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# **Couches interfaciales $\text{TiO}_2$ et $\text{NiO}$ déposées par CSD et PVD, pour cellules solaires organiques**

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THÈSE DE DOCTORAT  
Discipline : science des matériaux  
Spécialité : chimie du solide

*Présentée  
et soutenue publiquement par*

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# **Summary of the thesis in French**



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## Introduction générale

Le marché mondial de l'énergie est dominé par les énergies fossiles non renouvelables. L'exploitation intensive des ressources fossiles a été initiée au 18ème siècle par la révolution industrielle et elle continue à ce jour. Le développement rapide de nombreuses branches de l'industrie touche de façon spectaculaire presque tous les aspects de la vie quotidienne de chaque être humain. L'énergie d'origine fossile a induit un changement dans les transports, l'agriculture, l'industrie et les télécommunications. En plus de ces aspects industriels, la consommation d'énergie a un effet profond sur les conditions socio-économiques et culturelles actuelles. Cependant, l'énergie fossile est limitée et l'épuisement des ressources est prévu dans quelques décennies. En conséquence, les sources d'énergie alternatives sont nécessaires d'urgence pour maintenir des normes de style de vie pour l'avenir. Aujourd'hui, les gouvernements de nombreux pays investissent dans le développement des sources d'énergie renouvelables, qui proviennent de la lumière du soleil, du vent, la pluie et la chaleur géothermique. Cette énergie est considérée comme illimitée et bon marché. Cependant, le coût de production des énergies renouvelables reste trop cher par rapport à l'énergie des combustibles fossiles.

Parmi les sources d'énergie renouvelable, celle du soleil est la plus accessible dans toutes les régions du monde. Cette énergie primaire peut être convertie en chaleur ou en électricité via des capteurs solaires thermiques ou des cellules solaires photovoltaïques (PV), respectivement. L'utilisation de l'énergie solaire photovoltaïque a explosé ces dernières années, avec des développements prometteurs dans de nombreux pays. En 2010, le marché du photovoltaïque a connu une croissance sans précédent et une large utilisation de cette production d'énergie écologique et disponible. Sur une base mondiale, de nouvelles installations photovoltaïques d'environ 15 000 MW ont été ajoutés au cours de 2010, portant la capacité PV à près de 40.000 MW. Les cellules à base de Silicium cristallin (c-Si) constituent la technologie la plus commune et mature et représentent environ 80% du marché aujourd'hui. Les modules photovoltaïques commercialement disponibles au silicium convertissent 12 à 19% de la lumière du soleil incident en électricité et peuvent durer plus de 20 ans. Toutefois, les coûts de fabrication de modules photovoltaïques entraînent que la période de retour sur investissement est estimée à plusieurs années dans des conditions climatiques favorables.

Durant les dernières décennies, dans les laboratoires, sont développées des cellules solaires photovoltaïques organiques (OPV). Les réalisations récentes, dans ce domaine, ont montré que des prototypes de dispositifs permettent de convertir une partie raisonnable de la lumière du soleil en électricité. L'avantage le plus prometteur des cellules solaires organiques est leur coût de fabrication potentiellement faible. Elles peuvent être réalisées par des techniques d'impression ou de revêtement, qui permettent une production de grand volume sur des substrats de type flexible ou de verre. Pour cette technologie, les coûts de fabrication ne cessent de diminuer et devraient atteindre 0,50 € / W<sub>c</sub> en 2020. Un des facteurs qui limite le développement des cellules solaires organiques est la stabilité des composants organiques. Aujourd'hui les dispositifs à l'échelle du laboratoire fonctionnent pendant moins de 5000 heures et le problème de leur dégradation soulève de nombreuses questions non résolues.

Si plusieurs mécanismes sont proposés pour la décroissance de l'efficacité de l'OPV, la plupart des théories s'accordent que le mécanisme de dégradation dominant dans l'OPV non encapsulé est l'exposition de l'interface cathode-polymère organique à l'oxygène atmosphérique et à l'eau. Cela conduit à l'oxydation et à la délamination de la cathode métallique ainsi qu'à des réactions chimiques au sein des couches organiques. La thèse présente un concept d'amélioration des durées de vie des cellules solaires organiques par incorporation de matériaux semi-conducteurs inorganiques, qui permettent d'éviter l'interface polymères organiques-électrodes métalliques. Les matériaux inorganiques peuvent être déposés en couches minces sur les électrodes métalliques et jouer une fonction de couches collectrices de charge sélectives. Pour cet effet, le dioxyde de titane et l'oxyde de nickel ont été choisis comme semi-conducteurs de type n et p, respectivement.

## **Contenu de la thèse**

La thèse présente les méthodes pour la mise en forme de films minces d'oxydes de titane et de nickel. Deux façons seront étudiées. La première, est le dépôt à partir de solutions chimiques (CSD) qui est compatible avec la technique d'impression jet d'encre et offre un procédé à bas prix et la seconde est un dépôt physique en phase vapeur (PVD), qui offre l'opportunité de coûts de production modérés.



Le premier chapitre décrit un bref rappel historique du développement des cellules solaires organiques. Les résultats les plus récents en termes de performance, d'architecture et principe de fonctionnement sont présentés. Ce chapitre décrit les aspects économiques, les techniques de mise en oeuvre et les exigences pour augmenter les durées de vie de fonctionnement des cellules solaires organiques. La deuxième partie du chapitre présente le concept de cellules solaires organiques hybrides qui intègre des matériaux inorganiques. Les propriétés qui rendent l'oxyde de titane et l'oxyde de nickel des candidats intéressants pour les cellules solaires organiques ont été résumées. Les principes concernant les techniques de mise en oeuvre de ces oxydes sont également décrits.

Le deuxième chapitre décrit la synthèse de solutions colloïdales de  $\text{TiO}_2$ . La réaction est basée sur la conversion thermique du précurseur hydrolysable  $[\text{Ti}_8\text{O}_{12}(\text{H}_2\text{O})_{24}]\text{Cl}_8 \cdot \text{HCl} \cdot 7\text{H}_2\text{O}$  en particules de  $\text{TiO}_2$  à des températures modérées. La synthèse a été conçue pour permettre le dépôt de la suspension de particules par la technique d'impression jet d'encre. Les solvants organiques ont été utilisés comme milieu de dispersion pour satisfaire les exigences définies par la technique d'impression jet d'encre. Les solvants sont choisis pour leurs propriétés physiques et la présence d'eau a été réduite au minimum. La raison d'effectuer la synthèse dans des solvants organiques est liée à l'exigence de faible tension de surface, la gamme sélectionnée de viscosité et le relativement haut point d'ébullition du solvant des solutions colloïdales. Une des principales conditions est le dépôt de particules colloïdales à des températures relativement basses (inférieures à  $200^\circ\text{C}$ ). Par ailleurs, pour limiter les coûts et tenir compte de la stabilité thermique des polymères absorbeurs, il convient de proscrire un recuit ultérieur à haute température, donc la présence de tensio-actif a été évitée. Le procédé décrit ici est basé sur la méthode dite de médiation poly-ol. Le propylène glycol (1,2-propane-diol) a été choisi comme agent de dispersion pour les particules colloïdales. La sélection du propylène glycol est également liée à sa réactivité avec l'acide chlorhydrique à des températures élevées. Pendant l'hydrolyse du précurseur  $[\text{Ti}_8\text{O}_{12}(\text{H}_2\text{O})_{24}]\text{Cl}_8 \cdot \text{HCl} \cdot 7\text{H}_2\text{O}$ , l'acide chlorhydrique est un sous-produit. La réaction avec le propylène glycol permet d'éliminer la majorité des ions corrosifs. En effet, ces derniers sont considérés comme néfastes pour les équipements d'impression à jet d'encre. Ce chapitre décrit trois systèmes dans lesquels le propylène glycol est utilisé comme réactif direct ou indirect pour la synthèse. La première étape de l'hydrolyse du précurseur  $[\text{Ti}_8\text{O}_{12}(\text{H}_2\text{O})_{24}]\text{Cl}_8 \cdot \text{HCl} \cdot 7\text{H}_2\text{O}$  a été réalisée en présence de carbonate de propylène (4-méthyl-1,3-dioxolane-2-one) et d'eau. À des températures élevées (supérieures à  $100^\circ\text{C}$ ), ces solvants réagissent l'un avec l'autre pour donner du propylène glycol en tant que sous-produit, l'eau est

alors consommée. Dans la seconde partie, un système à trois composantes a été utilisé pour synthétiser des solutions colloïdales de  $\text{TiO}_2$ . Le carbonate de propylène, l'eau et le propylène glycol ont été utilisés pour obtenir des particules colloïdales très dispersées. Le dernier paragraphe décrit le système où le propylène glycol et l'eau ont été mis en oeuvre pour obtenir des colloïdes de  $\text{TiO}_2$ . Les produits ont été caractérisés par différentes techniques. Les propriétés physiques des solutions résultantes colloïdales ont été étudiées. Enfin, les particules colloïdales ont été déposés par spin-coating ou techniques d'impression à jet et testé comme couches semiconductrice de type n dans des cellules photovoltaïques organiques.

Le troisième chapitre décrit une méthode pour la synthèse d'hydroxyde de nickel colloïdal dans du propylène glycol. Les colloïdes obtenus ont été utilisés comme précurseur pour le dépôt de films minces d'oxyde de nickel et ont été testés comme couches conductrices de type p au sein de cellules solaires organiques hybrides. Les colloïdes ont été préparés en trois étapes afin de réaliser la synthèse et la purification de l'hydroxyde de nickel à partir de sous-produits. La première étape consiste en l'hydrolyse du sel de nickel (chlorure de nickel et de nitrate de nickel) par une base organique (hydroxyde de tétraméthyl ammonium) en utilisant un titrage acido-basique. La synthèse a été réalisée à deux températures différentes afin de modifier la stoechiométrie de l'hydroxyde résultant. La deuxième étape de la synthèse implique la floculation des espèces hydroxydes de nickel par l'addition d'un solvant choisi et la séparation des produits par centrifugation. Dans la dernière étape, l'hydroxyde de nickel est peptisé dans du propylène glycol dans le but d'obtenir des solutions colloïdales. Les films minces d'oxyde de nickel ont été obtenus par dépôt d'hydroxyde de nickel colloïdal par spin-coating suivi par des procédures de traitement thermique. Les produits ont été caractérisés à chaque étape de la préparation en vue de vérifier la structure cristallographique, la capacité de dispersion et la stoechiométrie des produits. Les films minces résultant ont été caractérisés par des techniques de microscopie électronique et l'homogénéité des couches déposées a été étudiée. Enfin, les films d'oxyde de nickel ont été testés comme couche de transport de trous dans des dispositifs organiques hybrides et les performances des cellules ont été présentées.

Le dernier chapitre décrit la fabrication de films minces d'oxyde de nickel par une technique de dépôt physique en phase vapeur. Le processus a été réalisé en utilisant deux réacteurs de dimensions différentes. Les films minces ont été obtenus par pulvérisation réactive de cibles de nickel utilisant de l'oxygène mélangé à de l'argon. L'influence de la pression partielle d'oxygène sur les propriétés des couches minces a été analysée. La première partie du chapitre décrit les paramètres du procédé pour un réacteur à l'échelle de laboratoire. La tension de décharge électrique de la cathode a été utilisée comme paramètre de contrôle du

procédé de pulvérisation de la cible métallique en vue du dépôt d'oxyde de nickel. Les films minces ont été caractérisés par différentes techniques en termes de structure cristallographique, de composition chimique, de croissance microstructurale, des propriétés optiques et de position du niveau de Fermi par rapport à la bande de valence. La deuxième partie du chapitre décrit l'élaboration d'échantillons d'oxyde de nickel en utilisant un réacteur PVD industriel. Le facteur d'échelle entre les surfaces des cibles est égal à 53,3. L'évolution des paramètres du processus a été analysée et comparée à ceux du réacteur de laboratoire. La troisième partie du chapitre décrit les résultats en cellules photovoltaïques hybrides organiques dans lesquelles les films d'oxyde de nickel ont été mis en œuvre comme couche collectrice de type p.

## **Contexte relatif aux cellules solaires organiques**

Le domaine du photovoltaïque organique a commencé au début du 19<sup>ème</sup> siècle. En 1906, Pochettino et Volmer ont mesuré, en 1913, la photoconductivité de l'anthracène solide. Mais les véritables recherches, sur le photovoltaïque organique, ont démarré dans les années 1950, quand des colorants organiques et des composés dérivés de la chlorophylle ont été étudiés. En 1958, Kearns et Calvin ont trouvé que des disques de phtalocyanine de magnésium revêtus d'un film mince de tétraméthyl p-phénylènediamine oxydée à l'air sont des systèmes organiques qui ne montrent que l'effet photovoltaïque. Les jonctions produisent une phototension de 200 mV et ont démontré un transfert d'électrons à partir de la phtalocyanine de magnésium vers la tétraméthyl p-phénylènediamine. En 1973, Ghosh et Feng ont élaboré une cellule solaire organique par insertion d'un film mince de tétracène entre des électrodes d'aluminium et d'or. La tension en circuit ouvert est de 0,6 V et l'efficacité de conversion de puissance atteignait 0,0001%. Cette découverte a amorcé le développement du photovoltaïque à une seule couche organique dans les années 1970. Dans les structures à une seule couche organique, la matière organique est insérée entre deux électrodes métalliques et la phototension est due à la différence des travaux de sortie des deux électrodes métalliques. En 1974, Gosh a amélioré le dispositif photovoltaïque en insérant une couche mince de phtalocyanine de magnésium entre des électrodes d'argent et d'aluminium. Le rendement de conversion des cellules à partir de la lumière blanche a atteint un rendement de conversion de 0,001%. En 1982, Chamberlain a publié un résultat de cellule solaire avec un rendement de

conversion de puissance de 0,3% avec de la lumière blanche. La cellule était composée de l'arrangement suivant : films minces d'aluminium, de mérocyanine dopé au chlore et d'or.

En 1986, Tang a proposé une nouvelle géométrie pour le photovoltaïque organique (OPV). La cellule est composée de deux couches organiques : une couche donneuse d'électrons telles que la phtalocyanine de cuivre et l'autre acceptrice dérivée de pérylène tétracarboxylique. Dans une telle structure, la photogénération de la charge est faiblement dépendante de la nature des électrodes métalliques, mais dépend fortement de l'interface entre les deux couches organiques. Cette solution améliore les propriétés photovoltaïques et a permis de franchir la limite de 1% pour une efficacité de conversion de puissance. Le concept a été une avancée pour le développement des cellules solaires organiques.

Dans ces deux couches de cellules solaires organiques (cellules solaires à hétérojonction), la génération efficace de charges survient seulement à environ 10 nm de l'interface entre les couches organiques. Toutefois, pour la plupart des couches organiques, l'épaisseur du film devrait être supérieure à 100 nm afin d'absorber la plupart de la lumière. Pour accroître l'efficacité de génération des charges dans toute l'épaisseur de la couche active, le scientifique a proposé d'utiliser des hétérojonctions interpénétrées. Ces hétérojonctions interpénétrées peuvent être obtenues en mélangeant deux matériaux organiques actifs. En conséquence, la surface de contact d'interface entre les deux couches actives augmente, conduisant à la génération de charges plus efficace.

En 1995, Yu a publié les résultats montrant des cellules solaires à base d'hétérojonction interpénétrée avec une efficacité de conversion de 2,9%. La poursuite du développement a été axée sur la composition du mélange, la morphologie du réseau et le développement de nouveaux matériaux organiques. La limite théorique d'efficacité des cellules solaire à hétérojonction interpénétrée est de 10%. Pour surmonter cet obstacle, des cellules solaires en tandem sont développées en parallèle avec les dispositifs à une seule couche. La cellule tandem est une connexion en série de deux cellules organiques qui permet d'augmenter la tension en circuit ouvert à deux fois celle d'une seule cellule. Pour les dispositifs tandem, la limite théorique de l'efficacité est de 15%. Outre les valeurs théoriques, les meilleurs rendements certifiés atteignent 8,13% pour une seule couche interpénétrée à hétérojonction en Juillet 2010 par Solarmer Energie Incorporation. En Novembre 2010, Heliatek et l'Institut de photophysique appliquée ont signalé un record d'efficacité certifiée de 8,3% pour une structure en tandem. Plus récemment, la société Konarka Technologies a rapporté une efficacité de 8,3% sur des cellules solaires photovoltaïques à une seule jonction organique d'une surface d'un centimètre carré. Soulignons enfin, la récente communication de

Heliatek GmbH (Dresde, en Allemagne), du 5 décembre 2011, qui a une fois de plus établi un nouveau record du monde (certifié Fraunhofer ISE) pour les cellules solaires organiques, avec une efficacité des cellules tandem de 9,8% pour une surface de 1,1 cm<sup>2</sup>, cellule fabriquée avec un procédé de dépôt à basse température. Les résultats de laboratoire sont encore loin des valeurs théoriques, mais en tenant compte du développement qui a eu lieu depuis 2001, les cellules solaires organiques sont très prometteuses et pourraient être en compétition avec les cellules solaires classiques en silicium cristallin, qui représentent aujourd'hui autour de 90% du marché photovoltaïque mondial.

## **Principe de fonctionnement des cellules solaires organiques**

Le processus de conversion de la lumière en courant électrique dans une cellule photovoltaïque organique est composé de quatre étapes:

- L'absorption d'un photon conduisant à la formation d'un état excité, la paire électron-trou (excitons),
- La diffusion des excitons sur le site de dissociation,
- La séparation des charges et la création de porteurs de charge libres (électrons et trous),
- Le transport des charges à l'anode (trous) et la cathode (électrons).

L'absorption des photons par une matière organique conduit à l'excitation de l'électron de la plus haute orbitale moléculaire occupée, HOMO (l'équivalent de la bande de valence dans un semi-conducteur inorganique massif) au plus bas orbitale inoccupée moléculaire, LUMO (bande de conduction) et laisse derrière lui un trou localisé. Ce processus ne mène pas directement à la création de charges électriques libres. Les électrons et les trous générés sont attirés entre eux par des interactions coulombiennes et conduisent à la création d'excitons. Afin de dissocier les paires électron-trou, il est nécessaire de générer un champ électrique interne. Ceci peut être réalisé dans la région de forte chute de potentiel au niveau des interfaces donneur-accepteur ou métal-semiconducteur, en fonction de l'architecture du dispositif photovoltaïque. Dans les architectures modernes (bicouche ou à hétérojonction interpénétrée) la dissociation des excitons est réalisée à l'interface donneur-accepteur.

Les matériaux donneur et accepteur ont des niveaux d'énergie (HOMO et LUMO) différents. A l'interface, une dissociation des excitons est réalisée par transfert de l'électron excité depuis le niveau élevé de l'énergie du donneur vers un niveau d'énergie inférieur de l'accepteur, ce qui est favorable énergétiquement. Pour les dispositifs à hétérojonction interpénétrée, la différence d'énergie entre donneur et accepteur affectent fortement la tension

de circuit ouvert des cellules solaires. Généralement, la différence entre HOMO du donneur et LUMO de l'accepteur est une limite pour la tension de circuit ouvert mesurée.

Après la séparation de charge, l'électron et le trou doivent être effectivement transportés aux électrodes. Les électrodes métalliques doivent être sélectionnées à l'égard de leurs travaux de sortie. Pour collecter les électrons, des matériaux de travaux de sortie sont favorables et des matériaux à faible travail de sortie sont préférables pour recueillir les trous.

## **Matériaux utilisés pour les cellules solaires organiques**

Les matières actives utilisées pour les cellules photovoltaïques organiques peuvent être des polymères, des oligomères ou des petites molécules. Ces matériaux sont des systèmes  $\pi$ -conjugués et ils sont souvent désignés comme semi-conducteurs organiques. Ils ont la capacité d'absorber les photons dans le domaine visible du spectre solaire, afin de créer des porteurs de charge. Les matières organiques doivent être capables de transporter des électrons à l'une des électrodes et des trous à l'autre. Ces matériaux sont classés en donneurs et accepteurs d'électrons.

La plupart des polymères semi-conducteurs sont des conducteurs à trou et sont appelés donneurs. Pour les polymères accepteurs d'électrons, de petites molécules sont fréquemment utilisées. Jusqu'à présent, les meilleurs accepteurs d'électrons sont des dérivés des molécules de fullerène.

Un des couples donneur-accepteur le plus fréquemment utilisé et étudié dans les cellules solaires à hétérojonction interpénétrée est un mélange de poly (3 - hexylthiophène) (P3HT) et de [6,6]-phényl-C(61) ester de l'acide butyrique (PCBM). L'avantage de ce mélange réside dans l'auto-organisation des polymères de P3HT avec les molécules de PCBM. De plus, des valeurs relativement élevées d'efficacité jusqu'à 5% ont été rapportées pour des systèmes optimisés. Le mélange P3HT:PCBM sous forme de couches minces présente une absorption dans la gamme 400-650 nm avec un gap d'environ 1.8 eV. Ces valeurs correspondent partiellement avec le spectre d'émission solaire. L'absorption de longueurs d'onde ne dépassant pas 650 nm limite la collecte à environ 20% des photons solaires. Le mélange P3HT:PCBM sera utilisé pour les cellules solaires hybrides décrites dans ce travail.

## **Couches interfaciales pour les cellules solaires organiques**

Dans les cellules solaires à hétérojonction interpénétrée, les couches actives sont insérées entre les électrodes avec des travaux de sortie différents. L'hétérojonction interpénétrée permet aux excitons d'atteindre facilement l'interface donneur-accepteur pour former des électrons et des trous. Cependant, cette configuration peut également être à l'origine de la recombinaison de charge et de réactions chimiques se produisant à l'interface organique / électrode. Ces problèmes peuvent être résolus par l'insertion de couches interfaciales. Une modification couramment appliquée à la cathode est le dépôt d'une couche très mince de LiF entre l'électrode métallique et le semiconducteur organique, pour améliorer le transfert d'électrons. Pour faciliter le transport des trous, le PEDOT:PSS très conducteur est déposé en contact avec l'anode. Cependant, l'utilisation de PEDOT:PSS reste problématique en raison de ses propriétés corrosives ( $\text{pH} < 1$ ). L'insertion de couches interfaciales améliore souvent les performances initiales des cellules solaires, mais ces couches ont une stabilité limitée dans le temps, menant à une certaine dégradation de la performance de la cellule avec le temps.

## **Concept de cellules solaires organiques et hybrides**

La raison de la dégradation rapide des cellules solaires organiques est évidemment liée aux composés atmosphériques tels que l'oxygène et l'eau, qui pénètrent dans la structure des cellules causant des dommages irréversibles. Le mécanisme de la dégradation n'est pas clair, mais on soupçonne que des réactions néfastes se produisent aussi aux interfaces polymères organiques-électrodes métalliques. Une des solutions pour comprendre le mécanisme de dégradation et dissocier l'influence des effluents atmosphériques de celle de l'interface métal-organique, consiste à insérer des couches interfaciales. Les expériences ont montré que le dépôt de couches interfaciales peut améliorer les performances des dispositifs photovoltaïques ( $V_{OC}$ ) et également éviter les réactions se produisant aux interfaces.

La condition principale pour les couches interfaciales est de contrôler leur capacité de transport de porteurs de charge vers les électrodes appropriées. Pour y parvenir, la surface de la cathode est modifiée par un semi-conducteur de type n et l'anode par une couche de type p.

Les cellules incorporant des couches interfaciales inorganiques sont appelées des systèmes hybrides. La tendance récente en matière de recherche inclue des couches interfaciales inorganiques car elles sont considérées comme plus stables que les couches organiques. Les plus fréquemment utilisées sont pour le type p :  $\text{MoO}_3$ ,  $\text{V}_2\text{O}_5$ ,  $\text{NiO}$  et pour le type n :  $\text{ZnO}$ ,  $\text{TiO}_2$ .

Dans ce concept, la couche active est localisée entre les semi-conducteurs dopés différemment. Deux architectures sont possible : NIP (classique) ou PIN (inversée), où P désigne le semi-conducteur de type p, I la couche active intrinsèque et N la couche de type n.

La différence entre ces deux types est due à la séquence dans l'empilement des semi-conducteurs sur un substrat conducteur transparent. Pour l'architecture PIN le semi-conducteur de type p est déposé sur l'électrode TCO tandis qu'il s'agit de la couche de type n pour la structure NIP. Les oxydes utilisés comme couches interfaciales sont généralement des semiconducteurs à large bande. Cette condition est impérative lorsque la couche interfaciale est déposée sur l'électrode avant (TCO) de telle sorte que l'accès des photons visibles à la couche active puisse effectivement avoir lieu. Les couches interfaciales jouent un double rôle: elles transportent uniquement les porteurs de charge sélectivement tout en bloquant l'accès à l'électrode aux porteurs de charge opposée. Le phénomène impose un bon alignement des niveaux d'énergie (VB et CB) d'oxydes par rapport à ceux des molécules organiques (HOMO et LUMO). Les couches interfaciales qui empêchent le transport de charge dans une seule direction sont appelés couches tampons. Pour les travaux présentés dans la thèse,  $\text{TiO}_2$  et  $\text{NiO}$  ont été sélectionnés en tant que couches tampon pour les cellules solaires organiques, ayant comme absorbeur, une heterojonction interpénétrée formée du polymère P3HT, mélangé avec des molécules de PCBM. Les cellules seront testées en termes de stabilité par insertion de  $\text{NiO}$  pour l'architecture PIN et de  $\text{TiO}_2$  pour la structure NIP. Les tests distincts permettent d'étudier la dégradation survenant sur les deux électrodes et de valider le concept de cellules solaires organiques hybrides stables.

Le cas idéal, où la dégradation sur les deux électrodes serait supprimée par les couches tampons de  $\text{TiO}_2$  et  $\text{NiO}$ , donne une possibilité d'intégration au sein de modules semi-transparents. La structure idéale peut être encapsulée par deux électrodes transparentes et mises en œuvre pour une application vitrage.



## Les procédés de mise en forme

Les cellules solaires organiques sont composées de plusieurs couches et presque chaque couche peut être obtenue par des techniques de mise en forme de films à partir de solutions. Ces techniques ont été largement explorées pour le papier, les polymères, et les industries textiles. Ils offrent des possibilités de production de grand volume et des prix bas, ce qui rend les cellules solaires organiques économiquement attractives sur le marché de l'énergie. La voie humide peut être divisée en techniques d'impression et de revêtement. Fondamentalement, la technique d'impression permet de réaliser des schémas en 2 dimensions. Les techniques d'impression comprennent : la sérigraphie, la tampographie, l'impression héliographique, l'impression flexographique et l'impression offset. Les techniques de revêtement sont considérées comme ayant des capacités de formation de schémas moins complexes et permettent de contrôler la formation de film en 0-dimension (pas de possibilité de créer un motif) ou 1-dimension (des modèles simples peuvent être formés). Les techniques de revêtement comprennent l'enduction centrifuge, la technique de Doctor Blade, le coulage en bande, la pulvérisation d'une solution, sous-die enduction, enduction au rideau, montage de la lame et le couteau-sur-bord de revêtement. Basé sur cette classification, l'impression jet d'encre peut être incluse à la fois dans les techniques d'impression et de revêtement. Elle autorise à la fois la formation de motifs complexes et de film continu. Le champ des cellules solaires organiques a été principalement développé, dans les laboratoires avec l'enduction centrifuge. La base de la méthode repose sur l'application d'une solution sur un disque horizontal en rotation, qui, après accélération (avec une vitesse contrôlée) induit l'éjection de l'excès de liquide. En conséquence, il reste un mince film sur le substrat. Les forces d'adhésion à l'interface liquide / substrat et la force centrifuge agissant sur le liquide en rotation impose un fort cisaillement du liquide et un écoulement radial.

La technique permet d'obtenir des films d'épaisseur très uniforme sur surface plane (jusqu'à  $\varnothing \geq 30$  cm) avec une bonne reproductibilité de l'épaisseur du film. La relation de l'épaisseur du film  $d$  est donnée par la formule empirique:  $d = k\omega^\alpha$  où  $\omega$  est la vitesse angulaire,  $k$  et  $\alpha$  sont des constantes empiriques liées aux propriétés physiques du solvant, du soluté et du substrat. La méthode peut être appliquée à des mélanges de solutions organiques et inorganiques. L'inconvénient du spin-coating est lié à la surface limitée et les déchets de matériaux significatifs, correspondant à ce qui est éjecté de la surface. D'autre part, le spin-

coating permet seulement un contrôle 0-dimensionnel de la structure du film créé. Les cellules solaires organiques sont des structures en couches et du point de vue de l'empilement des composants les uns sur les autres, les techniques de revêtement, sans possibilité de motif ne répondent pas aux exigences. C'est parce qu'il n'est pas nécessaire d'aligner une composante par rapport à un autre. Les cellules organiques sont généralement composées de l'empilement suivant : électrode métallique / couches organiques / électrode transparente. Le problème vient de la résistance relativement élevée pour les électrodes transparentes. Les techniques Zéro dimensions (p.ex spin-coating) sont appliquées pour la préparation de petits dispositifs pour lesquels les pertes résistives sont négligeables. La production de cellules de grande surface nécessite par exemple de longues bandes étroites de couches actives ou la structuration du réseau de contacts métalliques, qui peuvent compenser les pertes résistives et permettent de relier les cellules individuelles dans des modules.

Une des techniques qui offrent la formation de modèles complexes est l'impression jet d'encre. La technique d'impression jet d'encre devient de plus en plus populaire en raison de la commercialisation de dispositifs qui restent compatibles avec de nombreux solvants organiques. La commercialisation de têtes d'impression en céramique, résistantes à diverses formulations d'encre, offre de nombreuses possibilités aux expérimentateurs.

Cette technique peut être utilisée pour l'impression sur substrats flexibles plastiques et sur verre. Le principe de fonctionnement est basé sur la génération d'ondes de pression dans un canal rempli de liquide ou derrière celui-ci. Les ondes de pression peuvent être générées soit thermiquement ou piézo-électriquement. Le liquide est normalement conservé dans le canal à cause de la tension de surface à l'interface fluide / air, mais l'action des ondes de pression surmonte la tension superficielle et pousse le liquide hors de la buse, ce qui provoque la formation de gouttelettes. Les valeurs critiques de la pression dépendent principalement des propriétés rhéologiques du fluide, des dimensions des canaux et des buses. La pression de vapeur, le point d'ébullition, et la tension superficielle de l'encre sont des paramètres critiques pour la technologie d'impression jet d'encre.

Les imprimantes ont une limite de haute résolution jusqu'à 2880 dpi (points par pouce) ce qui signifie des capacités de structuration à l'échelle micrométrique. Habituellement, la technique d'impression est appliquée pour la formation de modèles bidimensionnels, mais des structures peuvent également être formées en 3-D. En outre, les appareils modernes offrent la possibilité de chauffer les substrats ou le fluide imprimé, ce qui permet de manipuler les paramètres physiques de l'encre en améliorant le mouillage du liquide sur différents types de substrats.

La technique d'impression jet d'encre peut être appliquée pour l'impression de toutes les composantes des cellules solaires organiques, y compris les électrodes transparentes d'ITO, les couches actives organiques, les connecteurs métalliques et donne l'occasion de l'appliquer aux cellules solaires organiques ayant des architectures différentes.

L'aspect économique du scaling-up de la production est souvent assimilable avec celui de la technologie roll-to-roll (R2R). Le concept de Roll-to-roll est basé sur la fabrication en continu de chaque composant tandis que le substrat est en mouvement. Le substrat est sous forme d'une longue feuille qui a une certaine souplesse mécanique. Pendant le processus d'impression ou de revêtement, le substrat se déplace à travers plusieurs rouleaux sur lequel les composants sont déposés. Le procédé R2R est considéré comme bon marché et des techniques de dépôt rapide et diverses peuvent être employées pour chaque étape de dépôt. Cependant jusqu'à présent, le choix de la technique la plus appropriée pour la réalisation des cellules solaires organiques n'est pas clairement établi et des efforts sont toujours en cours pour obtenir les meilleures performances sur des dispositifs plus grands que ceux préparés à l'échelle du laboratoire.

## **Objectifs du projet Solhypin**

Le travail présenté ici est une partie du projet ANR-Solhypin 2008-2011. Le projet prévoit la mise en œuvre de deux techniques différentes pour le dépôt de films minces semiconducteurs de  $\text{TiO}_2$  et  $\text{NiO}$ . L'un est un procédé par voie humide basée sur la chimie sol-gel en vue d'adopter le dépôt d'une technique d'impression jet d'encre, le second, moins difficile est le dépôt physique en phase vapeur pour satisfaire à l'exigence des conditions douces. La meilleure technique sera utilisée à la bonne place dans le processus d'élaboration des multicouches cellules solaires organiques. L'objectif de Solhypin est de produire des modules photovoltaïques de  $100 \text{ cm}^2$  qui démontre une dégradation de moins de 20% pendant plus de 5000 heures sous un éclairage continu, en commençant avec un rendement de conversion d'énergie aussi élevée que 3,5%.

## Contributions de chaque partenaires

Le projet ANR-Solhypin implique la participation de quatre unités :

### 1. Institut des Matériaux de Nantes (IMN)

Les objectifs de l'IMN sont la préparation de solutions colloïdales stables, qui, après dépôt, conduiront à des couches semi-conductrices de NiO de type p et de TiO<sub>2</sub> de type n. Les solutions colloïdales doivent être compatibles avec la technique d'impression jet d'encre et répondre aux exigences définies par le partenaire industriel (Ardeje). Le deuxième objectif est dédié aux dépôts de films minces de NiO par une technique de dépôt physique en phase vapeur dans un réacteur à l'échelle du laboratoire et explorer les conditions préalables pour le transfert du dépôt vers un partenaire industriel (SOLEMS SA).

### 2. Ardeje

Ardeje est une industrie spécialiste du jet d'encre, qui est en charge du dépôt de tous les composants de la cellule solaire hybride organique par la technique d'impression jet d'encre. Le dépôt comprend : des solutions colloïdales préparées à l'IMN, les solutions de couches actives organiques (P3HT:PCBM), les couches de transport de trous (PEDOT:PSS) et des collecteurs de courant métalliques (argent).

### 3. Solems S.A.

Solems est un fabricant de cellules solaires à base de silicium élaborées par les techniques PVD. Dans le projet Solhypin Solems est en charge du dépôt de films minces de NiO élaborés dans un réacteur à l'échelle industrielle.

### 4. CEA-INES

Le CEA-INES est l'unité coordonnatrice pour le projet. Le CEA-INES est en charge des tests de nouveaux matériaux pour cellules solaires organiques, produit par les trois partenaires mentionnées précédemment. Le CEA-INES est en charge d'optimiser les conditions de dépôt pour chaque couche et d'explorer les performances de cellules solaires incorporant les couches semi-conductrices inorganiques.

Le manuscrit présente la partie du travail qui a été élaboré à l'IMN, mais aussi un résumé des principaux résultats obtenus lors de la collaboration avec tous les participants.

## Exigences pour l'impression des solutions colloïdales

En général, les propriétés des encres doivent être adaptées à chaque périphérique d'impression particulier. Le cahier des charges exigé par le partenaire industriel impose les caractéristiques suivantes:

- Viscosité à la température d'impression entre 8-15 cP,
- Tension de surface entre 25-35 mN/m
- Point d'ébullition du solvant au-dessus de 120°C
- pH aussi proche que possible de la neutralité
- Granulométrie inférieure à 1  $\mu\text{m}$  dans une dispersion stable.

## Propriétés électriques de $\text{TiO}_2$

Le  $\text{TiO}_2$  non dopé et stoechiométrique à des températures modérées est un isolant. Ses propriétés électriques résulte de son réseau de défauts, qui dépendent fortement de la température et la pression partielle d'oxygène. A basse température et à pression d'oxygène partielle basse, le  $\text{TiO}_2$  est un semi-conducteur de type n et de la conductivité est attribuée à des lacunes d'oxygène dans le réseau cristallin (ou en surface).

Pour les cellules solaires organiques polymères,  $\text{TiO}_2$  en raison d'une conductivité de type n est un bon candidat comme couche de transport d'électrons. Cependant le transport efficace des porteurs de charge est lié à l'alignement des niveaux d'énergie par rapport aux niveaux d'énergie donneur-accepteur. Les trous et les électrons qui sont générés à l'interface P3HT - PCBM sont collectés au niveau des électrodes par une cascade d'alignement des niveaux d'énergie de couches semi-conductrices interfaciales. Le niveau de CB (niveau de Fermi) de  $\text{TiO}_2$  doit être inférieur à la LUMO du PCBM et supérieur (ou proche) du niveau de Fermi de l'électrode métallique de collecte (Al).

Pour les cellules solaires organiques polymères incorporant  $\text{TiO}_2$  comme couche interfaciale, le processus de transport d'électrons est photo-induit. Les expériences ont montré que la performance des cellules est considérablement diminuée lorsque le filtre UV a été introduit après la source de lumière. Ce comportement est réversible après retrait du filtre. Un phénomène similaire a été signalé pour les films minces de  $\text{TiO}_2$ , dont la conductivité a été

mesurée dans l'obscurité et la lumière avec des atmosphères de gaz différents.  $\text{TiO}_2$  pourrait constituer une protection importante vis-à-vis de l'oxygène / de l'eau et de l'effet de donneur sacrificiel dans l'OPV en raison de ses propriétés photocatalytiques et photophysiques. Le  $\text{TiO}_2$  absorbe la lumière à la longueur d'onde inférieure à 400 nm. Ainsi l'illumination par la lumière UV modifie les propriétés de la couche interfaciale de  $\text{TiO}_x$ . L'illumination du  $\text{TiO}_2$  favorisera les électrons de la bande de conduction qui peuvent interférer avec le transport d'électrons. La contribution néfaste de ce phénomène est l'oxygène. L'oxygène gazeux s'absorbe à la surface de  $\text{TiO}_2$  et tend à capturer les électrons pour produire le dioxygène qui agit comme piège des électrons. Ainsi, les électrons produits dans la majeure partie de  $\text{TiO}_x$  par illumination UV peut d'abord remplir des pièges d'électrons et contribuer au mécanisme de conduction.

## **Les propriétés optiques de $\text{TiO}_2$**

Le  $\text{TiO}_2$  est un semi-conducteur à large bande et la valeur du gap dépend du type polymorphe et de la taille des cristallites. Pour les formes les plus répandues, les valeurs sont dans la gamme suivante: 3 eV pour le rutile; 3,2 eV à 3,4 eV pour anatase, 3,4 eV pour brookite et 3,2 eV pour le  $\text{TiO}_2$  (B). La bande interdite élevée est une condition principale pour l'électrode avant (TCO) pour éviter de perdre dans la plage visible du spectre solaire. Une autre propriété intéressante de  $\text{TiO}_2$  est son indice de réfraction élevé ( $n = 2,48$  anatase - 2,56; brookite  $n = 2,58 - 2,70$ ; rutile  $n = 2,61 - 2,89$ ). Pour les cellules solaires organiques, les propriétés de réfraction de  $\text{TiO}_x$  peuvent être utilisées pour améliorer les performances du dispositif. Dans la cellule photovoltaïque, la lumière pénètre dans le dispositif par l'avant (transparent) des électrodes et il est réfléchi par l'arrière. Ainsi, la lumière passe à la couche active à deux reprises et une onde stationnaire est formée avec l'intensité du champ électrique léger ( $|E|$ ) maximum, quelque part au sein du matériau actif. L'absorption dans la couche active dépend de la distribution de la force électrique de la lumière et a une conséquence sur le nombre de porteurs de charge générés. L'absorption dans la couche active peut être optimisée par l'insertion de la couche  $\text{TiO}_x$  entre l'électrode arrière et la couche active. Dans ce concept la couche de  $\text{TiO}_x$  agit comme une soi-disant "entretoise optique". L'entretoise optique déplace le maximum du vecteur champ électrique de la lumière incidente dans la

couche active. L'insertion de l'entretoise optique permet d'améliorer l'efficacité de conversion de puissance d'environ 10% par rapport à un dispositif conventionnel.

## **Propriétés électriques de NiO**

L'oxyde de nickel non dopé et stoechiométrique est un isolant avec une résistivité dans la gamme de  $10^{-12}$  S/cm. NiO a tendance à être sous-stoechiométrique en raison de sites vacants en nickel. Les propriétés électriques de NiO résultent de son réseau de défauts et la conductivité rapportée pour l'oxyde non-stoechiométrique atteint  $10^{-3}$  S/cm. La création de lacunes de nickel dans le réseau entraîne que deux atomes de nickel voisins change leur état d'oxydation de  $\text{Ni}^{+2}$  à  $\text{Ni}^{+3}$  pour compenser la charge nette. Cela crée des trous et donne lieu à un comportement semi-conducteur de type p. Mais les propriétés semi-conductrices varient avec la température. Tel que préparé, NiO non stoechiométrique après traitement thermique tend rapidement vers la stoechiométrie et perd ses propriétés semi-conductrices de type p. Il a été rapporté que le processus après le recuit diminue drastiquement la concentration de porteurs de charge positive lorsque la température dépasse 200°C.

Pour une couche interfaciale semi-conductrice de type p, la bande de valence doit correspondre à la HOMO du donneur de trous pour faciliter le transport vers l'anode. L'alignement des niveaux d'énergie implique que NiO agisse comme une barrière de blocage pour les électrons. L'orbitale LUMO de P3HT et PCBM est à 3.0 eV et 4.0 eV respectivement. La bande de conduction de NiO est à 1.8 eV. Ceci fournit une barrière d'énergie d'environ 1.2 eV pour les électrons qui est donc favorable pour recueillir les trous à l'anode (ITO).

## **Propriétés optiques de NiO**

La valeur de « band-gap » de NiO est comprise entre 3.8 eV et 5.4 eV. La bande interdite est suffisamment élevée pour permettre aux photons visibles d'accéder à la couche active par l'électrode avant. La transparence de NiO dans le domaine visible est liée à sa stoechiométrie. Un oxyde de nickel sous-stoechiométrique montre une baisse de transmittance

par rapport au NiO stoechiométrique. Ce phénomène est attribué à la présence de  $\text{Ni}^{+3}$ , qui agissent comme des centres colorés.

## Conclusions du chapitre I

Dans le premier chapitre, l'histoire des cellules solaires plastiques a été résumée, en montrant les concepts les plus importants et révolutionnaires qui ont contribué aux développements dans ce domaine. Les aspects de performance pour les cellules organiques basées sur des simple couche, double couche et hétérojonction interpénétrée ont été discutés. Les dernières réalisations et les limites théoriques des rendements de conversion de puissance ont été présentées pour différentes architectures de cellules organiques. Les problèmes liés à la dégradation et la durée de vie courte de ces dispositifs ont été expliqués en termes de stabilité des matières organiques, corrosion des électrodes métalliques et influence des effluents atmosphériques. Les aspects économiques et les exigences pour la durée de vie des cellules solaires organiques ont été analysés en termes de besoins du marché et d'applications possibles pour les petits appareils électroniques ou les centrales professionnelles de production d'énergie. Le chapitre a présenté le concept de cellules solaires organiques hybrides incorporant des matériaux inorganiques semi-conducteurs en tant que couches interfaciales. Ces oxydes inorganiques pourraient jouer un rôle clé pour la protection des couches actives organiques sensibles au contact avec des électrodes métalliques. Ce concept permet d'éviter le contact couches organiques- électrodes métalliques et supprime les réactions chimiques qui se produisent sur les électrodes. Pour le matériau de cathode, le dioxyde de titane de type n est sélectionné. L'anode peut être protégé par l'oxyde de nickel de type p. Les propriétés semi-conductrices de ces oxydes proviennent de leur nature non-stoechiométrique. Le dioxyde de titane tend à être pauvre en oxygène et pour l'oxyde de nickel, des lacunes sur les sites de nickel se forment facilement. La configuration de bande électronique de ces semi-conducteurs correspond bien à l'HOMO et LUMO des niveaux d'énergie du couple donneur-accepteur organique et permet le transport de charge efficace vers les électrodes sélectives. Le mécanisme de la conductivité photoinduite de dioxyde de titane a été décrit, ainsi que ses propriétés de réfraction de lumière qui peuvent améliorer la distribution spatiale de la lumière dans la couche active et améliorer le nombre de porteurs de charge photogénérés. Le gap de  $\text{TiO}_2$  et NiO est suffisamment grand (supérieur à 3 eV) pour



permettre le dépôt de ces oxydes sur l'électrode avant transparente, sans pertes importantes dans le domaine visible du spectre solaire. Deux voies possibles ont été proposées pour la réalisation de couches inorganiques interfaciales. La première implique le dépôt par voie chimique à partir de solutions colloïdales, compatible avec la technique d'impression jet d'encre. Le second est axé sur le dépôt physique en phase vapeur, ce qui nécessite un équipement sous-vide. Les aspects économiques et pratiques de la mise en œuvre de ces techniques ont été analysés. Pour le processus de dépôt par jet d'encre, les propriétés physico-chimiques des solutions colloïdales ont été définies en ce qui concerne l'équipement. L'emploi de techniques industrielles donne une opportunité pour intensifier la production de cellules solaires hybrides organiques.

## Conclusions du chapitre II

Des solutions colloïdales de  $\text{TiO}_2$  ont été préparées par réaction d'hydrolyse de «  $\text{Ti}_8\text{O}_{12}$  » précurseur et de solvants organiques dans des conditions solvothermales à  $120^\circ\text{C}$ . Trois formulations ont été testées. La première formulation impliquait l'utilisation de mélange de deux solvants : l'eau et le carbonate de propylène. Ces solvants mélangés avec différents rapport molaire de  $R = [\text{H}_2\text{O}]/[\text{PC}]$  réagissent les uns avec les autres pour former le 1,2-propanediol. L'évolution de cette réaction affecte la stabilité des particules colloïdales qui se forment pendant l'hydrolyse du précurseur «  $\text{Ti}_8\text{O}_{12}$  ». La gamme examinée de  $R = [\text{H}_2\text{O}]/[\text{PC}]$  conduit à la synthèse de nanoparticules d'anatase dont le diamètre des cristaux primaires vaut environ 5 nm. Pour les valeurs faibles et élevées de  $R = [\text{H}_2\text{O}]/[\text{PC}]$  les particules s'agglomèrent fortement. Les conditions optimales pour synthétiser les colloïdes monodispersés ont été trouvées à  $R = [\text{H}_2\text{O}]/[\text{PC}] = 0,712$ . L'eau, qui est présente comme un réactif, est entièrement consommée au cours de la réaction qui dure 48 heures. La grande différence de viscosité entre les réactifs et les produits permet de contrôler la viscosité des solutions colloïdales finales et de l'ajuster à la valeur recommandée pour le jet d'encre. Tous les colloïdes examinés étaient photosensibles à l'exposition à la lumière ultraviolette. L'illumination des échantillons dans des conditions hermétiques entraîne l'amélioration du degré de dispersion des colloïdes agglomérés et cette procédure a été appliquée avant chaque dépôt sur les substrats. Les colloïdes ont été testés en termes de compatibilité avec la technologie jet d'encre et les dépôts ont été étudiés par MET. Pour la quantité ajustée de façon

optimale du matériel imprimé, les colloïdes déposés forment une couche de  $\text{TiO}_2$  distribuée de façon homogène sur des substrats TCO/verre.

La seconde formulation chimique pour la synthèse de solution colloïdale de  $\text{TiO}_2$  implique le carbonate de propylène, le 1,2-propanediol et de l'eau comme solvant. Dans cette formulation le carbonate de propylène réagit avec l'eau en milieu acide. La présence de 1,2-propanediol permet d'obtenir des colloïdes bien dispersées et plus concentrées dans un plus large éventail de  $R=[\text{H}_2\text{O}]/[\text{PC}]$  par rapport à la première formulation de la synthèse. Cependant, l'addition du 1,2-propanediol provoque une réaction incomplète entre le carbonate de propylène et de l'eau. L'eau résiduelle est indésirable, en raison de son fort impact sur la tension de surface, ce qui provoque un démouillage des solutions colloïdales sur les substrats.

La troisième formulation de solutions colloïdales est obtenue dans l'eau et le 1,2-propanediol. La quantité d'eau a été limitée afin d'obtenir des solutions colloïdales avec une tension de surface inférieure 40mN/m. Les synthèses conduisent à des particules très dispersées pour deux taux  $R=[\text{H}_2\text{O}]/[\text{PG}]$  examinés. Le ratio de mélange de solvants affecte aussi la taille des cristaux d'anatase. Pour  $R=[\text{H}_2\text{O}]/[\text{PG}]=0,171$ , la taille des cristallites est de 2 nm tandis que pour  $R=[\text{H}_2\text{O}]/[\text{PG}]=0,555$  la distribution de taille des cristaux d'anatase se situe dans la gamme de 4 à 10 nm. Toutefois, pour cette formulation, la viscosité des solutions colloïdales est trop élevée par rapport à celle recommandée pour l'impression jet d'encre.

Les trois formulations de la synthèse présentée dans le chapitre donnent une occasion de synthétiser des solutions colloïdales de  $\text{TiO}_2$  (anatase) monodispersées avec des diamètres de cristallites compris entre 2 et 8 nm. L'utilisation du propylène glycol, de carbonate de propylène et d'eau pour hydrolyser «  $\text{Ti}_8\text{O}_{12}$  », offre la possibilité de contrôler les paramètres physiques des solutions colloïdales par rapport aux valeurs recommandées pour l'impression jet d'encre. Les solutions colloïdales déposées sur des substrats de verre conducteur ont été utilisées comme une couche de transport de charge de type n pour les cellules solaires organiques. Tel que préparés, les dispositifs photovoltaïques montrent une efficacité de conversion de 3,7% et une durabilité de plus de 6500 heures avec une diminution du PCE limité à 17%. Le concept impliquant l'emploi de  $\text{TiO}_2$  comme couche protectrice a été validé au regard de la stabilité des cellules solaires organiques.

## Conclusions Chapitre III

Des solutions colloïdales d'hydroxyde de nickel ont été préparées avec succès dans les solvants organiques. Pour la synthèse, l'éthylène glycol et le propylène glycol sont utilisés pour leurs propriétés de contrôle de dispersion de particules et leurs paramètres physico-chimiques compatibles avec l'impression jet-technique. Le processus a été divisé en trois étapes : i) synthèse de l'hydroxyde, ii) séparation des particules d'hydroxyde des sous-produits et iii) stabilisation des particules en solution colloïdale. Deux sels de nickel différents ont été testés en tant que réactifs pour la synthèse: le chlorure de nickel et de nitrate de nickel. Les sels de nickel ont été hydrolysés par une base organique (hydroxyde de tétraméthylammonium) à deux températures différentes (à l'ambiante et 70°C). La température d'hydrolyse affecte la stoechiométrie des hydroxydes résultant et la taille des particules colloïdales. Pour les hydroxydes résultant les formules suivantes ont été proposées:  $\text{Ni}(\text{OH})_{1,7}\text{Cl}_{0,3}$ , lorsque le chlorure de nickel a été hydrolysé à température ambiante;  $\text{Ni}(\text{OH})_{1,67}(\text{NO}_3)_{0,33}$ , lorsque le nitrate de nickel a été hydrolysé à température ambiante, et  $\text{Ni}(\text{OH})_{1,82}(\text{NO}_3)_{0,18}$ , pour l'hydrolyse du nitrate de nickel à 70°C. Les hydroxydes préparés à température ambiante ont été stabilisés en tant que colloïdes avec un diamètre de particules de 9 nm. Les hydroxydes préparés à 70°C ont été stabilisés avec une taille de particule de 80 nm. Après évaporation du solvant à 120°C, les colloïdes ont été cristallisées dans la variété  $\alpha$ - $\text{Ni}(\text{OH})_2$  (brucite désordonnée), pour chaque synthèse. Le traitement thermique des hydroxydes à 400°C a permis d'obtenir des oxydes de nickel, via une déshydroxylation. Les études cristallographiques et thermogravimétriques montrent que les hydroxydes contiennent des molécules de glycols comme un élément structurel et / ou absorbée. La présence de glycols provoque des réactions inattendues dans le cas de la synthèse de l'utilisation du sel de nitrate de nickel titré à 70°C. L'analyse XPS prouve la présence de nitrites dans les échantillons d'hydroxyde et de carbures dans l'oxyde de nickel final. La synthèse en utilisant des précurseurs du chlorure de nickel, titrés à la température ambiante a été trouvée exempte de sous-produits de type hydroxyde ou oxyde. En outre, tous les échantillons examinés étaient contaminés en surface par des espèces carbonées : C=O, C-O et C-C / C-H. Les hydroxydes de nickel ont été déposés sur FTO (ASAHI 120) et ITO (PGO) par spin coating. Les oxydes de nickel ont été obtenus après des traitements thermiques à 120°C et 400°C. Les particules de NiO avaient une morphologie non uniforme et une distribution en taille non homogène. Les cristaux sont grossièrement sphériques ou rectangulaire avec une taille variant entre 5 et

20 nm. Le dépôt par spin-coating permet d'obtenir des films poreux de NiO répartis sur le substrat, mais avec des discontinuités locales. Le démouillage des colloïdes sur les substrats de verre conducteur, ainsi que la viscosité trop élevée ont été ajustés par l'ajout d'un co-solvant, l'éther méthylique du dipropylène glycol.

Les films minces de NiO ont été testés comme couche conductrice de type p dans les cellules solaires organiques hybrides. Les couches de NiO ont été obtenues à partir des hydroxydes colloïdaux décrits ici. La meilleure performance a été enregistrée pour les couches de NiO synthétisés à partir des précurseurs  $\text{Ni}(\text{OH})_{1,7}\text{Cl}_{0,3}$  et  $\text{Ni}(\text{OH})_{1,82}(\text{NO}_3)_{0,18}$  et conduit à 1% de rendement. Le PCE pour NiO obtenus à partir de  $\text{Ni}(\text{OH})_{1,67}(\text{NO}_3)_{0,33}$  était proche de 0,5%. Ces valeurs ne sont pas satisfaisantes par rapport aux cellules optimisées avec PEDOT:PSS comme couche de transport de trous. Les cellules ayant des dépôts NiO avait une  $V_{oc}$  et des valeurs de FF presque deux fois inférieures, à celles rapportées à la référence PEDOT: PSS. Ces valeurs indiquent que les NiO présentés ici ont un caractère p faiblement marqué. Une des raisons possibles de la faible efficacité des cellules photovoltaïques peut être attribuée à la contamination des dépôts par les espèces carbonatées. Une autre raison peut être due à une inadéquation des niveaux d'énergie entre NiO et P3HT:PCBM. Enfin, la concentration de porteurs de charge positive dans les échantillons de NiO peut être faible et les couches qui en résulteraient pourraient agir comme des isolants.

Le protocole de synthèse de l'hydroxyde de nickel dans le glycol offre la possibilité d'obtenir une dispersion homogène des particules sous forme de solution colloïdale. La dispersion de particules permet ainsi d'obtenir des dépôts homogènes d'hydroxydes et d'oxydes de nickel. Cependant les couches de NiO résultant montrent de mauvaises performances en tant que matériau de type p dans les cellules solaires organiques hybrides.

## Conclusions du chapitre IV

Dans le quatrième chapitre, le dépôt de films minces d'oxyde de nickel a été mené en plasma réactif en utilisant le nickel métallique comme cible, et un mélange de gaz oxygène/argon. Le dépôt a été effectué pour deux réacteurs ayant des dimensions différentes. Le processus a été contrôlé par un ajustement de la tension de la cathode. Pour les deux réacteurs, la réponse en tension cathodique présente le même profil en fonction de la composition du gaz (oxygène/argon). Le profil unique de tension de cathode a été utilisé pour

trouver des conditions de travail des processus de pulvérisation lorsque le courant de décharge a été changé. La réponse en tension de la cathode a été considérée comme une indication du degré de réaction entre l'oxygène et la cible pulvérisée. Pour le réacteur de laboratoire, en utilisant ce diagnostic, nous avons montré que les films minces déposés présentaient des orientations préférentielles. Selon le profil de tension cathodique, les films minces de NiO ont été orientés selon la direction cristallographique [111] ou [002] (description dans un réseau pseudo cubique). Comme conséquence de l'orientation préférentielle, l'augmentation de l'épaisseur des films entraîne une évolution de la microstructure spécifique. De plus, le profil de tension de cathode nous a permis d'ajuster la stoechiométrie des films déposés. Les échantillons déposés au maximum absolu de tension de la cathode étaient proches de NiO stoechiométrique. Pour chaque décharge particulière de courant, dans la région riche en oxygène, la tension de cathode a chuté vers le bas et du  $\text{Ni}_{1-x}\text{O}$  sous stoechiométrique a été déposé. La stoechiométrie de NiO influe directement sur les propriétés optiques des couches minces. Les échantillons, élaborés dans des conditions où NiO était proche de la stoechiométrie, présentent la plus grande transparence. Les échantillons déposés dans la région riche en oxygène, où la structure de nickel NiO a montré des lacunes en nickel, conduisent à une chute de la transmission de la lumière. Les expériences réalisées à l'aide réacteur industriel ont montré que la croissance cristallographique des films minces de NiO n'est pas seulement liée au profil de tension de la cathode. Les films minces déposés sont caractérisés par une croissance dans la direction cristallographique [111] indépendamment du profil de tension cathodique. En fait, les conditions de dépôt n'étaient pas exactement les mêmes que pour le réacteur de laboratoire. La croissance cristallographique des films minces de NiO est probablement liée à des aspects énergétiques des adatoms. Les principales différences entre les deux réacteurs sont : la distance cible-substrat et le champ magnétique des magnétrons. Ces deux paramètres affectent sensiblement l'aspect énergétique des adatoms. Outre la croissance de la structure cristallographique de NiO, les échantillons déposés dans un réacteur industriel suivent la même tendance en matière de transparence. Dans la région riche en oxygène, les échantillons ont montré moins de transmittance. Les tests des couches minces déposées comme une couche tampon dans les dispositifs photovoltaïques organiques ont prouvé que le film de NiO lacunaire peut agir comme couche de transport de charge de type p. Les meilleures performances ont été enregistrées pour des films minces d'oxyde de nickel déposés dans les conditions riches en oxygène. Pour les films minces de NiO optimisés, l'efficacité de conversion d'énergie sont de l'ordre de 2,6%. Cependant, la durée de vie des dispositifs reste limitée. Les cellules fabriquées ont montré une perte de 20%

de l'efficacité de conversion d'énergie après 24 heures d'éclairage continu. La surface des films minces déposés présenterait de fortes interactions avec les effluents atmosphériques. Ces espèces de surface absorbées peuvent modifier la configuration de la bande électronique du dépôt de NiO et affecter les propriétés de transport de charge des couches minces.

## Conclusions générales

Le concept de cellules solaires organiques contenant des oxydes inorganiques semi-conducteurs est une solution très prometteuse pour prolonger le temps de vie de ces dispositifs. Au cours de ce travail nous avons mis en œuvre le dioxyde de titane et l'oxyde de nickel, comme couches de transport de charge sélective pour les dispositifs photovoltaïques organiques. La configuration théorique de la structure électronique de ces oxydes est en bon accord avec les niveaux HOMO et LUMO de P3HT: PCBM de la couche organique active. Le bon alignement du niveau d'énergie est un facteur crucial pour une collecte des charges efficaces vers les électrodes métalliques. Aussi le gap de ces semi-conducteurs est suffisamment important et donne une opportunité pour l'incorporation de NiO et de TiO<sub>2</sub> sur l'électrode avant transparente, sans perte significative de l'absorption de la partie visible du spectre solaire. Le manuscrit présente la synthèse et les techniques de dépôt de ces deux oxydes semi-conducteurs. Le dioxyde de titane a été élaboré par voie chimique en solution dans des solvants organiques. Les films minces d'oxyde de nickel ont été déposés par deux méthodes: procédé par voie chimique en solution et dépôt physique en phase vapeur. Tout d'abord, le dépôt à partir d'une solution chimique implique la synthèse de l'hydroxyde de nickel qui exige un recuit thermique supplémentaire pour former l'oxyde de nickel. Le deuxième procédé de dépôts de films minces d'oxyde de nickel a été élaboré par pulvérisation réactive. Les propriétés physiques des films minces dépendent fortement du choix du processus de l'élaboration. Par conséquent, l'efficacité des cellules solaires organiques intégrant TiO<sub>2</sub> et NiO comme des couches interfaciales a été affectée. Les films minces de dioxyde de titane ont été obtenus par la méthode sol-gel à partir d'un précurseur de titane hydrolysable tel que « Ti<sub>8</sub>O<sub>12</sub>> ». Trois types de formulation ont été proposés pour stabiliser les solutions colloïdales contenant des nanocristallites de TiO<sub>2</sub>, tout en respectant le cahier des charges de l'impression jet d'encre.

La première formulation impliquait l'utilisation de mélange de solvants tels que l'eau et le carbonate de propylène. En présence du précurseur «  $\text{Ti}_8\text{O}_{12}$  », ces solvants réagissent à la température de  $120^\circ\text{C}$  les uns avec les autres pour former le 1,2-propanediol. La réaction des solvants est importante pour contrôler trois aspects. Premièrement, il permet de préparer des solutions colloïdales de viscosité désirée dans un processus par étapes. Deuxièmement, le solvant réactionnel influe sur la stabilité des particules colloïdales. Troisièmement, il permet d'éliminer l'eau de la solution colloïdale. La présence d'eau est indésirable vis à vis de l'impression jet d'encre. Sa tension superficielle élevée pourrait affecter les propriétés de mouillage des colloïdes. Les meilleures conditions ont été trouvées pour un mélange de solvant de  $R = [\text{H}_2\text{O}]/[\text{PC}] = 0,712$ . Pour ce ratio de solvants, la solution colloïdale est composée de nanoparticules monodisperses et présente une valeur de la viscosité adaptée. Pour un rapport de mélange de solvants différents  $R = [\text{H}_2\text{O}]/[\text{PC}]$  les particules colloïdales s'agglomèrent et les paramètres physiques de la solution ne correspondent pas aux exigences de l'impression jet d'encre. Indépendamment du ratio de  $R = [\text{H}_2\text{O}]/[\text{PC}]$ , les cristaux primaires de particules colloïdales sont de taille proche de 5nm et cristallisent sous forme de  $\text{TiO}_2$  anatase. En raison de la petite taille des particules, les colloïdes sont sensibles à l'exposition de la lumière ultraviolette. Un éclairage prolongé par les UV, sans contact avec l'oxygène, a entraîné une amélioration du degré de dispersion des particules initialement agrégées.

La seconde formulation chimique pour la synthèse de solution colloïdale de  $\text{TiO}_2$  implique le carbonate de propylène, le 1,2-propanediol et de l'eau comme solvant. Dans cette formulation le carbonate de propylène réagit avec l'eau et la présence de 1,2-propanediol, permet d'obtenir les colloïdes bien dispersés dans un large éventail de  $R = [\text{H}_2\text{O}]/[\text{PC}]$  comparativement à la première formulation de synthèse. Cependant, ce protocole de synthèse limite la réaction entre l'eau et le carbonate de propylène. L'eau résiduelle peut affecter les capacités de mouillage des solutions colloïdales.

La troisième formulation pour la synthèse de  $\text{TiO}_2$  colloïdal implique l'utilisation de l'eau et de 1,2-propanediol. Cette composition chimique régit la forte dispersion des particules colloïdales et contrôle la taille des cristaux primaires. Pour les faibles  $[\text{H}_2\text{O}]/[\text{PC}]$ , les particules synthétisées sont proches de 2nm. Pour les ratio plus élevés de  $[\text{H}_2\text{O}]/[\text{PC}]$ , les particules colloïdales ne sont pas homogènes en taille et s'étalent sur une gamme de diamètres allant de 4 à 10 nm.

Pour résumer le rôle de chaque solvant lors de la synthèse de colloïdes, les conclusions suivantes peuvent être formulées. L'eau avec sa constante diélectrique élevée, est nécessaire pour dissoudre les cristaux de «  $\text{Ti}_8\text{O}_{12}$  ». La quantité d'eau affecte les phénomènes de

croissance cristalline. La vitesse d'hydrolyse du précurseur d'oxyde de titane est de l'ordre de quelques secondes ou minutes lorsque le pH est égal à quatre, proche de la valeur du point de charge nulle. En conséquence, un excès d'eau favorise la formation d'un précipité amorphe. Le rôle du carbonate de propylène est d'éliminer l'eau de la solution colloïdale par la réaction d'hydrolyse de l'ester qui conduit à la formation 1,2-propanediol. Le carbonate de propylène a un impact sur la viscosité des solutions colloïdales. Le 1,2-propanediol est un agent de dispersion des particules fraîchement nucléées qui régit la stabilité à long terme des colloïdes à des températures élevées (jusqu'à 120°C).

Les colloïdes de  $\text{TiO}_2$  préparés par les procédés décrits ont été utilisés pour l'élaboration de couches minces pour cellules solaires organiques. Les solutions ont été déposées sur l'électrode avant transparente et ont été testées en configuration inversée du dispositif solaire. Les meilleurs résultats ont été obtenus pour la solution  $R=[\text{H}_2\text{O}]/[\text{PC}]=0,712$ . La cellule solaire organique a montré une efficacité de conversion d'énergie initiale de 3,7% avec une perte de 17% après 6500 heures d'éclairage continu. Le dépôt de  $\text{TiO}_2$  comme couche interfaciale valide le concept de stabilité des cellules solaires organiques.

La solution colloïdale  $R=[\text{H}_2\text{O}]/[\text{PC}] = 0,712$  a été utilisée pour élaborer des films minces par la technique d'impression jet d'encre. Le processus a abouti à des dépôts homogènes sur l'ensemble du substrat ( $5 \times 5 \text{ cm}^2$ ). Les paramètres physiques des solvants ont été correctement ajustés pour la fiabilité du processus d'impression. Les expériences préliminaires ont démontré la compatibilité des colloïdes avec les équipements industriels, mais la propriété légèrement acide peut provoquer des problèmes liés à des phénomènes de corrosion.

Les films minces d'oxyde de nickel ont été préparés par voie chimique en solution par réaction acido-basique de nitrate de nickel ou de chlorure de nickel avec de l'hydroxyde de tétraméthylammonium. Ces réactions sont réalisées en présence de différents solvants tels que le glycol 1,2 propanediol et l'éthylène. L'échange acido-basique permet d'obtenir des particules colloïdales d'hydroxyde de nickel. En fonction de la température de la réaction, la stoechiométrie des hydroxydes diffère. La synthèse effectuée à température ambiante conduit à la formation de  $\text{Ni}(\text{OH})_{1,7}\text{Cl}_{0,3}$  et  $\text{Ni}(\text{OH})_{1,67}(\text{NO}_3)_{0,33}$ , pour l'hydrolyse de chlorure de nickel et de nitrate de nickel, respectivement. La synthèse à 70°C entraîne la formation de  $\text{Ni}(\text{OH})_{1,82}(\text{NO}_3)_{0,18}$ , pour l'hydrolyse du nitrate de nickel. Tels que préparés, les colloïdes ont été purifiés et les sous-produits ont été séparés par sédimentation à l'aide d'acétone et redispersés dans 1,2-propanediol. La procédure permet d'obtenir une solution colloïdale stable



d'hydroxyde de nickel, qui après dépôt cristallise dans une forme  $\alpha$ -Ni(OH)<sub>2</sub>. Lors du protocole de synthèse, la gamme de température influe sur la taille des particules colloïdales d'hydroxyde. Les colloïdes préparés à température ambiante, après redispersion étaient composés de particules de 9 nm. La synthèse à 70 ° C conduit à des particules plus grosses dont le diamètre moyen est de 80 nm.

Afin de transformer l'hydroxyde de nickel en oxyde de nickel, deux traitements thermiques ont été appliqués. D'abord l'un à 120°C afin d'éliminer l'excès de solvants et un second à 400°C pour déshydrater les hydroxydes. L'analyse XPS a montré que l'oxyde de nickel préparé à partir du précurseur Ni(OH)<sub>1,82</sub>(NO<sub>3</sub>)<sub>0,18</sub> contenait du carbure de nickel de pollutions. L'analyse DRX suggère la présence d'impuretés métalliques de nickel dans le cas de l'oxyde de nickel, préparé à partir de Ni(OH)<sub>1,67</sub>(NO<sub>3</sub>)<sub>0,33</sub>. La synthèse de l'hydroxyde de nickel en milieu glycolé provoque des réactions chimiques inattendues. En raison du caractère réducteur des molécules de glycol l'oxyde de nickel peut être réduit en nickel lors du traitement thermique. Comme dans le cas de la synthèse des colloïdes de TiO<sub>2</sub>, le 1,2-propanediol s'avère un solvant efficace stabiliser les particules colloïdales d'hydroxyde de nickel. Les solutions colloïdales d'hydroxyde de nickel ont été utilisées pour l'élaboration de cellules solaires organiques dans une architecture classique. Bien que, les cellules solaires ont montré des résultats insatisfaisants, le meilleur rendement de conversion d'énergie atteint était proche de 1%. La faible performance peut être le résultat de la présence de polluants mis en évidence sur la surface des particules. En plus de la présence de carbure de nickel possible et de nickel métallique à la surface de particules telle que préparée, l'oxyde de nickel a été affectée par la présence d'espèces carbonées. Une autre explication, possible peut être liée aux propriétés semi-conductrices de l'oxyde de nickel tel que préparé. Les rapports bibliographiques suggèrent que l'oxyde de nickel perd son caractère semi-conducteur de type p et devient isolant, lorsqu'il est chauffé à des températures élevées. Peut-être, le processus de recuit thermique doit être optimisé afin de contrôler les propriétés semi-conductrices de NiO.

Les films minces d'oxyde de nickel ont été déposés par pulvérisation réactive de cibles de nickel métal en présence d'oxygène et d'argon comme un mélange de gaz de travail. Le dépôt a été effectué pour trois différents courants de décharge. Le contrôle du processus de pulvérisation a été réalisé par analyse de la tension de décharge. Pour différentes valeurs de courant de décharge, le signal cathodique a donné une réponse caractéristique quand on augmente la pression partielle d'oxygène. En utilisant ce diagnostic, les films minces déposés ont montré qu'ils croissaient avec des orientations préférentielles. Selon le profil de tension cathodique des films minces de NiO sont orientés selon les directions cristallographiques

[111] ou [002]. Comme conséquence de l'orientation préférentielle, l'augmentation de l'épaisseur des films entraîne une évolution de la microstructure spécifique. La tension de cathode de diagnostic a également été utilisée pour contrôler la stoechiométrie des films minces de  $\text{Ni}_{1-x}\text{O}$  et leurs propriétés optiques. La tension de décharge de diagnostic a été appliquée pour contrôler le processus de pulvérisation dans le réacteur industriel de SOLEMS. L'augmentation de la pression partielle d'oxygène dans le mélange de gaz de travail a entraîné une évolution du signal de tension cathodique similaire. Toutefois, la croissance de la structure cristallographique de NiO semble indépendante de la tension de décharge. Les films minces déposés sont toujours orientés selon la direction cristallographique [111].

Les films minces préparés par procédé de pulvérisation cathodique réactive ont été utilisés pour élaborer des cellules solaires organiques dans les architectures classiques. Les cellules ont montrées des performances très faibles pour les films minces déposés à des valeurs relativement faibles et modérées de la pression partielle d'oxygène. Les performances des cellules solaires ont été améliorée significativement lorsque les films ont été déposés à des pressions partielles d'oxygène élevées. Pour ces conditions, l'oxyde de nickel devrait être non-stoechiométrique et présenter un caractère semi-conducteur de type p. Les valeurs les plus élevées de rendement de conversion sont obtenus pour des dépôts ayant une épaisseur de 20nm. Les rendements de conversion sont 2,6% et 1,8% pour l'échelle du laboratoire et dans le réacteur industriel, respectivement. Cependant, ces cellules subissent une dégradation rapide et perdre plus de 20% du rendement initial après 20 heures d'éclairage continu. L'origine de la dégradation rapides peut être liée aux espèces de surface absorbées. L'analyse XPS montre la présence d'hydroxyde de nickel, d'eau et des espèces carbonées. Les articles de la littérature récente ont montré que les propriétés électroniques de NiO sont fortement affectées par l'exposition aux polluants atmosphériques. Les cellules solaires présentées ici ont été assemblés au moins quelques jours après la préparation de l'échantillon et aucun soin particulier n'a été donné à la protection des échantillons de polluants atmosphériques. Le contrôle du traitement de surface et la protection de l'échantillon pourrait être la clé pour l'obtention de cellules solaires organiques stables et efficaces ayant une couche de transport de charge de NiO.





## General introduction

The world energy source is dominated by combustion of non renewable fossils. The vigorous exploitation of fossils was initiated during the 18<sup>th</sup> century by the industrial revolution and it continued up to this day. The rapid development of many domains of the industry has dramatically affected almost all aspect of daily life for every human being. The energy coming from fossils made changes in transports, agriculture, manufacturing, and telecommunication. Despite the industrial aspects, the energy consumption has a profound effect on socio-economic and cultural conditions of these times. However, fossils energy is limited and exhaustion of resources is predicted in few decades. In consequence, alternative sources of energy are urgently needed to maintain standards of way of life, for the future. Nowadays the governments of many countries invest in developing renewable energy sources, which comes from sun light, wind, rain and geothermal heat. This energy is considered as unlimited and cheap. However, the production cost of renewable energy remains too expensive as compared to the fossil fuel energy.

Among renewable energy sources, sunlight is the most accessible in every part of the world. This primary energy can be converted in heat or in electricity via solar thermal collector or photovoltaic (PV) solar cells, respectively. The use of PV solar energy has soared in recent years, with promising developments in many countries.<sup>1</sup> During 2010, the PV market has shown unprecedented growth and wide-spread use of this environmentally friendly and well-distributed source of power generation. On a global basis, new PV installations of approximately 15,000 MW have been added during 2010, taking the entire PV capacity to almost 40,000 MW.<sup>2</sup> Crystalline silicon (c-Si) is the most common and mature technology representing about 80% of the market today. The commercial silicon photovoltaic modules convert 12 to 19 % of the incident sun light into electricity and they can last over 20 years. However, the manufacturing costs of photovoltaic modules causes that the payback period is estimated to last over several years, in favorable climate conditions.

In the last decades, in laboratories, are developed organic photovoltaic (OPV) solar cells. The recent achievements in that field have shown that prototype devices can convert a reasonable part of sun light into electricity. The most promising advantage of organic solar cells is a potentially low manufacturing cost. They can be processed by printing or coating techniques, which permit high volume production on flexible or glass type substrates. For that technology, manufacturing costs is constantly decreasing and they are expected to reach 0.50€/W by 2020. One of the factors which limit the development of organic solar cells is the

stability of organic materials. Nowadays, laboratory scale devices operate for less than 5000 hours and degradation problem arise from number of unresolved issues.

There have been many proposed mechanisms for the decay in OPV efficiency, but most theories agree that the dominant degradation mechanism, in unencapsulated OPVs, is the exposure of the organic-cathode interface to atmospheric oxygen and water. This leads to oxidation and delamination of the metal cathode as well as to chemical reactions within the organic layers. The thesis presents a concept for improving the lifetimes of organic solar cells by incorporation of inorganic semiconductive materials, which allows avoiding organic-metallic interface. The inorganic materials can be deposited as thin films on the metallic electrodes and play a function of selective charge transporting layers. For that purpose, titanium dioxide and nickel oxide were selected as n- and p-type semiconductors, respectively.

The thesis presents the methods for processing thin films of titanium and nickel oxides. Two ways of implementation have been applied. The first one is chemical solution deposition (CSD) which is compatible with ink-jet printing technique and offers low price processing and the second one is physical vapor deposition (PVD), which gives an opportunity for moderate price production.

Before presenting the experimental results, the first chapter gives a brief historical report of the development of organic solar cells. The last achievements in performance, architectures and principle of working are presented. This chapter describes economical aspects, processing techniques and requirements for extending operating lifetimes of organic solar cells. The second part of chapter introduces the concept of hybrid organic solar cell which incorporates inorganic materials. The properties which make titanium oxide and nickel oxide interesting candidates for organic solar cells were summarized. The principles regarding implementation techniques for those oxides are also given.

The second chapter describes the synthesis of colloidal solutions of titanium dioxide nanocrystallites using a laboratory made titanium precursor and organic solvents. The size and crystallographic structure of nanoparticles were investigated by HRTEM and XRD. The stability of colloidal solutions was analyzed by photon correlation spectroscopy and zetametry. The physical properties of colloids were controlled in order to maintain compatibility with ink-jet printing equipment. Thin films were deposited by spin-coating or ink-jet printing and were characterized by SEM, AFM and spectroscopic techniques. The performance of organic solar cells having titanium oxide layers was tested.

The third chapter describes the synthesis of nickel hydroxide colloidal solutions. The colloids were synthesized using organic solvents, two nickel salts and organic base. The deposition and thermal annealing of colloidal nickel hydroxide allows us to obtain nickel oxide thin films. The colloids were characterized in terms of dispersion degree and were optimized for ink-jet printing process. The prepared materials were analyzed in terms of crystallographic structure, morphology and chemical composition. Finally, the organic solar cells having nickel oxide thin films were tested.

The last chapter presents the preparation of nickel oxide thin films by physical vapor deposition technique. The thin films were obtained by reactive sputtering of metallic nickel target using oxygen and argon mixture. The influence of oxygen partial pressure on properties of thin films was analyzed. The experience using laboratory scale reactor was transferred towards the industrial-scale device. The organic solar cells having nickel oxide thin films were tested.

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<sup>1</sup> Renewable Energy Projections as Published in the National Renewable Energy Action Plans of the European Member States, European Environment Agency, ECN-E--10-069, 1 February 2011.

<sup>2</sup> Solar photovoltaic electricity empowering the world, European Photovoltaic Industry Association (EPIA) 2011





# Chapter I: Concept of hybrid organic solar cell

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## Introduction

Currently the polymer organic solar cells constitute an emerging technology, which has shown a rapid progress during the last decade. Promising results are obtained in laboratories, causing industrial interest for large scale production. A main advantage of organic solar cells is their low cost processing. This low cost gives an opportunity for cheaper solar energy. However, the technology of organic photovoltaics still needs to be improved before commercialization. The main problem arises from stability issues. The organic solar cells undergo degradation and they show moderated operating lifetimes. The suspected mechanism of degradation is related to the interface with metallic electrodes which are in contact with the polymeric active layer. One possible way to solve this problem lies in the insertion of interfacial layers to avoid the metallic-organic contact.

In the following chapter, a historical brief overview is given for organic photovoltaics. The materials, principle of working, architectures and problems related with stability of organic photovoltaics are discussed. This chapter presents the marked or market needs and economical aspects which have to be satisfied for the commercialization of organic photovoltaic technology. The fabrication methods, which are currently used and those which are potentially interesting are going to be introduced to the reader. Finally, the problematic of the thesis is explained in details. This chapter presents a concept of hybrid organic solar cells, which incorporates inorganic semiconductive layers of  $\text{TiO}_2$  and  $\text{NiO}$ . The objective is to elaborate photovoltaic modules on a pre-industrial scale and the project involves participation of four partnership units. The role of each unit and goals of the project will be defined. The fabrication methods and requirements for the materials, produced by the collaborative units are given. The properties which make  $\text{TiO}_2$  and  $\text{NiO}$  interesting candidates for organic solar cells are also discussed.

## I.1 Organic photovoltaics devices

### I.1.1 Historical background

The beginning of the development of solar cells is often attributed to the discovery of the French physicist *Alexandre Edmund Becquerel*<sup>3</sup>. In 1839, Becquerel accidentally discovered the photovoltaic effect while experimenting with an electrolytic cell made up of two metal electrodes. He measured a current when platinum electrodes, coated by silver chloride or silver bromide in aqueous solution were illuminated by light. He postulated that certain materials would produce small amounts of electric current when exposed to light. However, *Becquerel's* discovery could not find any practical use and was limited to observation phenomenon. Thirty years later in 1873, the British engineer *Willoughby Smith* published a report about photoconductivity of elemental selenium<sup>4</sup>. In 1876, *William Adams* with his student *Richard Day*, discovered that illuminating a junction between selenium and platinum has a photovoltaic effect<sup>5</sup>. They built a simple device and showed for the first time that a solid material could create electricity.

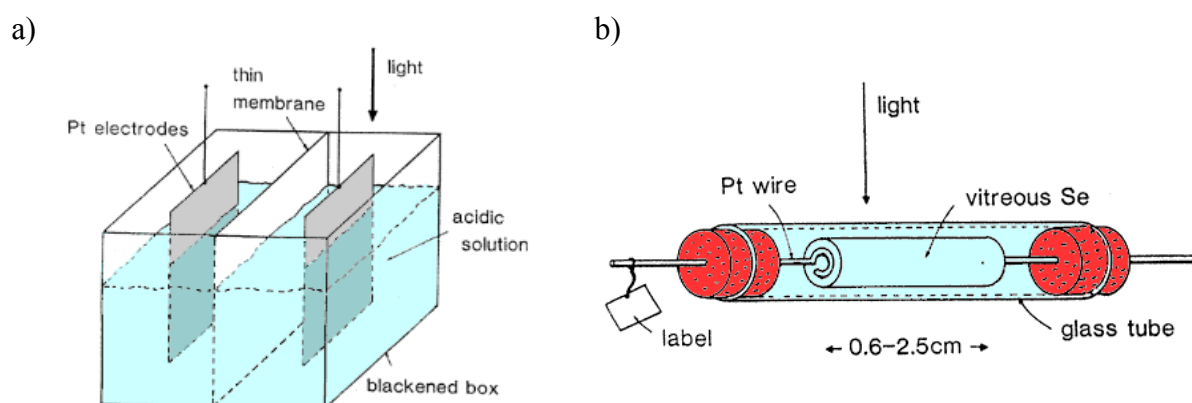


Figure 1. First photovoltaic devices discovered by<sup>6</sup>: a) *Becquerel*, b) *William Adams* and *Richard Day*.

These two discoveries have formed a background for the first solar cell, which resemble the devices we know nowadays. In 1883, the American inventor *Charles Fritts* set up a solar cell, which was made of very thin selenium wafers. He was able to create thin films of selenium by compressing molten selenium on a metal plate (brass). The selenium layer was covered with ultra thin, nearly transparent layer of gold and the device had efficiency less than 1%. *Fritts's*

devices were very inefficient, but they proved the idea of using light as an energy source to produce electricity.

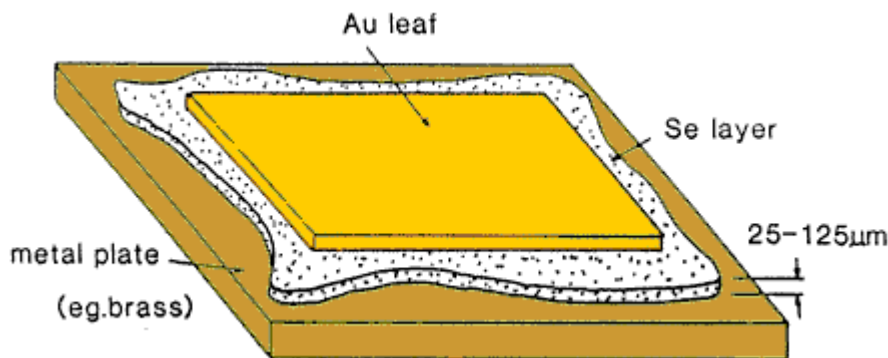


Figure 2. *Fritts's* thin-film Selenium wafer from 1883<sup>6</sup>.

It took several years before scientists truly understood what was going on. The explanation came with the development of quantum theory and understanding of the nature of light. The author of the most comprehensive theoretical work about the nature of light was *Albert Einstein*. He postulated that light is made up of packets of energy, called photons. In 1905 Einstein was able to theorize the phenomenon of photoelectric effect, which was observed previously by *Heinrich Hertz* in 1887<sup>7</sup>. The theory claimed that the energy of photons is sufficient to excite electrons, bound into solids up to higher energy levels where they are moving. The photoelectric effect considered the behavior of electrons in metals, but the theory was revolutionary and explained very well the absorption of photons regarding to the frequency of light. The early solar cells elaborated by *Becquerel*, *Adams* and *Fritts* were devices with semiconductor-metal junction. In semiconductors, when the light is absorbed, the excited electrons are transferred from the low energy states within the material but quickly relaxed back to the ground state. In metal-semiconductor structures, the excited electrons flow through the external circuit due to electronic asymmetry of the junction. The theoretical explanation for metal-semiconductor contact was developed by *Walter Schottky* (Munich, Germany) and *Neville Mott* (University of Bristol, England) in the 1930s. The further development of solar cells was related to the progress of silicon electronics and manufacture of p-n junction. The p-n junction is formed at the boundary of p-type and n-type semiconductors and provides better photovoltaic behavior than at the metal-semiconductor interfaces. The beginning of modern photovoltaic technology is often dated to 1954, when three researchers (*Gerald Pearson*, *Daryl Chapin* and *Calvin Fuller*) at the Bell Laboratories reported a silicon solar cell, which converted sun light with an efficiency of 6%.<sup>8</sup>

The development of solar cells from the beginning was dominated by inorganic materials and organic photovoltaic technology remained in the shadow. The field of organic photovoltaics has started at the beginning of the 19<sup>th</sup> century<sup>9</sup>. In 1906, *Pochettino* and *Volmer* in 1913 observed photoconductivity in solid anthracene. But the real investigation of organic photovoltaics came later in the 1950s, when organic dyes and chlorophyll compounds were studied. In 1958, *Kearns* and *Calvin*<sup>10</sup> found that magnesium phthalocyanine disks coated with a thin film of air-oxidized tetramethyl p-phenylenediamine do show the photovoltaic effect. The junction produced a photovoltage of 200 mV and gave an evidence of electron transfer from magnesium phthalocyanine to tetramethyl p-phenylenediamine. In 1973, *Ghosh* and *Feng*<sup>11</sup> built an organic solar cell by insertion of thin film of tetracene between aluminium and gold electrodes. The device had an open circuit voltage of 0.6 V and power conversion efficiency of 0.0001%. This discovery initiated the development of single layered organic photovoltaics in the 1970s. In single layered organic structures, the organic electronic material (Figure 3) is inserted between metallic electrodes and the photovoltage is due to the difference in work functions of both metallic electrodes. In 1974, *Gosh*<sup>12</sup> improved the photovoltaic device by inserting thin film of magnesium phthalocyanine between silver and aluminium electrodes. The cell conversion efficiency for the white light reached 0.001%. In 1982, *Chamberlain*<sup>13</sup> published a result showing a solar cell with power conversion efficiency of 0.3% for white light. The cell was composed of thin films of aluminium, chlorine-doped merocyanine and gold.

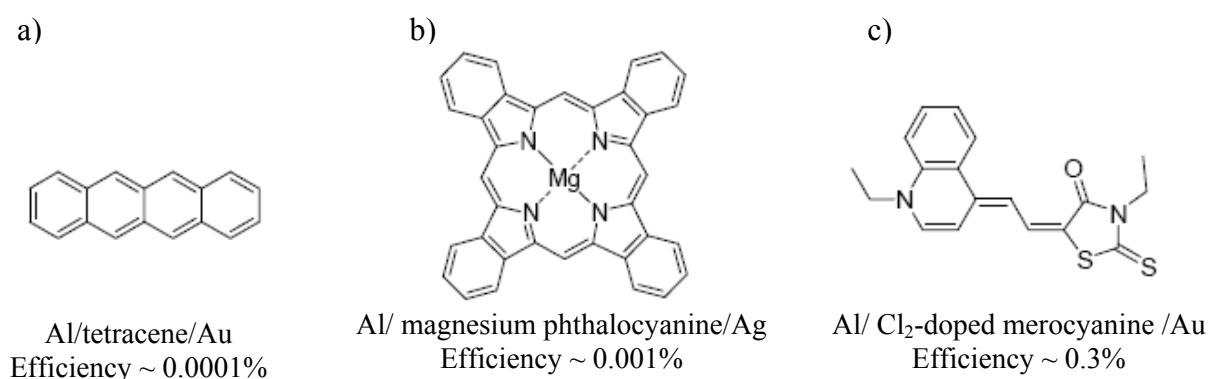


Figure 3. Single layered organic solar cells elaborated by: a) *Ghosh* and *Feng* in 1973, b) *Ghosh* in 1974, c) *Chamberlain* in 1982.

In 1986, *Tang*<sup>14</sup> proposed a new design for organic photovoltaics (OPV) (Figure 4). He fabricated a cell composed of two organic layers: copper phthalocyanine and perylene tetracarboxylic derivative. In such a structure, the photogeneration of charge is weakly dependent on the nature of metallic electrodes but strongly depends on the interface between both organic layers. This solution improved the photovoltaic properties and crossed the barrier limit of 1% for power conversion efficiency. The concept was a breakthrough for the development of organic solar cells.

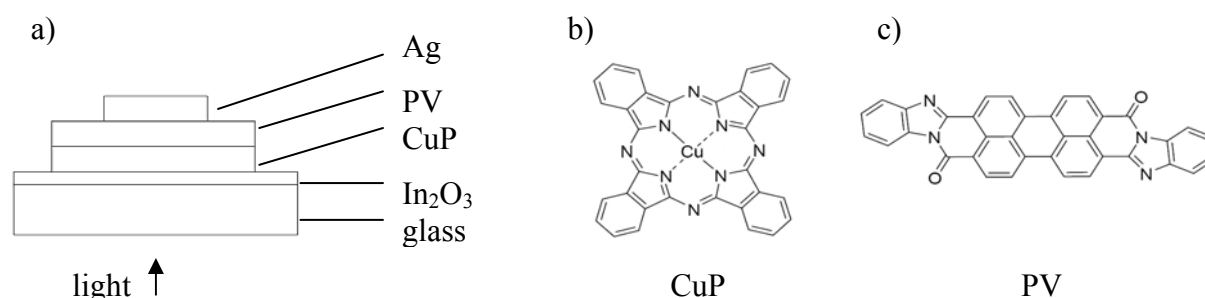


Figure 4. Heterojunction solar cell proposed by *Tang* in 1986: a) cross-section view, b) copper phthalocyanine, c) perylene tetracarboxylic derivative.

In these two layered organic solar cells (heterojunction solar cells), the effective generation of charges occurs only at about 10 nm from the interface between both organic layers. However, for most organic layers, the film should be thicker than 100 nm in order to absorb most of the light. To increase the effectiveness of charge generation in the entire thickness of the active layer, scientists proposed to use dispersed heterojunction. Dispersed (or bulk) heterojunction can be achieved by blending two organic active materials. In consequence the interface contact area between two active layers increases, leading to more efficient charge generation.

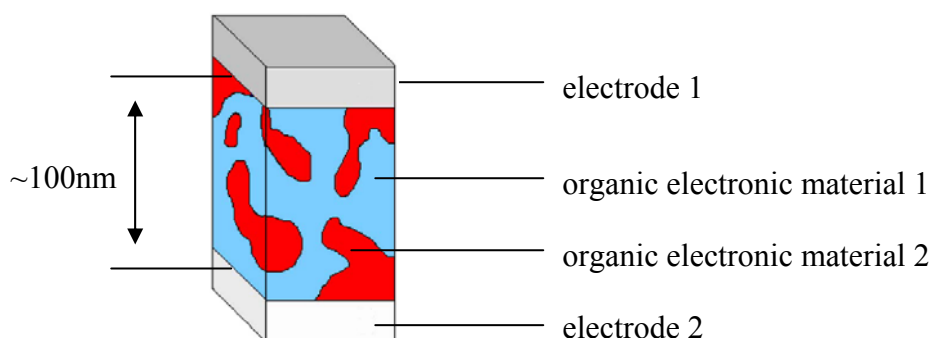


Figure 5. Dispersed heterojunction between two electrodes.

In 1995 Yu<sup>15</sup> published results showing solar cells based on dispersed heterojunction with power conversion efficiency of 2.9%. Further development was focused on the blend composition<sup>16</sup>, network morphology<sup>17</sup> and development of new organic electronic materials<sup>18</sup>. The theoretical limit of efficiency for dispersed bulk heterojunction solar cells is 10%<sup>19</sup>. To overcome this barrier, tandem solar cells are being developed in parallel. In the tandem cell, two organic cells are connected in series allowing an increase in the open circuit voltage to twice that of a single device. For tandem design, the theoretical limit of efficiency is 15%. Beside the theoretical values, the best certified results of 8.13% for single layer bulk heterojunction was reported in July 2010 by Solarmer Energy Incorporation. In November 2010, Heliatek and Institute of Applied Photophysics have reported a certified efficiency record of 8.3% with tandem structure. More recently, a single-junction organic photovoltaic solar cell with a surface area of one square centimeter has been demonstrated by Konarka Technologies to have 8.3% efficiency.<sup>20</sup> The laboratory results are still far from theoretical values, but taking into account the vigorous development (Figure 6) which took place since 2001, the organic solar cells are very promising and might be a competition for traditional crystalline silicon solar cells, which nowadays represent around 90% of the world photovoltaic market<sup>21</sup>.

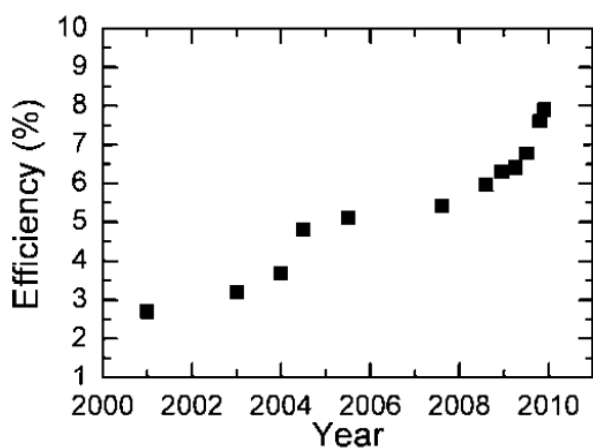


Figure 6. Efficiency evolution of best research in organic solar cells from 2001<sup>22</sup>.



### I.1.2 Principle of working

The process of converting light into electric current in an organic photovoltaic cell is composed of four steps:

- absorption of a photon leading to the formation of an excited state, the electron-hole pair (exciton),
- excitons diffusion to the dissociation site,
- charge separation and creation of free charge carriers (electron and holes),
- charge transport to the anode (holes) and cathode (electrons).

The absorption of photons by an organic material leads to excitation of the electron from the highest occupied molecular orbital, HOMO (equivalent to the valence band in bulk inorganic SC) to the lowest unoccupied molecular orbital, LUMO (conduction band) and leaves behind a localized hole. This process does not directly lead to the creation of free electric charges. The generated electrons and holes are attracted together by columbic interactions and create so-called excitons. In order to dissociate the electron-hole pairs, a build-in electric field is needed. This might be achieved in the sharp drop potential region at the donor-acceptor or metal-semiconductor interfaces, depending on the architecture of the photovoltaic device. In modern architectures (bilayer or bulk heterojunction) the dissociation of excitons is realized at the donor-acceptor interface. The concept of donor-acceptor is illustrated in Figure 7.

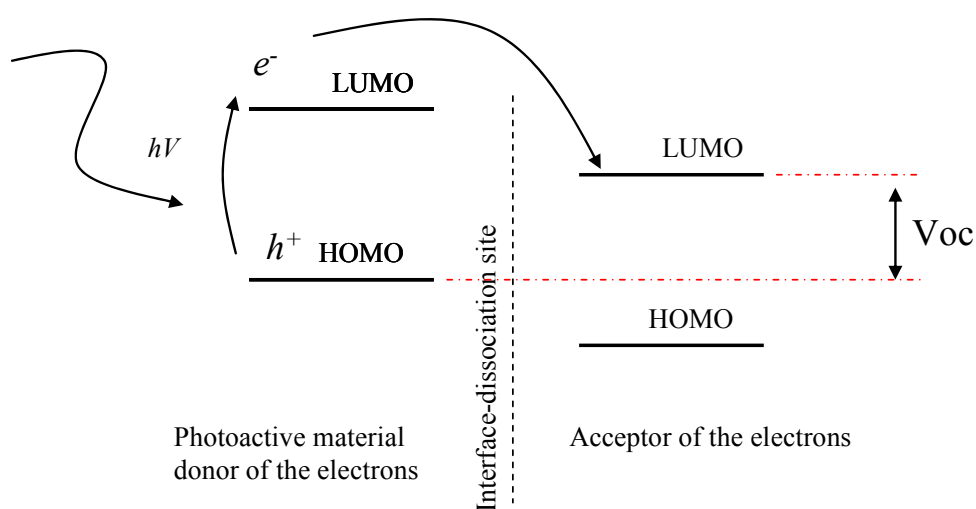


Figure 7. Energy diagram of excitons dissociation (HOMO-highest occupied molecular orbital, LUMO-lowest unoccupied molecular orbital,  $V_{oc}$ -open circuit voltage).

Donor and acceptor materials have different energy levels (HOMO and LUMO). At their interface, a dissociation of the excitons is achieved by a transfer of the excited electron from the higher energy level of the donor to a lower energy level of the acceptor, which is energetically preferential. For the bulk heterojunction devices, the energy difference between charge transporting states strongly affects the open circuit voltage of the solar cell. Generally, the difference between HOMO of the donor and LUMO of the acceptor is a limit for the measured open circuit voltage.

After charge separation, the electron and hole should be effectively transported to the electrodes. Metallic electrodes have to be selected with respect to their work functions. To collect the electrons high work function materials are favorable and low work function material to collect the holes.

### **I.1.3 Donor-acceptor materials used for organic solar cells**

The active materials used for organic photovoltaic cells can be polymers, oligomers or small molecules. These materials are  $\pi$  conjugated systems and they are often referred as organic semiconductors. They have to absorb the photons in the visible range of the solar spectrum in order to create charge carriers. The organic materials must be able to transport electrons to one of the electrode and holes to the other one. These materials are classified as electron donors and electron acceptors.

Most of the semiconductive polymers are hole conductors and called donors. For electron acceptors polymers and small molecules are frequently used. Up to now, the best electron acceptors are derivatives of fullerene molecules. The Figure 8 shows some examples of donor and acceptor materials used for organic solar cells.

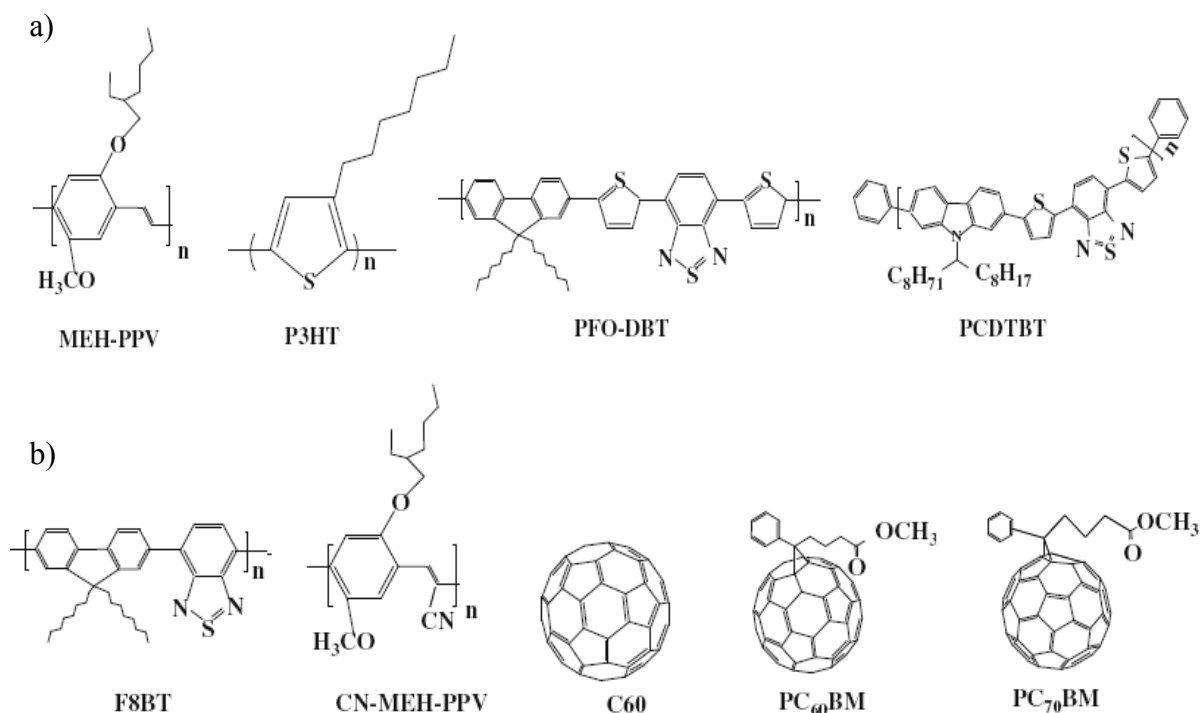


Figure 8. Example of organic semiconductors used in polymer solar cells<sup>23</sup>: a) donors, b) acceptors.

One of the most frequently used and investigated donor-acceptor couple in the bulk heterojunction solar cells is a blend of poly (3- hexylthiophene) (P3HT) and [6, 6]-phenyl-C(61) butyric acid ester (PCBM). The advantage of that blend is its facility in self-organization of P3HT polymer with PCBM molecules<sup>24,25</sup>. Additionally, relatively high values of efficiencies, up to 5%, have been reported for optimized systems<sup>26</sup>. The blend of P3HT:PCBM as thin film has a broad absorption spectrum (Figure 9) in the range of 400-650 nm, with a band gap of approximately 1.8eV<sup>27</sup>.

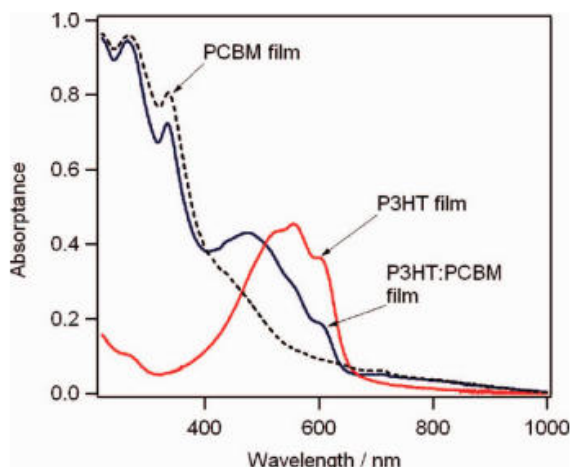


Figure 9. Absorbance spectrum of P3HT film, PCBM film, and P3HT:PCBM film (1:2 w/w).<sup>27</sup>

This characteristic feature partially matches with the solar emission spectrum. The absorption of wavelengths limited to 650 nm gives an opportunity to collect about 20% of the solar photons<sup>28</sup>. The blend of P3HT:PCBM will be used for the hybrid solar cells described in this work.

#### I.1.4. Interfacial layers for organic solar cells

In the bulk heterojunction solar cells, the active layers are inserted between electrodes with different work functions. The bulk heterojunction arrangement facilitates the excitons to reach the donor-acceptor interface to form electron and holes. However this configuration may favour charge recombination and chemical reactions may also occur at the organic/electrode interface. These problems can be solved by insertion of interfacial layers. A commonly applied modification of the cathode is the deposition of a very thin LiF layer between the metal electrode and the organic semiconductor to improve the electron transfer. To facilitate the transport of the holes, the highly conductive PEDOT:PSS is deposited in contact with the anode. However, the use of PEDOT:PSS remains problematic because of its corrosive properties ( $\text{pH} < 1$ ). The insertion of interfacial layers often improves the initial performance of solar cells but these layers have short time stability, leading to some degradation of the cell performance with time.

### **I.1.5. Lifetime and degradation of organic solar cells**

In the history of organic solar cells, the main effort was focused to improve the power conversion efficiencies, but less importance was given to stability issues. Nowadays, the organic solar cells convert a reasonable part of solar spectrum, which make them potential candidates on the photovoltaic market. However, silicon based solar cells may last up to 25 years at least, thus the lifetime of organic solar cells must be improved to be technologically interesting.

The first early reports for stability of organic devices came in the 1990s (Figure 10). At that time, the lifetime of OPV was in the range of hours and the degradation mechanism was not well defined. Nowadays, there is a rough division between chemical and physical degradation studies. The physical degradation considers the reorganization of the materials over time period or at elevated temperatures. In bulk heterojunction devices, the cell performance depends on the microstructure arrangement of the donor-acceptor network. It is now clear that this structure is not static once it has been formed. Small organic molecules like PCBM and polymers like P3HT may still have some freedom to diffuse slowly or reorganize over time especially at elevated temperature<sup>34</sup>. The chemical degradation is ascribed to several aspects. The first one includes diffusion of oxygen and water towards the organic active layers<sup>29</sup>. For example, it was found that in fullerene thin-films, oxygen degrades the carrier mobility by several orders of magnitude<sup>30</sup>. It was also found for P3HT that oxygen exposure increases the number of trap sites and decreases the charge carrier mobility.<sup>31</sup> The mechanism of degradation by oxygen is not clear but it is also suspected to induce photochemical reactions implying the polymers<sup>34</sup>. Another problem is the degradation of the electrodes. One of the most frequently used layers to improve the hole conduction is the commercially available PEDOT:PSS conductor. It is highly hygroscopic and acidic in the presence of absorbed water and it causes etching of the ITO electrode<sup>32</sup>. On another hand, the cathode material usually involves low work function materials, which are easily oxidized by oxygen and water. The oxidation products destroy the ohmic contact at the organic-metallic interface and they affect the performance of the solar device. It was reported that the nature of the cathode material strongly affects the lifetime of the organic solar cells<sup>33</sup>.

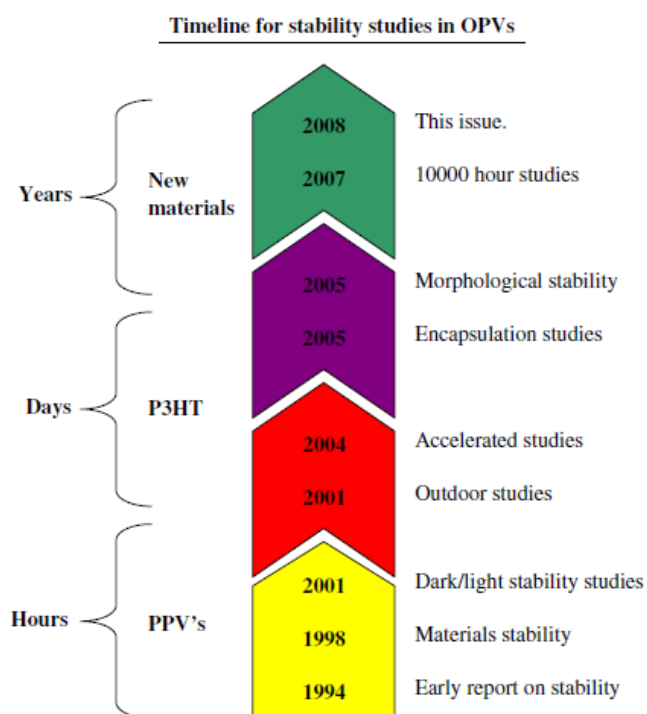


Figure 10. A graphical overview of the field of stability and degradation of polymer solar cells. The lifetime under atmospheric conditions and the typical material is estimated on the left-hand side<sup>34</sup>.

Currently, the lifetime of organic devices lies in the range of months<sup>35</sup>. The improvement in stability was mainly achieved by encapsulation methods<sup>36, 37</sup>, modification of the architectures of the devices and insertion of various interfacial layers between electrodes<sup>23</sup>. Among those studies, one promising solution is the use of interfacial layers. The suggested function of those layers is the protection of the organics from the metallic electrodes, as well as the modification of the work function of the metal. In addition, buffer layers also improve the stability of the solar cells by preventing the diffusion of oxygen and/or water vapour into the device<sup>38</sup>.

The most convenient and simplest method to examine the lifetime of the solar cells is to plot the cell power conversion efficiency as a function of time. The power conversion efficiency is directly related to the other parameters like  $V_{oc}$ ,  $I_{sc}$ , FF and it reflects how the cell degrades. In a standard architecture employing P3HT/PCBM blend, organic hole transporting layer as anode and metal (Ca/Al) cathode, the typical profile for the efficiency loss can be divided into two regimes (Figure 11). The first region is called burn-in period. The efficiency follows there an exponential decay. It is considered as an ageing of the device. This

loss in efficiency varies in time and magnitude depending on the polymer system. The burn-in period is followed by a nearly linear loss in efficiency. That region is considered as a cathode ageing and interface degradation. The lifetime is defined by the point at which the efficiency has dropped by 20% from the start of the linear decay period<sup>39</sup>.

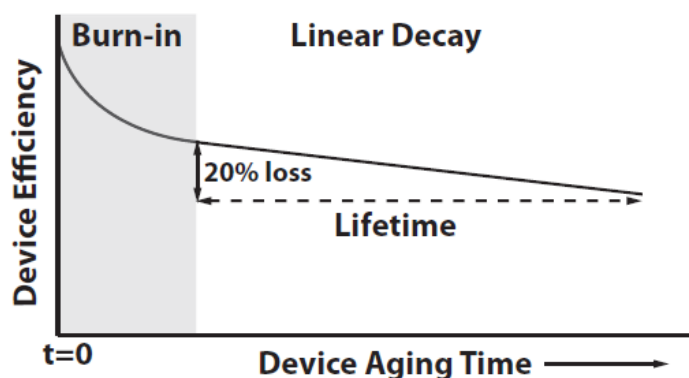


Figure 11. Typical decay curve of power conversion efficiency for polymer solar cell<sup>39</sup>.

Since the lifetime of organic photovoltaics is extended to the orders of months some methods were applied for accelerating the degradation phenomenon. One of the most common methods is the ageing of the device at elevated temperatures. For example, the ageing of the cell in the standard architecture (ITO/PEDOT:PSS/P3HT-[60]PCBM/Al) at 60°C was found to accelerate the degradation by a factor of 6 in ambient atmosphere<sup>40</sup>. The degradation of the solar cells is strictly affected by chemical and photochemical processes which vary with temperature and ambient atmosphere. From that reason, evaluation of the lifetime measurements should be some how standardized in order to compare the results obtained by different research groups. For that purpose the importance should be given to:

- the incident light intensity and the spectrum of the incident light,
- the temperature during the experiment,
- the atmosphere (i.e. humidity, oxygen content, glove box, vacuum, encapsulation method).

#### **I.1.6. Market needs**

The factors which determine the economical aspects of solar energy includes the manufacture costs, lifetime and efficiency of the photovoltaic devices. Practically, the competition between different photovoltaic modules is based on the price which has to be

paid for delivering a certain amount of power. The unit which is often used to express the “economical attractiveness” is the power costs as function of cell efficiency,  $\$/W_p$  (dollar per Watt<sub>peak</sub>).<sup>41</sup> This evaluation does not take into account the efficiency per surface area of modules and the lifetime of the devices. Currently the silicon based photovoltaic modules cost above  $2\$/W_p$  (Figure 12) and operate over 20 years with power conversion efficiencies up to 20%.

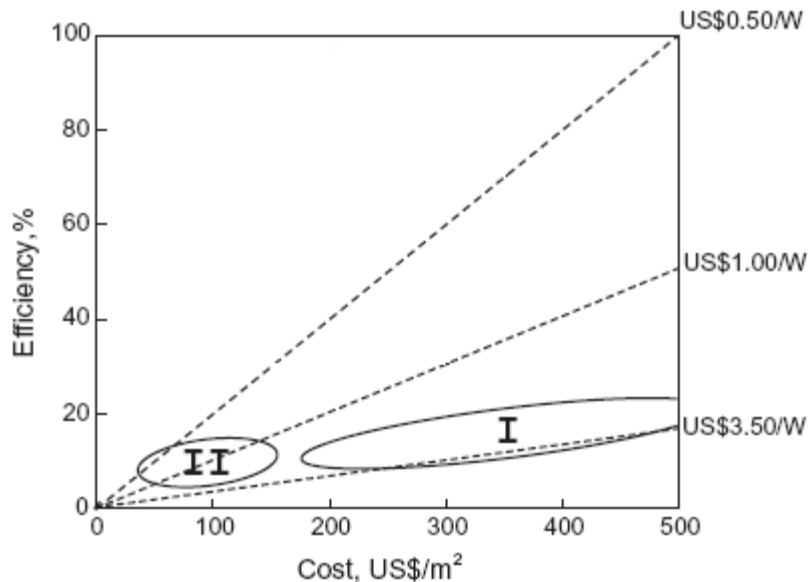


Figure 12. Photovoltaic power costs as function of cell efficiency and module cost: Zone I - commercial available photovoltaics (Silicium); zone II – CIGS, CdTe, DSSC and solution processable organic photovoltaics<sup>42</sup>.

The price of  $2\$/W$  makes the silicon-based photovoltaics the most expensive source of electricity on the energy market. The vigorous development of organic solar cells attracts more and more attention because of their potentially low production costs and quite reasonable predicted efficiencies (10-15%). The values of efficiency are still lower than for silicon devices. However their predicted processing costs may yield in lower price per Watt ( $\sim 0.5\$/W$ ). This economical balance allows obtaining cheaper energy but utilizing the accessible surface area in a less effective manner. However, to satisfy the market needs the lifetime of organic devices should be extended to the range of years.

The requirements for the lifetime strongly depend on the potential application. The photovoltaic market can be roughly divided into two categories: the consumer and professional market. The consumer market concerns the mobile devices which are used in daily life and for which the energy demand is low<sup>43</sup>. For example: the list can enclose small devices such as watches, radios, thermometers, calculators, LCD displays, sensors, mobiles



phones, TV remote controls, computer keyboard and mice. Those devices are produced in a high scale, they have a relatively low price and the price competition between manufactures is high. The average usage time for consumer electronics is usually limited to 5 years. In that segment of market, the organic photovoltaics have a strong potential, because of the compromise between low price, low power demand and moderate lifetimes. The professional market considers the energy production (solar cells installed on buildings or roofs). In that case, the efficiency as well as long operating times is important. In this segment, the lifetime of solar cells should exceed the 5-10 years, not only because of pay-back time but also due to practical aspects related to the exchange of modules.

### **I.1.7. Processing methods**

Organic solar cells are composed of several layers and almost each layer can be obtained by solution derived film-forming techniques. The solution derived techniques have been extensively explored for paper, polymer, and textile industries. They offer high volume production and low price, which makes the organic solar cells economically attractive on the energy market. The wet film-forming methods can be divided on printing or coating techniques. Basically the mean of printing indicates that a complex pattern can be formed in 2-dimensions. Printing techniques include: screen printing, pad printing, gravure printing, flexographic printing and offset printing. Coating techniques are considered to have abilities to form less complex patterns and control the film formation in 0-dimension (no ability to create patterns) or 1-dimension (stripped patterns can be formed). Coating techniques include spin-coating, doctor blading, casting, spray coating, slot-die coating, curtain coating, slide coating and knife-over-edge coating. Based on that classification, only jet-printing can be included into both printing and coating techniques. It offers complex patterning as well as formation of continuous films<sup>44</sup>.

The field of organic solar cells in laboratories was developed mainly with spin-coating technique. The method is based on applying a solution onto an horizontal disc in rotation, which after acceleration (with a controlled speed) results in ejection of the excess liquid and only a thin film remains on the substrate. Alternatively the solution may be applied to the spinning substrate. The adhesive forces at the liquid/substrate interface and the centrifugal forces acting on the rotating liquid result in strong shearing of the liquid and radial flow<sup>45</sup> (Figure 13).

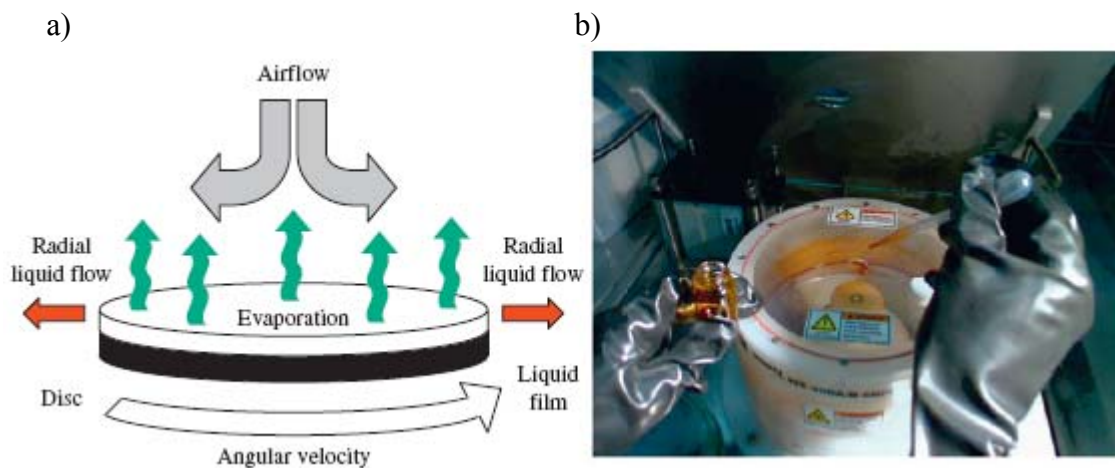


Figure 13. Illustration of the spin-coating technique<sup>44</sup>: a) schematic view, b) image.

The technique allows one to obtain highly uniform film thickness over the planar area (up to  $\varnothing \geq 30\text{cm}$ ) with a good reproducibility of the thickness. The relation for film thickness  $d$  is given by the empirical formula:  $d = k\omega^\alpha$ , where  $\omega$  is the angular velocity,  $k$  and  $\alpha$  are empirical constants related to physical properties of the solvent, solute and substrate<sup>44</sup>. The method can be applied to inorganic and organic solution mixtures. The disadvantage of spin-coating technique is related to the limited surface areas and significant wastes of materials, which are ejected from the surface. On another hand, the spin coating allows only 0-dimensional control of the created film pattern.

The organic solar cells are layered structures and from the point of view of stacking the components one onto another, the coating techniques without pattern abilities could pass the requirements. This is because there is no need for aligning one component in respect to another one. The organic cells are usually composed of stacking of: metal electrode/organic layers/transparent electrode. The problem is coming from the relatively high resistance of transparent electrodes. Zero-dimensional techniques (e.g. spin-coating) are applied for construction of small devices for which sheet resistive loss is negligible. The production of larger devices requires for example preparation of long narrow strips of active layers or the network patterning for metallic contacts, which can compensate the resistive losses and enable to connect the individual cells into modules. From that reason, the deposition of components is favorable in 2-dimensions.

One of the techniques offering complex pattern formation is ink jet-printing (Figure 14). The ink-jet printing technique becomes more and more popular because of the

commercialization of devices which remain compatible with many organic solvents. That popularization was achieved by fabrication of ceramic printing heads which are resistant to many ink formulations, giving large opportunities for experimentalists<sup>44</sup>.

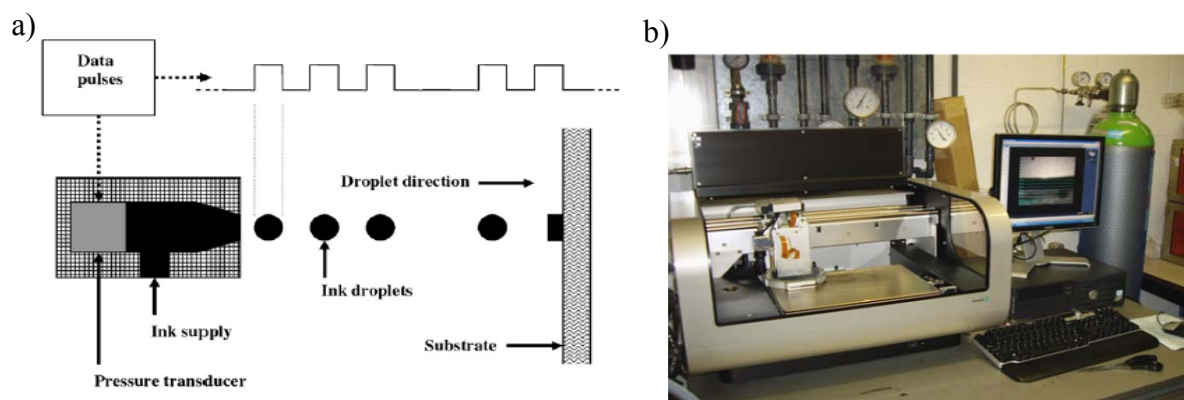


Figure 14. Illustration of the ink-jet printing technique<sup>44</sup>: a) schematic view, b) image

It can be used for printing on flexible, plastic as well as rigid glass substrates. The working principle is based on the generation of pressure waves in a channel filled with fluid or behind it. The pressure waves can be generated either thermally or piezo-electrically<sup>46</sup>. The fluid is normally retained in the channel due to surface tension at the fluid/air interface, but the action of pressure waves overcomes the surface tension and pushes away the fluid from the nozzle, causing droplet formation. The critical values of pressure mainly depend on the rheological properties of the fluid, the dimensions of channels and nozzles. The vapour pressure, boiling point, and surface tension of the inks are critical parameters for ink-jet printing technology<sup>47</sup>.

The printers have a high resolution limits up to 2880 dpi<sup>48</sup> (dots per inch) which means patterning abilities on the micrometer scale. Usually, printing technique is applied for the formation of 2-dimensional patterns; however 3-D structures can also be formed (Figure 15). In addition, manufactures of modern devices offer the possibility to heat up the substrates or the printed fluid, which allows one to tune the physical parameters of the ink and this leads to improve the fluid wetting on various types of substrates<sup>48</sup>.

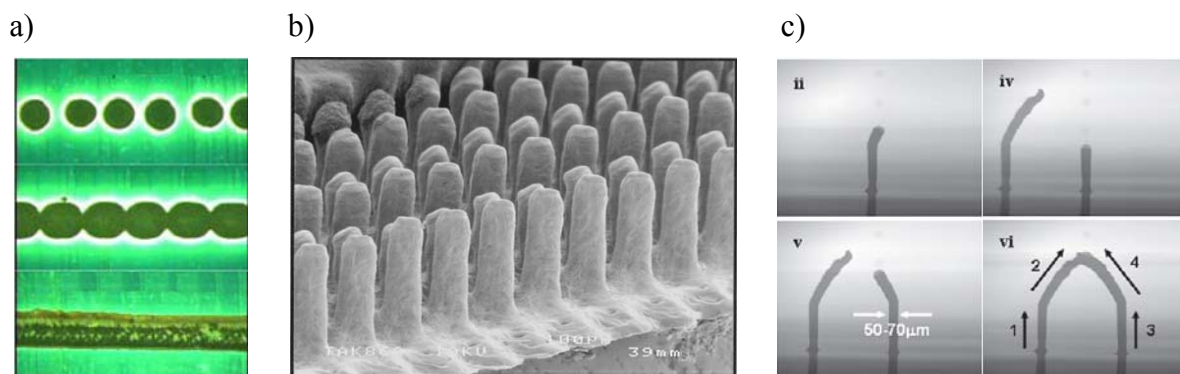


Figure 15. Examples of ink-jet printing: a) silver contact<sup>49</sup> (diameter of the droplet 160  $\mu\text{m}$ ), b) pillars of lead zirconium titanate<sup>50</sup> (height of 400  $\mu\text{m}$ ), c) micro bridge made of gold<sup>51</sup>.

Ink-jet printing technique can be applied for printing all the components of organic solar cell including ITO transparent electrodes<sup>52</sup>, organic active layers<sup>47</sup>, metallic connectors and gives an opportunity for scaling-up organic solar cells having various architectures.

The economical aspect of scaling-up the production is often identified with roll-to-roll (R2R) technology. Roll-to-roll concept is based on the continuous fabrication of each component while the substrate is moving. The substrate is of a long sheet presenting some mechanical flexibility. During the process of printing or coating, the substrate is moving through several rolls on which the components are deposited. Figure 16 shows the schematic representation of the process for a standard architecture of organic solar cell employing ITO/PEDOT:PSS/P3HT:PCBM/Ca/Al.

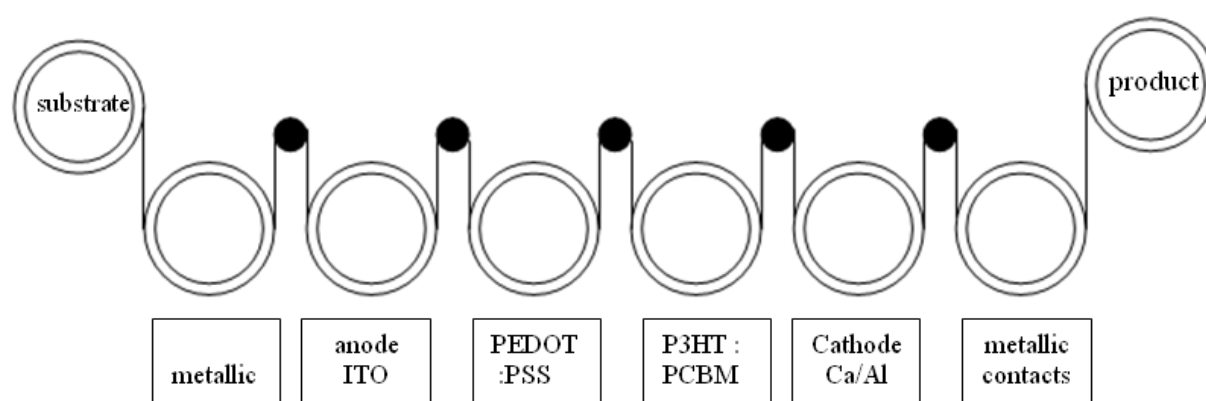


Figure 16. Process steps for roll-to-roll manufacturing of organic solar cells.

The R2R process is regarded to be cheap, fast and various deposition techniques can be employed for each deposition step. However up to know, it is not clear yet which technique is

the most suitable for processing of organic solar cells and efforts are being done to obtain the best performance for devices bigger than those prepared at the laboratory scale.

## **I.2 The hybrid organic photovoltaic**

### **I.2.1 Concept of hybrid organic solar cell**

The fast degradation of organic solar cells is obviously related to atmospheric pollutants (oxygen and water), which penetrate the cells structure causing irreversible damage of the components. The mechanism of degradation is still not clear but it is suspected that detrimental reactions may also occur at the organic-metal electrode interfaces. One of the solutions to understand the degradation mechanism and dissociate the role of atmospheric pollutants from metallic-organic interface is to insert interfacial layers. The experiments have shown that deposition of interfacial layers can improve the performance of photovoltaic devices<sup>53</sup> ( $V_{oc}$ ) and also prevent the reaction from occurring at the interfaces<sup>54</sup>.

The main condition for interfacial layers is to control their ability to transport the charge carriers towards the right electrodes. To achieve this, the cathode surface is modified by n-doped and the anode by p-type doped semiconductor. This concept is valid for organic as well as for inorganic materials. The cells incorporating inorganic interfacial layers are called hybrid systems. The recent trend in research involves inorganic interfacial layers<sup>55</sup> because these are considered to be more stable than the organic ones. The most frequently used are for p-type:  $MoO_3$ ,  $V_2O_5$ ,  $NiO$  and for n-type:  $ZnO$ ,  $TiO_2$ .

The concept of sandwiching the active layer between differently doped semiconductors is described as P-I-N (classic) or N-I-P (inverted) architectures, where P is p-type semiconductor, I is intrinsic and N is n-type semiconductor (Figure 17).

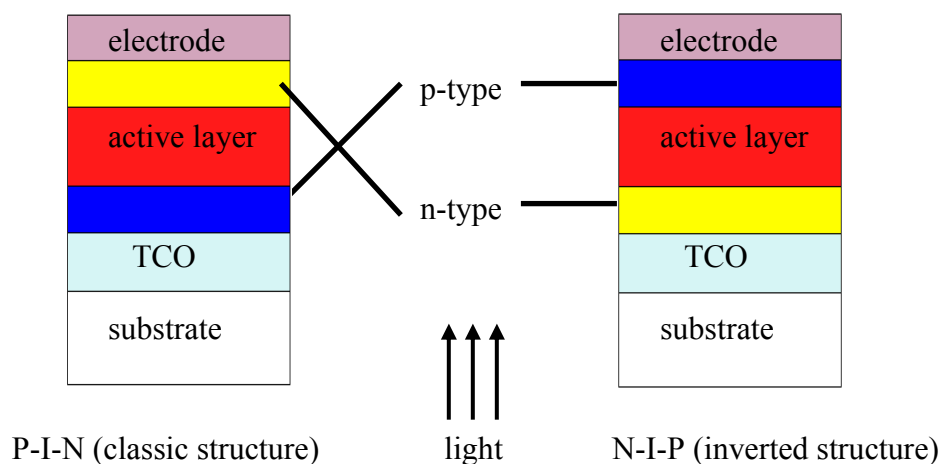


Figure 17. Schematic illustration of P-I-N and N-I-P architectures for organic solar cells.

The difference between these two types lies in the sequence in stacking the semiconductors on the transparent conductive substrate. For P-I-N architecture the p-type semiconductor is deposited on TCO electrode while this is the n-type for N-I-P structure.

The oxides used as interfacial layers are usually wide band gap semiconductors. The wide band gap is especially required when the interfacial layer is deposited on the front electrode (TCO) and access of visible photons to the active layer is necessary. The interfacial layers play a dual role: they selectively transport only one kind of charge carriers while blocking the other one to access the electrode. The phenomenon is achieved by proper alignment of energy levels (VB and CB) of oxides with respect to the organic molecules ones (HOMO AND LUMO). The interfacial layers which prevent the charge transport only in one direction are called buffer layers.

For the work presented in the thesis,  $\text{TiO}_2$  and  $\text{NiO}$  were selected as buffer layers for organic solar cells, having as absorber, standard polymer bulk heterojunction of P3HT:PCBM blend. The cells will be tested in terms of stability by insertion of  $\text{NiO}$  for P-I-N architecture and  $\text{TiO}_2$  for N-I-P structure. The separate tests allow one to examine the degradation occurring on both electrodes and validate the concept of stable hybrid organic solar cells.

The ideal case, where degradation on both electrodes will be suppressed by  $\text{NiO}$  and  $\text{TiO}_2$  buffer layers, gives also an opportunity for integration of semitransparent modules. The ideal structure (Figure 18) can be encapsulated by two transparent electrodes and implemented for windows application.

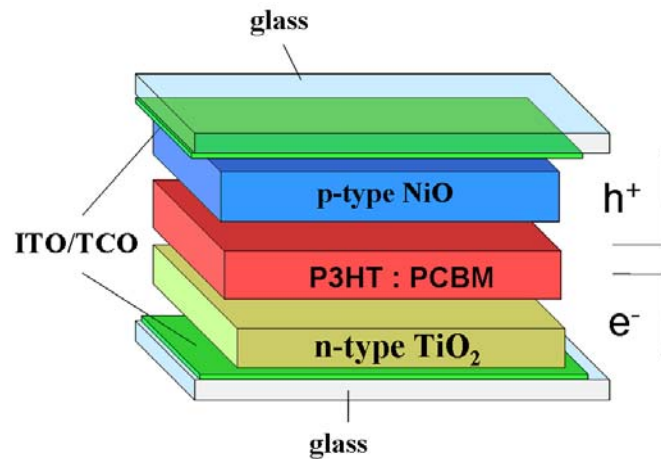


Figure 18. Concept of semitransparent hybrid organic solar cell.

### I.2.2 Objectives of the Solhypin project

The work presented here is part of an ANR- project Solhypin lasting from 2008 to 2011. The project predicts implementation of two different techniques for deposition of  $\text{TiO}_2$  and  $\text{NiO}$  semiconductive thin-films. One involves wet processes based on sol-gel chemistry in order to adopt deposition by ink-jet printing technique. And the second one is less challenging: vapour deposition to satisfy the requirement of mild conditions. The best technique will be used at the right place in the elaboration process of the multilayer organic solar cells. The objective of Solhypin is to produce photovoltaic modules of  $100 \text{ cm}^2$  active area which demonstrates a degradation less than 20% over 5000 hours under continuous illumination, starting with a power conversion efficiency as high as 3.5%.

### I.2.3 Partnership units and fabrication methods

The ANR-Solhypin project involves participation of four partnership units:

1. Institut des Matériaux de Nantes (IMN)

The goals for IMN are to produce stable colloidal solutions, which after deposition process will create p-type  $\text{NiO}$  and n-type  $\text{TiO}_2$  semiconductive layers. The colloidal solutions have to be compatible with the ink-jet printing technique and pass the requirements defined by the industrial partner (ARDEJE). The second goal is dedicated to deposition of  $\text{NiO}$  thin films by physical vapour technique in the

laboratory scale reactor and to explore preliminary conditions for the industrial partner (SOLEMS S.A.).

2. ARDEJE

ARDEJE is a fluid jetting industry, in charge of deposition all components of the hybrid organic solar cell by-ink jet printing technique. The deposition includes: colloidal solutions prepared at IMN, organic active layers (P3HT:PCBM), hole transporting layers (PEDOT:PSS) and metallic current collectors (silver).

3. Solems S.A.

Solems is a manufacturer of silicon-based solar cell elaborated by PVD techniques. In the Solhypin project Solems is in charge of deposition of NiO thin films elaborated in an industrial scale reactor.

4. CEA-INES

CEA-INES is the coordinator unit for the project. CEA-INES is in charge of testing new materials for organic solar cells, produced by the three previously mentioned units. CEA-INES will optimize the deposition conditions for each layer to explore the best performance of solar cells incorporating inorganic semiconductors.

The manuscript presents part of the work which was elaborated by the IMN, but it also summarizes the main results obtained during collaboration with all participants.

#### **I.2.4. Requirements for printing of colloidal solutions**

In general, ink properties have to match to each particular printer device. The requirements given by the industrial partner are listed below:

- viscosity at printing temperature between 8-15 cP,
- surface tension between 25-35 mN/m
- boiling point of the solvent above 120°C
- pH as close to neutrality as possible
- particle size below 1µm in a stable dispersion.

The viscosity of the solvent determines the fluid flow in the narrow capillaries of the printer. It should be in the range, which allows refilling of the channels on time for a continuous delivery of the droplets. The surface tension is important for two reasons. It affects the droplet formation during the printing process and this parameter is responsible for the



formation of the so-called satellites (Figure 19), when the fluid evolves into spherical drops connected by thin fluid filaments. These smaller satellite droplets are detrimental to the deposit quality. The surface tension cannot be too low because it may prevent formation of stable droplets and this also leads to some ink wetting around the nozzles. Secondly, the surface tension also impacts the behaviour of the droplet when they reach the substrate. Too high surface tension may cause dewetting and accumulation of the liquid in some domains of the substrates, causing unhomogeneity of the deposit.

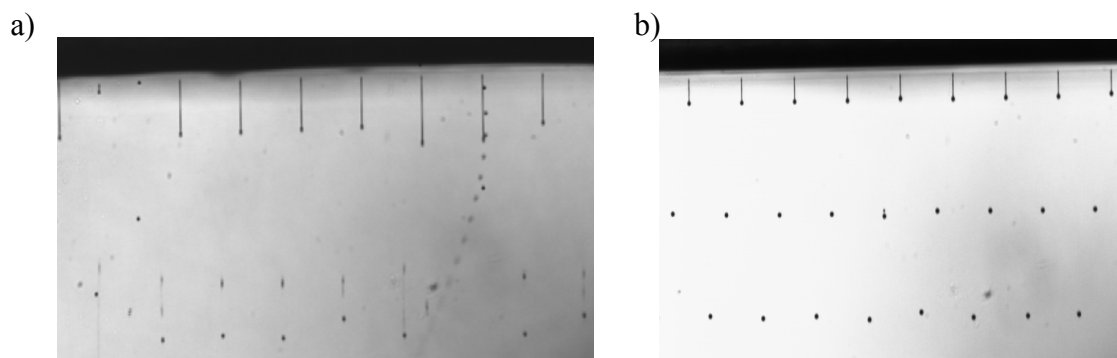


Figure 19. Stroboscopic photographs for the formation of the droplets during printing process: a) formation of so-called satellites, b) formation of well defined droplets. images taken by ARDEJE.

The boiling point (vapour pressure) of the solvent has to be high enough to prevent from eventual evaporation of the small droplets, which are ejected from the nozzles, before they reach the substrate. The pH of the ink is supposed to be as close to neutral as possible to avoid corrosion of printing equipment but also ink should not react with substrates (transparent conductive electrodes or polymers). The last parameter is the maximal size of colloidal particle or aggregates which should not exceed  $1\mu\text{m}$  to avoid clogging of printing nozzles and capillary channels.

## I.3 Properties of titanium dioxide as a transparent n-type charge transporting layer

### I.3.1 Differences polymorph of titanium dioxide for organic solar cells

At the present day, titanium dioxide crystallize as 11 polymorphic forms. Four of them can be found in the nature: anatase<sup>56,57</sup>, brookite<sup>58</sup>, rutile<sup>59</sup> and  $\text{TiO}_2(\text{B})$ <sup>60,61,62,63</sup>. Three are artificially obtained in the laboratories and are stable at ambient conditions:  $\text{TiO}_2(\text{H})$ <sup>64,65</sup>,  $\text{TiO}_2(\text{R})$ <sup>66</sup> and  $\text{TiO}_2\text{-II}$ <sup>67, 68</sup>. Four others are stable only at high pressures:  $\text{TiO}_2\text{-III}$ <sup>69</sup>,  $\text{TiO}_2\text{-OI}$ <sup>69</sup>,  $\text{TiO}_2\text{-OII}$ <sup>70</sup> and  $\text{c-TiO}_2$ <sup>71</sup>. Table 1 summarizes the crystallographic parameters of each allotropic form of  $\text{TiO}_2$ .

Table 1. Crystalline parameters for polymorphs of  $\text{TiO}_2$ .

| Polymorphic type of $\text{TiO}_2$ | Lattice constant |        |        |             | Crystallographic system | Space group    |
|------------------------------------|------------------|--------|--------|-------------|-------------------------|----------------|
|                                    | a (Å)            | b (Å)  | c (Å)  | $\beta$ (°) |                         |                |
| Anatase                            | 3,777            | 3,777  | 9,501  | 90          | tetragonal              | <i>I41/amd</i> |
| Brookite                           | 9,174            | 5,449  | 5,138  | 90          | orthorhombic            | <i>Pbca</i>    |
| Rutile                             | 4,594            | 4,594  | 2,9586 | 90          | tetragonal              | <i>P42/mnm</i> |
| $\text{TiO}_2(\text{B})$           | 12,163           | 3,735  | 6,513  | 107,29      | monoclinic              | <i>C2/m</i>    |
| $\text{TiO}_2(\text{H})$           | 10,182           | 10,182 | 2,966  | 90          | tetragonal              | <i>I4/m</i>    |
| $\text{TiO}_2(\text{R})$           | 4,9022           | 9,459  | 2,9583 | 90          | orthorhombic            | <i>Pbnm</i>    |
| $\text{TiO}_2\text{-II}$           | 4,531            | 5,498  | 4,900  | 90          | orthorhombic            | <i>Pbcn</i>    |
| $\text{TiO}_2\text{-III}$          | 4,606            | 4,986  | 4,933  | 99,17       | monoclinic              | <i>P21/C</i>   |
| $\text{TiO}_2\text{-OI}$           | 9,046            | 4,834  | 4,621  | 90          | orthorhombic            | <i>Pbca</i>    |
| $\text{TiO}_2\text{-OII}$          | 5,163            | 2,9898 | 5,966  | 90          | orthorhombic            | <i>Pnma</i>    |
| $\text{c-TiO}_2$                   | 4,516            | 4,516  | 4,516  | 90          | cubic                   | <i>Fm3m</i>    |

Among stable polymorphs, only four of them have been applied for photovoltaic devices. For solar cells,  $\text{TiO}_2$  is mainly used because of its electron transporting ability. Number of references describes the use of  $\text{TiO}_2$  for Dye Sensitized Solar Cells (DSSC). In that case brookite<sup>72</sup>, rutile<sup>73</sup> and anatase<sup>74</sup> or mixtures of those phases<sup>75</sup> were tested, but also one short report about  $\text{TiO}_2(\text{B})$ <sup>76</sup> is available. For polymer organic solar cells, available reports are limited to anatase<sup>77</sup> or amorphous form of  $\text{TiO}_2$ . Summarizing the reports, the anatase is the most frequently used polymorph. The  $\text{TiO}_2$  layers for photovoltaics are usually

deposited by sol-gel processing<sup>80</sup> on conductive glass or plastic substrates. The liquid titanium precursors after deposition are often amorphous and post annealing process is required to crystallize the particles. The reason of popularity of anatase is probably due to facility of stabilization by sol-gel processing and limited post annealing temperatures ( $\leq 450^\circ\text{C}$ )<sup>77</sup>.

### I.3.2 Electrical properties

Undoped and stoichiometric  $\text{TiO}_2$  at moderated temperatures is an isolator.<sup>78</sup> The electrical properties of titanium dioxide arise from its lattice defects, which strongly depend on temperature and oxygen partial pressures. At low temperatures and low oxygen partial pressures, the  $\text{TiO}_2$  is a n-type semiconductor and the conductivity is ascribed to oxygen vacancies in the crystal lattice<sup>79</sup>.

For polymer organic solar cells, n-type conductivity makes  $\text{TiO}_2$  a good candidate as an electron transport layer. However efficient transport of charge carriers is related to alignment of energy levels with respect to donor-acceptor energy levels. The holes and electrons which are generated at the polymer blend interface P3HT:PCBM are collected at the electrodes by a cascade of energy level alignment of semiconductor interfacial layers (Figure 20). The CB level (Fermi level) of  $\text{TiO}_2$  has to be lower than the LUMO of PCBM and higher (or close to) the Fermi level of metal collecting electrode (Al).

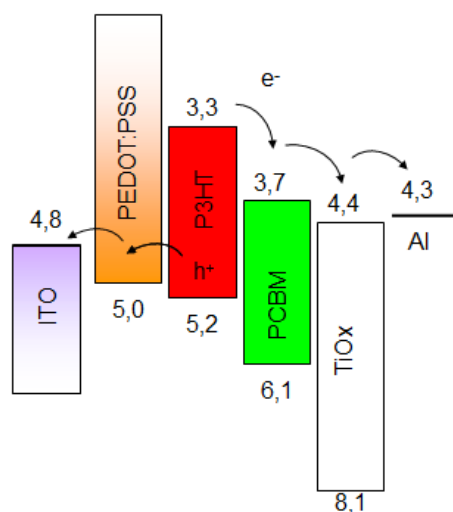


Figure 20. Bands diagram for organic solar cell having  $\text{TiOx}$  buffer layer<sup>80</sup>.

For polymer organic solar cells incorporating  $\text{TiO}_2$  interfacial layer, the electron transport process was found to be photo-induced. The experiments showed that the cell performance drastically decreased when UV filter was introduced to the source of light. This

behavior was reversible after filter removal (Figure 21). Similar phenomenon was reported for  $\text{TiO}_2$ <sup>81</sup> thin films, for which the conductivity was measured in the dark and light irradiation with different gas atmospheres.

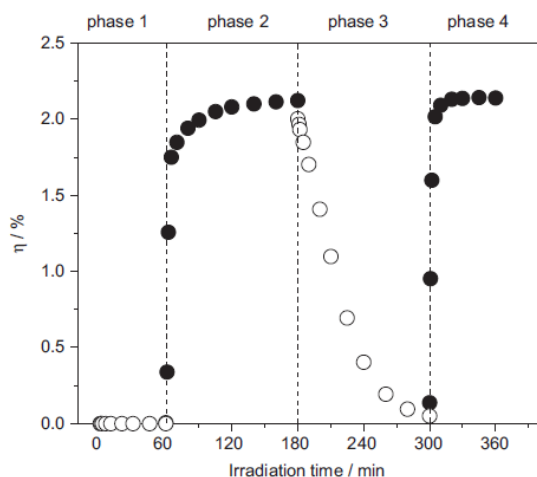


Figure 21. Irradiation time dependence of the power conversion efficiency for the ITO/ $\text{TiO}_x$ /PCBM:P3HT/ PEDOT:PSS/Au inverted-type solar cell under light irradiation of AM 1.5G-  $100 \text{ mW/cm}^2$  with (open circle) and without UV cut filter (filled circle)<sup>82</sup>.

$\text{TiO}_2$  could have a substantial oxygen/water protection and scavenging effect in OPV due to its photocatalytic and photophysical properties. The  $\text{TiO}_2$  absorbs the light with the wavelength below 400 nm. Thus, illumination by UV light is changing the properties of  $\text{TiO}_x$  interfacial layer. The UV illumination of  $\text{TiO}_2$  will promote electron to the conduction band which can interfere with the electron transport. The detrimental contribution to this phenomenon is oxygen. Gas oxygen absorbs on the surface of  $\text{TiO}_2$  and tends to capture the electrons to produce  $\text{O}_2^-$ , which acts as electron traps<sup>81</sup>. Thus the electrons produced in the bulk of  $\text{TiO}_x$  by UV illumination may first fill electron traps and then contribute to conduction mechanism<sup>83</sup>.

### I.3.3 Optical properties

$\text{TiO}_2$  is a wide band gap semiconductor and the band gap value depends on the polymorphic type and crystallite size. For the most popular allotropes, the values are in the following range: 3 eV for rutile<sup>84</sup>; 3.2 eV to 3.4 eV for anatase<sup>85, 86</sup>; 3.4 eV for brookite<sup>87</sup> and

3.2 eV for  $\text{TiO}_2(\text{B})$ <sup>88</sup>. The high band gap is a main condition for the front electrode (TCO) to avoid losses in the visible range of the solar spectrum.

Another interesting property of  $\text{TiO}_2$  is its high refractive index (anatase  $n=2,48 - 2,56$ ; brookite  $n=2,58 - 2,70$ ; rutile  $n=2,61 - 2,89$ )<sup>89</sup>. For organic solar cells, the refraction properties of  $\text{TiO}_x$  can be used to improve the device performance. In the photovoltaic cell, the light enters the device through front (transparent) electrode and it is reflected from the back (non-transparent electrode). Thus, the light went through the active layer twice and a standing wave is formed with the light electrical field strength ( $|E|$ ) maximum somewhere in the bulk of the device<sup>90</sup>. The absorption within the active layer depends on the distribution of the light electrical strength and has a consequence on the number of generated charge carriers. The absorption within the active layer can be optimized by insertion of the  $\text{TiO}_x$  layer between the back electrode and active layer. In this concept the  $\text{TiO}_x$  acts as a so-called “optical spacer”. Optical spacer shifts the maximum of the electrical field vector of the incident light into the active layer (Figure 21). The insertion of optical spacer was found to improve the power conversion efficiency of about 10% in respect to conventional device<sup>80</sup>.

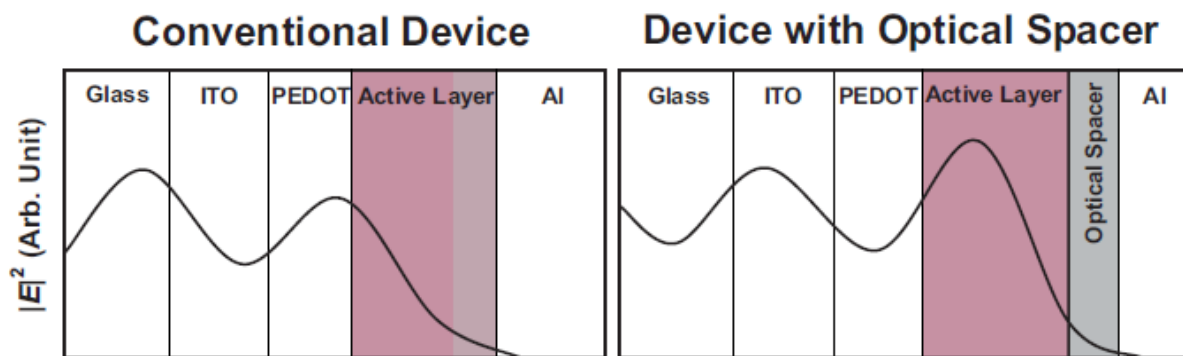


Figure 21. Schematic representation of the spatial distribution of the squared optical electric field strength  $|E|^2$  inside the devices with a structure of ITO/PEDOT/active layer/Al (left) and ITO/PEDOT/active layer/optical spacer/Al (right)<sup>80</sup>.

### **I.3.4 Deposition techniques<sup>91</sup>**

The choice of deposition method is usually determined by considering the desired properties of thin films. There are many published techniques for producing deposits of  $\text{TiO}_2$ , which can be classified into two categories:

- (1) Deposition from vapour phase
- (2) Chemical solution deposition

Deposition from a vapour phase allows one to control the stoichiometry, morphology, properties and leads to uniform and dense deposits of good quality. However, it often requires high temperatures and it is necessary to operate under vacuum. As a result, the process is expensive and energy consuming.

In comparison, the deposition by chemical solution is a relatively easy to implement and inexpensive technique. The chemical deposition processes operate at relatively low temperatures, thus the well crystallized deposits often requires heat treatment after deposition. The choice of substrate (plastic, glass, wood or paper) for chemical solution deposition techniques strongly depends on the post annealing temperature.

#### **I.3.4.a. Deposition from a vapour phase**

Physical from a vapour phase can be divided into two categories: physical vapor deposition (PVD) and chemical vapor deposition (CVD).

##### ***Physical Vapour Deposition (PVD)***

This method is performed by vapor deposition from the source to the substrate in a low pressure chamber. It can be performed by thermal methods or by bombardment of the target surface by high energy particles, such as  $\text{Ar}^+$  (Sputtering). The physical vapor deposition includes:

##### ***-Thermal evaporation***

The target is heated at high temperatures to generate a vapor pressure of about  $10^{-1}$  Pa and the vapor condenses on the colder substrate to form the deposit. The heating is realized by thermal resistors (tungsten wire, metal layers, etc.). The important parameters which

determine properties of the deposits are: substrate temperature, deposition pressure, chemical composition of the target and deposition rate. The advantages of thermal evaporation technique are: relatively fast deposition rate, good adhesion of thin films, a dense microstructure and easy control of the stoichiometry.

#### *-Sputtering*

In this technique, the target is the cathode and the anode may be the substrate. The target is bombarded by high energy ions which eject the atoms. The latter condense on the substrate to form a thin layer. Different techniques can be distinguished according to the method: DC sputtering (a current of high voltage is applied directly), RF sputtering (an alternative high voltage is applied). These sputtering methods can operate with a magnetron which enhances the magnetic field across the target to produce more energetic ions. The DC reactive technique will be discussed in details in section I.4.4.

#### *-Laser ablation or pulsed laser deposition (PLD)*

It is a technique involving the removal of the material from a solid surface by irradiating it with a laser beam. At low laser flux, the material is heated by the absorbed laser energy and evaporates or sublimates. At high laser flux, the material is typically converted to plasma.

#### ***Chemical Vapor Deposition (CVD)***

The CVD is an alternative technique between chemical solution deposition and physical vapor depositions processes. The CVD process does not always require vacuum equipment. Basically, the liquid precursor at low saturated vapor pressure is carried to the reactor by a gas flow and it is deposited on the substrate. The liquid precursor undergoes chemical reactions with a gas phase before reaching the substrate or on the substrate. There are three basic techniques of chemical vapor deposition: thermal CVD, plasma enhanced CVD (PECVD) and laser CVD (LCVD). The thermal CVD and laser CVD operate at elevated temperatures. The plasma enhanced CVD allows one to promote chemical reactions at lower temperatures.

The source material for CVD process is a gas, a volatile liquid, or a sublimated solid. The material should be stable at room temperature, should be sufficiently volatile and the reaction temperature must be lower than the melting point of the substrate. The properties of the deposit depend on vapor pressure of the precursor, power of the plasma (PECVD),

thermodynamics of the process, substrate temperature. This method is suitable for high speed growth of thin films. It can be applied for deposition of metals, semiconductors, oxides in amorphous or crystalline forms. Due to high quality of deposits and low costs, the CVD techniques are widely used.

#### **I.3.4.b. Chemical solution deposition (CSD)**

Chemical Solution Deposition or sol-gel processing, involves a liquid phase as the mass transfer media. The process usually requires that the precursor which is in a liquid phase undergoes chemical transformation to form solids. The thin film formation might go through several steps including: formation of colloidal suspension in a solvent (sol), gelation (gel), evaporation of the solvent (drying), and thermal treatment, if necessary. Each of these particular steps can be controlled and gives the opportunity for manipulation of crystal growth, aggregation, coalescence or self-assembling of particles forming thin films, thus controlling the film quality. Chemical solution deposition usually refers to low temperatures and deposits often require post annealing treatment to gain crystalline forms. Currently sol-gel chemistry gives the opportunity to synthesize variety of materials or coatings and this may be an alternative to vapour deposition techniques, which require high-price equipment. In the laboratories, thin films are deposited using two major approaches: spin-coating or dip coating. The chemical solution deposition can be applied by industrial techniques (printing or coating), which permit complex pattern formation of deposited thin films (see paragraph I.1.7.).

#### **I.3.5 Stabilization of colloidal solutions**

In 1903, Ostwald formulated a definition of colloidal solution as a continuous phase at which one phase is dispersed in another one. The dispersed phase is composed of particles with the dimensions of 1 nm to 1000 nm, which undergo Brownian motion. When the particles are sufficiently close, they stick and aggregate because of van der Waals attraction. There aggregation can be prohibited by three mechanisms (Figure 22):

1. Electrostatic stabilization. Colloidal particles often carry an electrical charge and therefore attract or repel each other.



2. Steric stabilization. The large bulky molecules (surfactants, polymers) are attached to the surface of particles preventing them from close contact.
3. Depletion stabilization. The unanchored (free) polymeric molecules creating repulsive forces between the approaching particles.

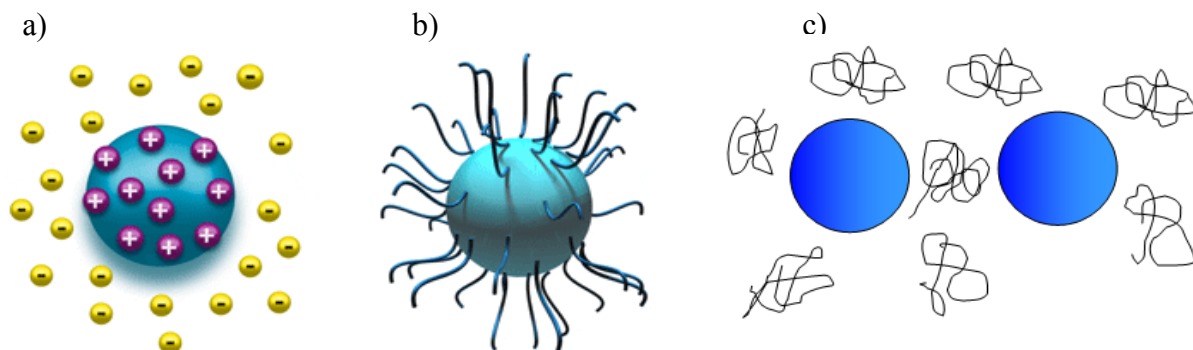


Figure 22. Schematic representation of dispersion mechanism<sup>92</sup>: a) electrostatic, b) steric, c) depletion stabilization.

The Electric Double Layer (EDL) is a one of the fundamental models which describes the electrostatic stabilization of particles in solution. The model describes the variation of the electric potential near the particle surface (Figure 23). The electrical potential has a maximum value on the surface of particles and drops to zero while increasing the distance from particle. The surface of colloidal particles usually is terminated by differently charged chemical groups. For example for oxides the particle surface can be ionized by adjusting the pH of solution and leads to the surface equilibrium:  $\text{M-OH} + \text{H}^+ \leftrightarrow \text{M-OH}_2^+$  in acidic medium and  $\text{M-OH} + \text{OH}^- \leftrightarrow \text{M-O}^- + \text{H}_2\text{O}$  in basic solution. Due to electrostatic attraction the counter ions are absorbed on the particle surface and create the so-called Stern plane. The distance of counter ions from the particle surface is determined by its solvation radius. The second layer is the so-called diffuse layer. The electrical potential in the diffuse layer is lower thus ions and counter ions are distributed with a concentration gradient determined by influence of electric attraction and thermal motion. When the colloidal particle is moving in the liquid medium, the electrostatic shell composed of ions and counter ions (also particle of liquid phase) follows the displacement of particle. The boundary of this plane is called slipping plane or shear plane. The value of electrical potential at the slipping plane is called zeta potential ( $\zeta$ ).

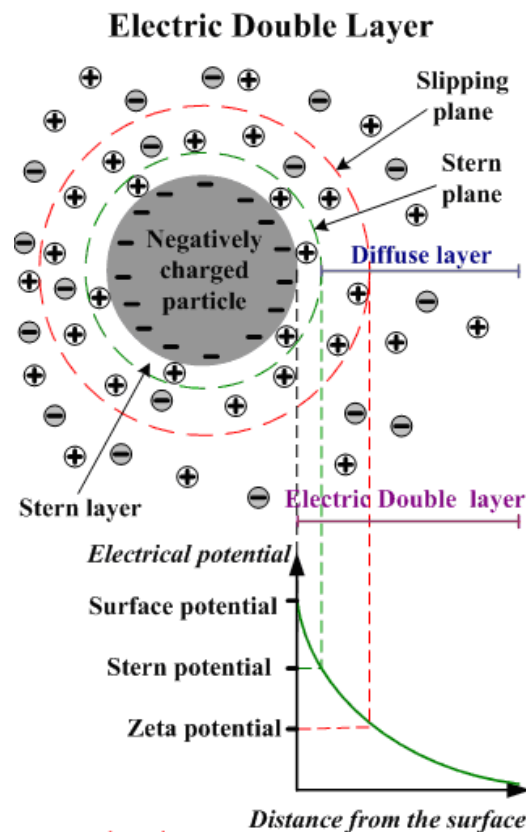


Figure 23. Model of the electric double layer.

The value of zeta potential determines the kinetic stability of the suspension, because a higher value means stronger repulsive interactions between the separated particles, which prevents them from aggregation.

Steric stabilization is a mechanism, which explains the ability of certain additives to prevent the particle from agglomeration. The additives include large molecules like polymer or surfactants which are absorbed on particle surface and by their bulky structures inhibit particle aggregation. Systems which are sterically stabilized tend to remain dispersed even at high salt concentrations or under conditions where the zeta potentials of the surfaces are reduced to near zero.

## **I.4 Properties of nickel oxide as a transparent p-type charge transporting layer**

### **I.4.1. Nickel oxide as a component in organic solar cells**

Nickel oxide crystallizes in one polymorphic form only. It is generally accepted that it adopts the NaCl cubic structure with Fm3m as space group. However cubic symmetry is only stable at elevated temperatures. In ambient conditions the real symmetry is rhombohedral with the space group R-3m. The distortion of rhombohedral lattice is low at ambient temperatures and leads to XRD diffraction peaks at similar positions (see details at IV.1.2.). Probably from this reason the literature reports simplify the NiO structure as a cubic phase.

The application of NiO for photovoltaics is currently limited to polymer organic solar cells, but there are also many works in progress dealing with NiO layers, in inverse Dye Sensitized Solar Cells<sup>93,94</sup>. The recent reports for employing NiO in polymer organic solar cells are related to the trend of finding an optimal p-type interfacial layer. The trend was initiated at 2008 when *Marks*<sup>95</sup> reported organic solar cell showing 5.2% of power conversion efficiency and excellent stability. Since that time, few groups published results on similar devices, however with lower performance<sup>96</sup>.

### **I.4.2 Electrical and properties**

Undoped and stoichiometric nickel oxide are isolators with a resistivity in the range of  $10^{-12}$  S/cm<sup>97</sup>. NiO has a tendency to be under-stoichiometric due to nickel vacancies. Electrical properties of NiO arise from its lattice defects and reported conductivities for non-stoichiometric oxide reaches  $10^{-3}$  S/cm<sup>98</sup>. Creation of nickel vacancy in the lattice causes that two neighbouring nickel atoms change their oxidation state from  $\text{Ni}^{+2}$  to  $\text{Ni}^{+3}$  to compensate the net charge<sup>99</sup>. This creates holes and gives rise to p-type semiconductive behaviour. But semiconductive properties were found to vary with temperature (Figure 24)<sup>100</sup>. As prepared, non-stoichiometric NiO after heat treatment rapidly turns to stoichiometry and it loses its p-type semiconductive properties<sup>101</sup>. It was reported that post annealing process drastically decreases the concentration of positive charge carriers when heated above 200°C.

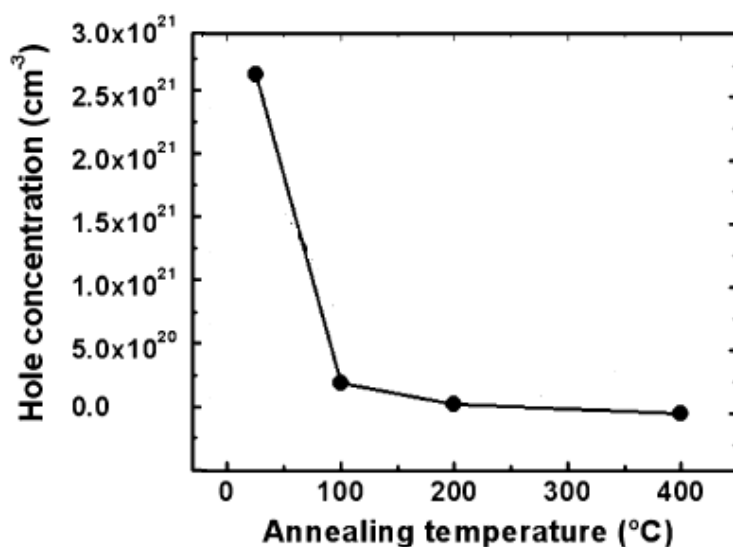


Figure 24. Concentration of holes in NiO versus annealing temperature in nitrogen atmosphere<sup>100</sup>.

Figure 25 shows the appropriate alignment of energy levels for NiO with respect to the standard donor-absorber materials used for organic solar cells. For a p-type semiconductive interfacial layer material, the valence band is required to match the HOMO of the donor to facilitate hole transport towards the anode. The alignment of energy levels causes that NiO acts as a blocking barrier for the electrons. The LUMO orbital of P3HT and PCBM is at 3.0 eV and 4.0 eV respectively. The conduction band of NiO is at 1.8 eV. This provides an energy barrier of about 1.2 eV for electrons. This barrier blocks the electrons and allows harvesting of the holes at the anode (ITO).

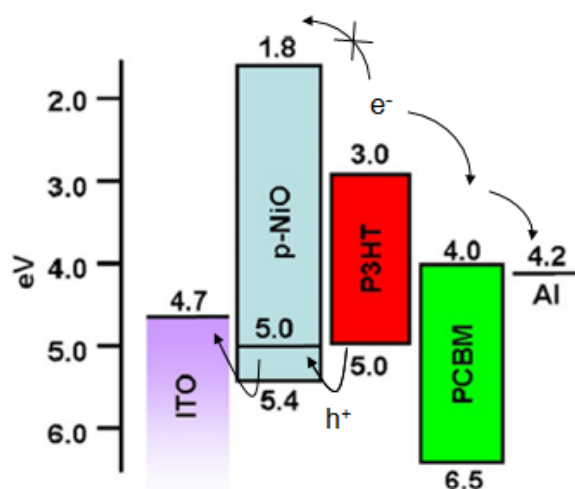


Figure 25. Bands diagram for organic solar cell having NiO buffer layer<sup>95</sup>.

### I.4.3 Optical properties

Reported value of the band gap for NiO is ranging between 3.8 eV<sup>102</sup> and 5.4 eV<sup>103</sup>. The band gap is sufficiently high in order to allow the visible photon to access the active layer through the front electrode. The transparency of NiO in the visible range is related to its stoichiometry. Under-stoichiometric Ni<sub>1-x</sub>O shows lower transmittance in respect to the stoichiometric NiO one. This phenomenon is ascribed to the presence of Ni<sup>3+</sup>, which act as a color centers<sup>104</sup>.

### I.4.4 Deposition of NiO by reactive sputtering<sup>105</sup>

Sputtering bases on the bombardment of the target by energetic particles. The impact of those energetic particles ejects the target atoms which condense on the substrate. The figure 25 shows the principle of sputtering process in a direct current mode (DC), which permits sputtering of the conductive targets.

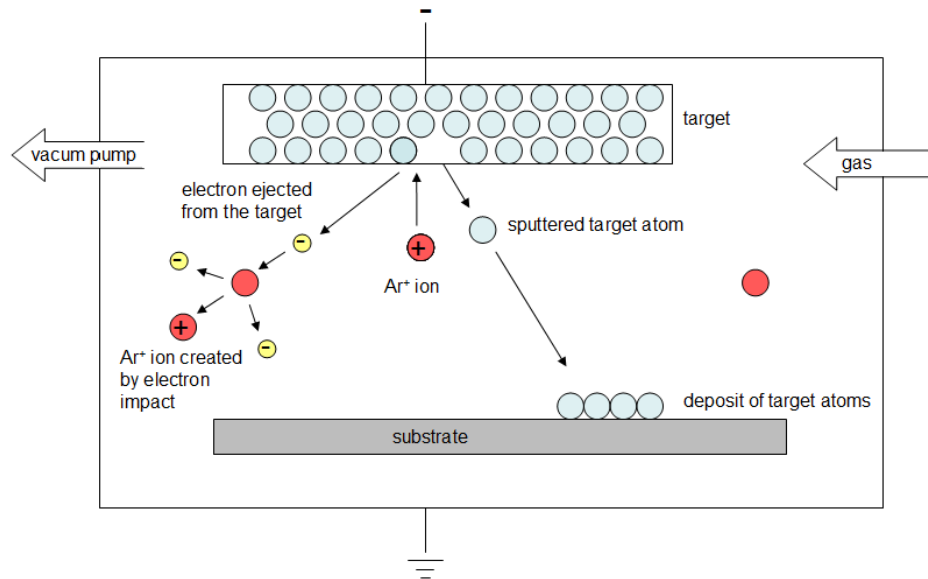


Figure 25 . The principle of sputtering process.

When the potential difference is applied between two electrodes in a chamber at low pressures, a glow discharge is created. The inert gas (usually argon) is used for the bombardment of the target. The material which is sputtered, called target is placed as a cathode and the substrate is either connected to the ground or electrically isolated (floating potential). The negative potential, which is applied to the cathode, is in the range of some hundred volts. The potential difference between two electrodes results in the liberation of the

electrons, which are accelerated by the electric field and collide with inert gas molecules causing ionization. Those ionized gas molecules and free electrons create a plasma state of matter. The ions ( $\text{Ar}^+$ ) are attracted by the cathode. The momentum transfer leads to ejection of the cathode atoms, which condense on the substrate. The impact of the ionic bombardment on the target causes emission of secondary electrons, which sustain the plasma discharge.

In order to improve the ionization of the gases, magnets are placed behind the target. This method, called magnetron sputtering, allows an increase of deposition rates, a reduction of the working gas pressure and a decrease of the discharge voltage applied to the cathode. The effect of the magnetron is based on trapping the electrons by the magnetic field next to the cathode. This allows an increase of the probability for the electrons to collide with the gas molecules. The trajectory of the electrons follows the lines of magnetic fields created by the magnetron. There are many configurations of magnetrons (Figure 26), like balanced or unbalanced (type 1 or type 2)<sup>106</sup> which can improve the crystallinity of the deposited films<sup>107</sup>.

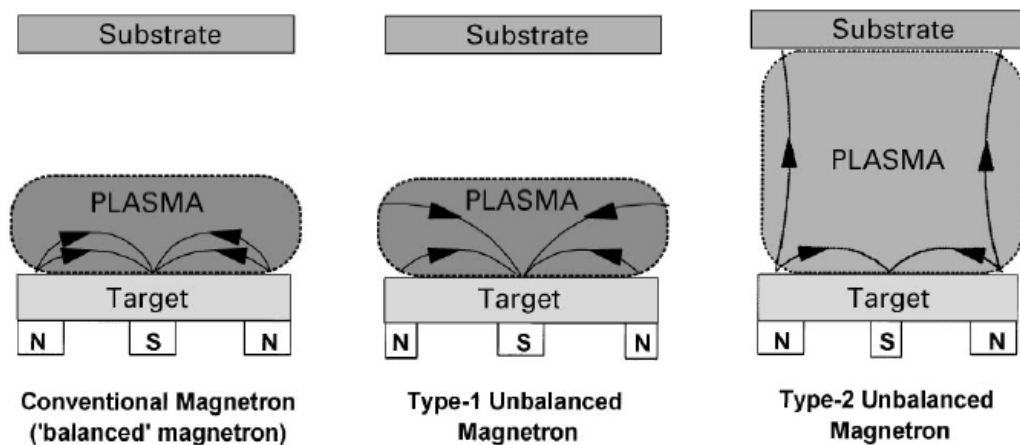


Figure 26. Schematic representation of plasma confinement for various configuration of the magnetron<sup>106</sup>.

For conventional balanced magnetron, the lines of magnetic field are confined between the central and outer poles of the magnetron. Consequently the plasma is trapped close to the target substrate. In unbalanced magnetrons, the lines of magnetic field are directed towards the substrate and plasma can occupy larger space and be shifted towards the substrate. This solution gives an opportunity for more efficient deposition with no needs to bias the substrate.

The sputtering process allows deposition of materials in two modes: the direct deposition of the target metal on the substrate in the presence of inert gas, or the deposition of the metal

in the presence of reactive atmosphere (ex. oxygen or nitrogen). In the second mode, the reactive gas reacts chemically with the target metal and results in deposition of thin films having different chemical composition. For the reactive sputtering mode the inert gas can be partially or totally replaced by the reactive gas.

## **Conclusions of chapter I**

In this chapter, the history of plastic solar cells was outlined, showing the most important and revolutionary concepts which contributed to developments in that field. The aspects of performance for single layer, bilayer and bulk heterojunction based organic cells was discussed. The last achievements and theoretical limitations of power conversion efficiencies were presented for various architectures of organic cells. The problems related to degradation and short lifetime of those devices was explained in terms of stability of organic materials, corrosion of metallic electrodes and influence of atmospheric pollutants. The economical aspects and requirements for the lifetime of organic solar cells were analyzed in terms of market needs and possible application for small electronic devices or professional power plants for energy production. The chapter presented the concept of hybrid organic solar cell incorporating inorganic semiconductive materials as interfacial layers. Those inorganic oxides could play a key role for the protection of sensitive organic active layers from the contact with metallic electrodes. This concept allows avoiding organic-metallic contact and suppresses the chemical reactions occurring on the electrodes. For the cathode protecting material the n-type titanium dioxide was selected. The anode can be protected by the p-type nickel oxide. The semiconductive properties of those oxides arise from their non-stoichiometric nature. The titanium dioxide tends to be oxygen deficient and for nickel oxide, nickel vacancies are easily formed. The electronic band configuration of those semiconductors matches well with the HOMO and LUMO energy levels of organic donor-acceptor couple and allows an efficient charge transport to the selective electrodes. The mechanism of photo-induced conductivity of titanium dioxide was described, as well as its refractive light properties which can improve the spatial distribution of light within the active layer and improve the number of photogenerated charge carriers. The band gap of  $\text{TiO}_2$  and  $\text{NiO}$  is sufficiently large (above 3 eV) causing that they can be deposited on the front transparent electrode without significant losses in the visible range of solar spectrum. Two possible ways were proposed for the realization of inorganic interfacial layers. The first one

involves: chemical solution deposition employing colloidal solutions, compatible with ink-jet printing technique. The second one is focused on: physical vapor deposition, which requires vacuum equipment. The economical and practical aspects of implementation of those techniques were analyzed. For deposition process by ink-jet printing, the physico-chemical properties of colloidal solutions were defined in respect to equipment. The employment of industrial techniques gives an opportunity for scaling-up the production of hybrid organic solar cells.



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## **Chapter II: Synthesis and characterization of TiO<sub>2</sub> colloidal solutions**

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## Introduction

The chapter describes the synthesis of  $\text{TiO}_2$  colloidal solutions. The reaction bases on thermal conversion of hydrolysable  $[\text{Ti}_8\text{O}_{12}(\text{H}_2\text{O})_{24}]\text{Cl}_8\cdot\text{HCl}\cdot 7\text{H}_2\text{O}$  precursor into  $\text{TiO}_2$  particles at moderated temperatures. The synthesis was designed to enable the deposition of the particle suspension by ink-jet printing technique. The organic solvents were used as a dispersion medium to pass requirements delineated by ink-jet printing technique. Solvents were selected by their physical properties and presence of water was restricted to the minimum. The reason to perform synthesis in organic solvents was related to the requirement for low surface tension, selected range of viscosity and relatively high boiling point of colloids solvent. One of the main conditions was the deposition of colloidal particles at relatively low temperatures (lower than  $200^\circ\text{C}$ ) and limitation of post annealing process, thus the presence of surfactant was avoided. The process described herein is based on the so-called poly-ol mediated method<sup>108</sup>. Propylene glycol (1,2 propane-diol) was chosen as a dispersive agent for colloidal particles. The selection of propylene glycol was also related to its reactivity with hydrochloric acid at elevated temperatures. During hydrolysis of  $[\text{Ti}_8\text{O}_{12}(\text{H}_2\text{O})_{24}]\text{Cl}_8\cdot\text{HCl}\cdot 7\text{H}_2\text{O}$  precursor, hydrochloric acid is produced as a by-product. The reaction with propylene glycol allows a significant limitation of corrosive ions. Indeed, the latter are considered to be detrimental for ink-jet printing equipment. This chapter describes three systems where propylene glycol was used as indirect or direct reactant for the synthesis. In the first paragraph the hydrolysis of  $[\text{Ti}_8\text{O}_{12}(\text{H}_2\text{O})_{24}]\text{Cl}_8\cdot\text{HCl}\cdot 7\text{H}_2\text{O}$  precursor was carried out in propylene carbonate (4-Methyl-1,3-dioxolan-2-one) and water. At elevated temperatures (above  $100^\circ\text{C}$ ), those solvents react one with the other resulting in propylene glycol as a by-product, and the water is successfully consumed. In the second part, the 3 component system was used to synthesize colloidal solutions of  $\text{TiO}_2$ . Propylene carbonate, water and propylene glycol were used to obtain the highly dispersed colloidal particles. The last paragraph describes the system where propylene glycol and water were used to obtain  $\text{TiO}_2$  colloids. The products were characterized by various techniques. The physical properties of the resulting colloidal solutions were estimated. Finally, the colloidal particles were deposited by spin-coating or jet printing techniques and tested as n-type layers in photovoltaic organic cells.

## II.1. Synthesis of colloidal solution in the mixture of propylene carbonate and water

Nanosized anatase particles can be synthesized from  $[\text{Ti}_8\text{O}_{12}(\text{H}_2\text{O})_{24}]\text{Cl}_8 \cdot \text{HCl} \cdot 7\text{H}_2\text{O}$  titanium precursor in the mixture of propylene carbonate and water. Heating this suspension induces the titanium precursor to undergo hydrolysis leading then to the nucleation of titania particles. The role of used solvents as a dispersive agent for  $\text{TiO}_2$  particles is discussed. Various solvent mixtures of propylene carbonate and water were examined to find an optimum composition for dispersion of colloidal particles.

### II.1. Protocol of synthesis

The colloidal solutions were prepared using titanium precursor  $[\text{Ti}_8\text{O}_{12}(\text{H}_2\text{O})_{24}]\text{Cl}_8 \cdot \text{HCl} \cdot 7\text{H}_2\text{O}^{109}$ , propylene carbonate (Sigma-Aldrich 99.7%) and milli-Q water. Before synthesis the crystals of titanium precursor were eluted several times by ethanol and dried in nitrogen flow. For each synthesis,  $\text{Ti}_8\text{O}_{12}$  crystals were dissolved in the appropriate amount of water by vigorous stirring. After crystal dissolution propylene carbonate (PC) was added. As prepared, the reactants were poured in the teflon vessels (47 mL volume) and autoclaved at  $120^\circ\text{C}$  for 48 hours. The heating rate was approximately  $300^\circ\text{C}/\text{hour}$ . After synthesis the autoclaves were let to cool down room temperature and they were carefully opened in order to slowly release the pressure in gaseous carbon dioxide. Table 1 presents the amount of reactants involved during the synthesis. The samples were denoted by the initial ratio of solvents used:  $R=[\text{H}_2\text{O}]/[\text{PC}]$ . The concentrations of colloidal solutions refer to the precursor concentration and were established to be in the range of  $0.05 \text{ mol.L}^{-1}$  in  $\text{TiO}_2$ .

Table 1. Amount of reactants taken for the synthesis of colloidal  $\text{TiO}_2$  for initial solvent mixture of  $\text{H}_2\text{O}$  and PC.

| Solution No.                         | 1            | 2            | 3            | 4            | 5            | 6            |
|--------------------------------------|--------------|--------------|--------------|--------------|--------------|--------------|
| $\text{Ti}_8\text{O}_{12}$ (g)       | 0.18         | 0.18         | 0.18         | 0.18         | 0.18         | 0.18         |
| $\text{H}_2\text{O}$ (mole)          | 0,056        | 0,111        | 0,139        | 0,167        | 0,194        | 0,222        |
| PC(mole)                             | 0.195        | 0.195        | 0.195        | 0.195        | 0.195        | 0.195        |
| $R=[\text{H}_2\text{O}]/[\text{PC}]$ | <b>0,285</b> | <b>0,570</b> | <b>0,712</b> | <b>0,855</b> | <b>0,997</b> | <b>1,140</b> |

### II.1.2. General scheme of the synthesis

The synthesis of colloidal solutions was controlled by three parallel reactions. The Figure 27 presents the general scheme of the synthesis. The first considered reaction is the hydrolysis of  $[\text{Ti}_8\text{O}_{12}(\text{H}_2\text{O})_{24}]\text{Cl}_8 \cdot \text{HCl} \cdot 7\text{H}_2\text{O}$  precursor and nucleation of  $\text{TiO}_2$  particles. The conversion of  $\text{Ti}_8\text{O}_{12}$  results in the formation of hydrochloric acid and water as by-products. The second reaction (ester hydrolysis) occurs between propylene carbonate and water. This reaction is initiated by protons coming from the hydrolysis of the titanium precursor, which acts as catalyst. The products are 1,2-propandiol (propylene glycol) and carbonic acid<sup>110</sup>. As carbonic acid is not stable, it decomposes into water and carbon dioxide. The third considered reaction is the neutralization of hydrochloric acid present in the system. In that case, 1,2-propanediol undergoes nucleophilic substitution, where one of the hydroxyl groups from alcohol is exchanged by chlorine ion.

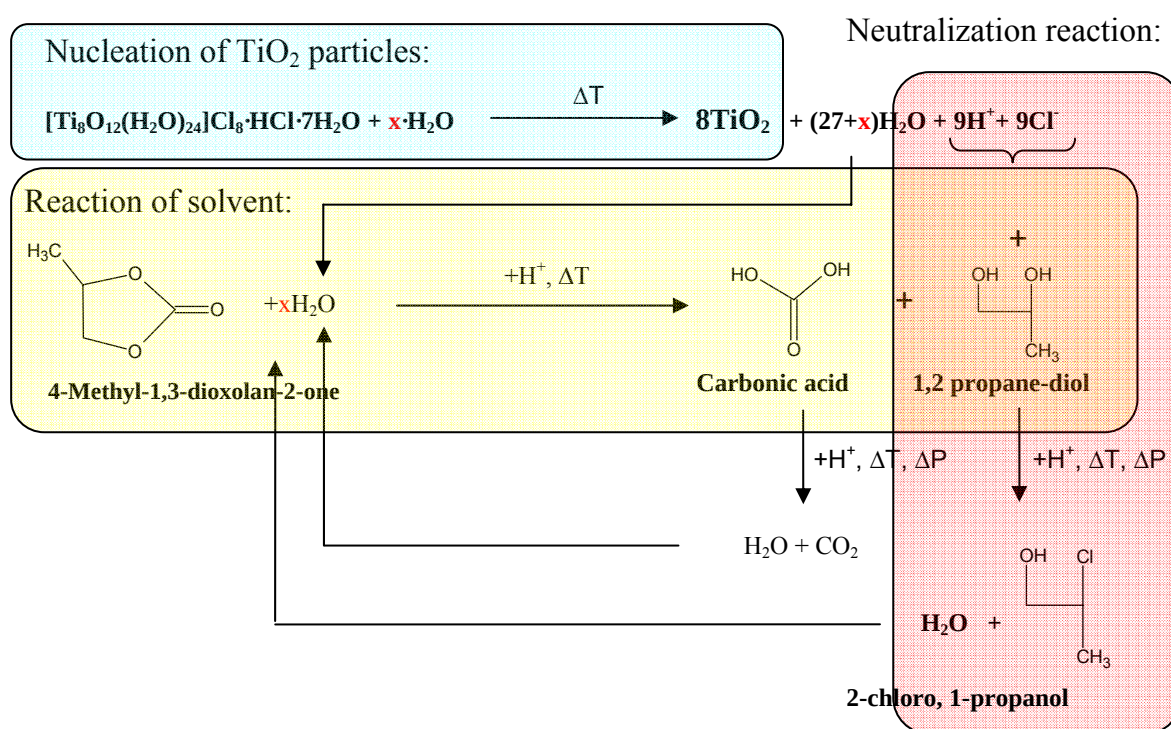


Figure 27. Synthesis of colloidal solutions  $\text{TiO}_2$ .

In all the three parallel reactions water is produced as by-product. Excess of propylene carbonate allows reducing the amount of water to a negligible level. The equilibrium of conversion for propylene carbonate is reached when no more water is available. Each considered reaction and resulted products were characterized in the following paragraph.

### II.1.3. Characterization of products

#### II.1.3.a). Crystallographic structure: XRD, electronic diffraction and HRTEM

The crystal structure of products was identified by X-ray diffraction using a SIEMENS D 5000 diffractometer operating in Bragg Brentano mode ( $\text{CuK}\alpha$ , stepsize of  $0,01^\circ\theta$  with and step time 1sek.). The crystallographic structure of colloidal particles was characterized after evaporation of the solvent. The colloids were dried at  $120^\circ\text{C}$  under air conditions for 24 hours. Figure 28 shows the X-ray diffraction patterns obtained for products prepared at various composition of solvent mixture of  $R=[\text{H}_2\text{O}]/[\text{PC}]$ . All samples possessed evident peaks characteristic of anatase variety. The diffraction peaks are broad, indicating on small crystalline domains. For increasing ratio of solvents  $[\text{H}_2\text{O}]/[\text{PC}]$ , a small signal at  $2\theta\sim 31^\circ$  is appearing, this can be ascribed to traces of brookite.

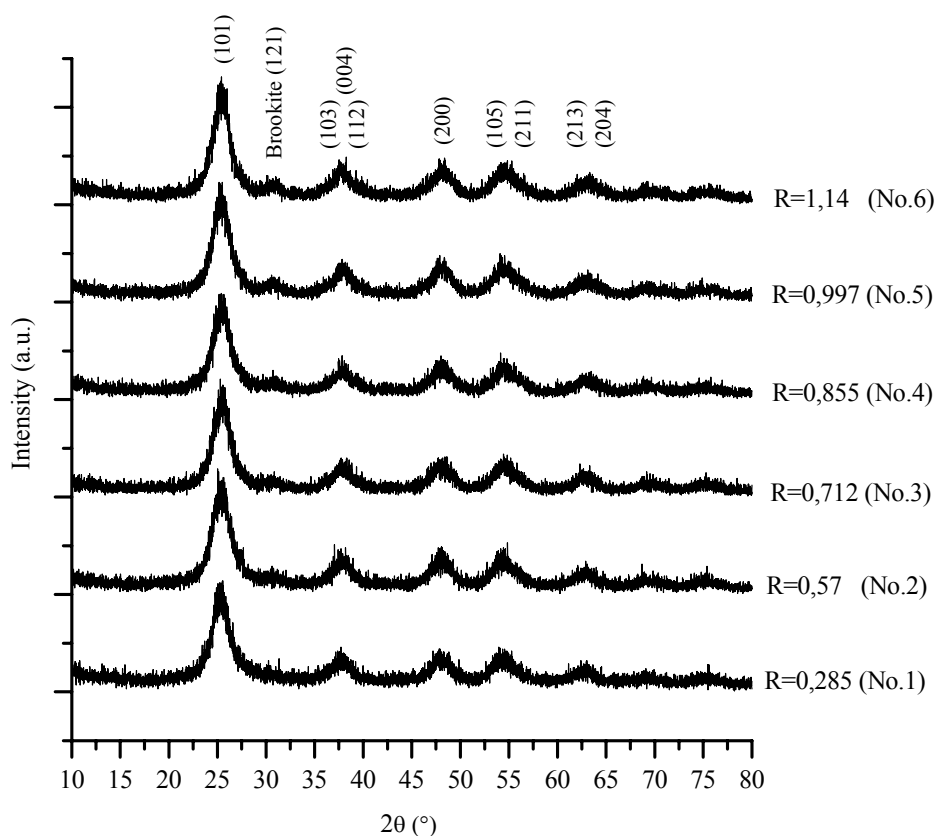


Figure 28. X-ray diffraction patterns for powders obtained by drying the colloidal solutions (No.1 to 6).

The XRD patterns show that initial composition of solvents  $[\text{H}_2\text{O}]/[\text{PC}]$  does not significantly affect the crystallinity of the synthesised colloids. For each experiment the diagrams are

almost identical, but samples prepared in water-rich mixture, contain brookite as an impurity. The brookite phase was not detected only in the sample prepared at  $R=[\text{H}_2\text{O}]/[\text{PC}]=0.285$  (No.1 ).

Transmission electron microscopy (TEM) studies were carried out with a Hitachi H9000NAR operating at 300 kV. Figure 29 shows the high resolution image of particles obtained by immersing a TEM grid in the colloidal solution (No.2) and drying in air at room temperature.

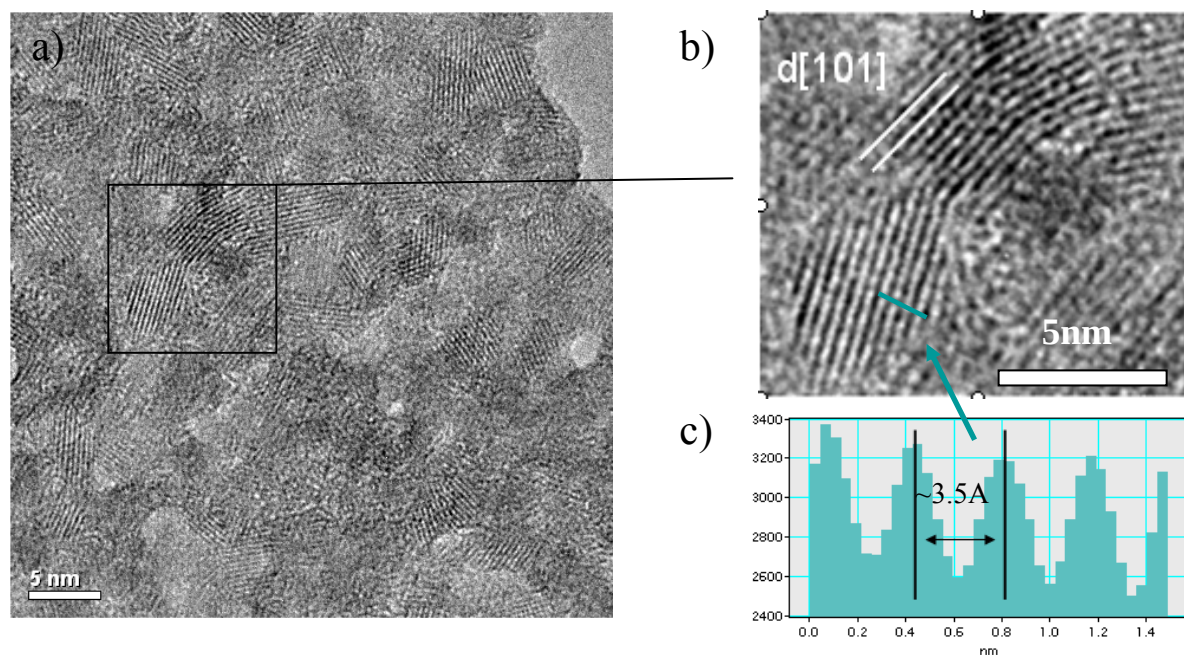


Figure 29 TEM image of colloidal solution No.2 ( $R=0.57$ ): a) at magnification 400 000, b) zoom at crystals with exposed (101) anatase plane, c) histogram along a green line

Due to relatively high concentration in titanium ( $0.05 \text{ mol.L}^{-1}$ ), the colloids create a dense film on the TEM grid and isolated particles were not observed. The individual grains have roughly spherical shape with a diameter around 5 nm. The crystals are randomly oriented in respect to the electron beam and only some of the particles expose lattice planes. The most frequently appearing d-spacing (estimated from histograms Figure 29c) gives an average value of  $3.5 \text{ \AA}$ , which is in agreement with the largest [101] distance of anatase. The images show distortion of crystallographic structures and defective nature of prepared anatase nanocrystals. Similar images were obtained for samples prepared for various ratio  $R=[\text{H}_2\text{O}]/[\text{PC}]$ . Figure 30 shows the TEM image for sample No.5 ( $R=0.997$ ). The particles are still superimposed because upon evaporation the colloids tend to agglomerate, which makes it difficult to observe as isolated crystals. The size of particles can be rather estimated from dashed domains of the image and seems to be in the range of 5 nm.

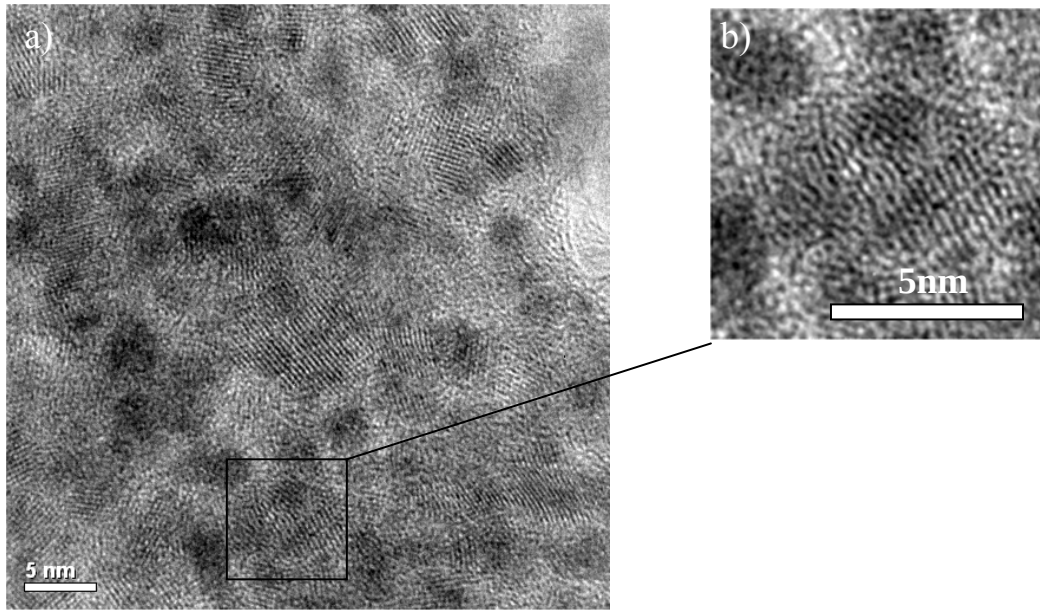


Figure 30. TEM image of colloidal solution No.5 ( $R=0.997$ ): a) at magnification 400 000, b) zoom at crystals with distorted lattice planes.

The estimation of crystallographic distances was performed by selective area electronic diffraction (SAED). The examined region was selected using an aperture with 300 nm diameter, which is much higher than the individual crystallite domains. The diffraction results in rings indicating on random crystals arrangement (Figure 31).

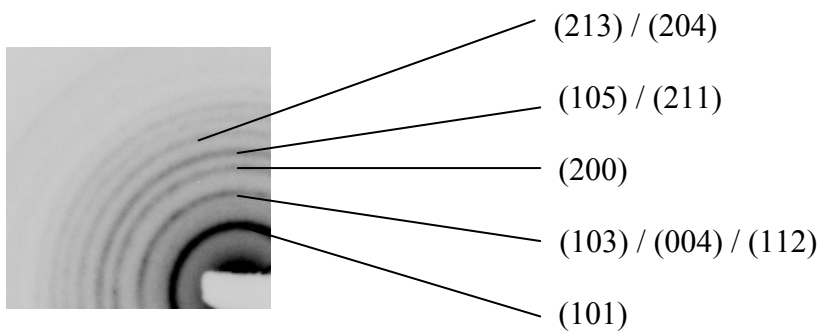


Figure 31. TEM image of electronic diffraction: selected area of colloidal solution No.2 deposited on grid.

The experimental determination of lattice distances was estimated for the first five diffraction rings. Due to small crystallite size, all of the lattice distances attributed to anatase can not be recognized as unique diffraction rings. Lattice spacings of similar dimensions

superimpose and are detected as one intense ring. It was the case of the 2<sup>nd</sup>, 4<sup>th</sup> and 5<sup>th</sup> rings. Complementary, the lattice spacings were calculated from X-ray diagrams from Bragg's Law. Extracted values are listed in Table 2 and compared with the reference.

Table 2. Lattice distance of nanocrystalline anatase extracted from SAED and XRD for sample No.2 (R=0.57) and compared with a reference (JCPDS 21-1272).

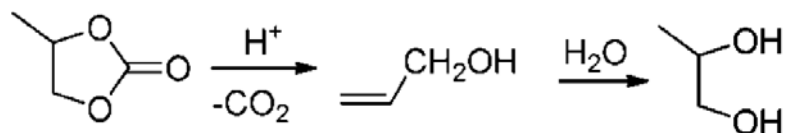
| Diffraction ring | Lattice distance measured by SAED (Å) | Lattice distance measured by XRD (Å) | Lattice distance reference (Å) | Index <i>h</i> | Index <i>k</i> | Index <i>l</i> |
|------------------|---------------------------------------|--------------------------------------|--------------------------------|----------------|----------------|----------------|
| 1 st             | 3.42                                  | 3.503                                | 3.520                          | 1              | 0              | 1              |
| 2nd              | 2.34                                  | 2.376                                | 2.431                          | 1              | 0              | 3              |
|                  |                                       |                                      | 2.378                          | 0              | 0              | 4              |
|                  |                                       |                                      | 2.332                          | 1              | 1              | 2              |
| 3rd              | 1.87                                  | 1.892                                | 1.892                          | 2              | 0              | 0              |
| 4th              | 1.65                                  | 1.683                                | 1.6999                         | 1              | 0              | 5              |
|                  |                                       |                                      | 1.6665                         | 2              | 1              | 1              |
| 5th              | 1.45                                  | 1.478                                | 1.493                          | 2              | 1              | 3              |
|                  |                                       |                                      | 1.4808                         | 2              | 0              | 4              |

In both cases estimated distances are in close agreement to the anatase lattice spacings. The exception is the largest (101) which seems to be smaller than the one reported for bulk anatase. This can be due to size-dependent changes in crystallite lattice. In general oxide lattice tend to expand at extremely reduced crystallite size<sup>111</sup>. By the contrast the data for nano-anatase reports non linear size dependent evolution of lattice parameters for nano crystals in the size range of 5-12nm<sup>112</sup>.

### II.1.3.b). Viscosity of colloidal solutions

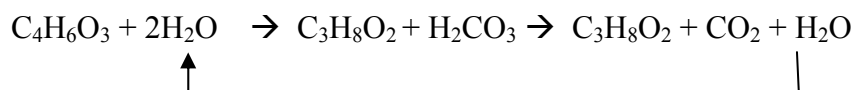
One reason why propylene carbonate was selected for the synthesis of colloidal solutions was its reactivity with water. Water as a solvent with high dielectric constant is necessary to dissolve Ti<sub>8</sub>O<sub>12</sub> crystals before solvothermal treatment. However, for the purpose of ink-jet printing the presence of water has to be reduced. Propylene carbonate is a cyclic ester and like all esters it undergoes hydrolysis reaction when catalysed by protons in the presence of water. The products of esters hydrolysis are usually alcohols and carboxylic acids. In the case of propylene carbonate, the hydrolysis leads to the formation of 1,2-propanediol and carbonic acid (H<sub>2</sub>CO<sub>3</sub>). Carbonic acid at elevated temperatures (and acidic environment)

decomposes rapidly to water and carbon dioxide. Another mechanism of acidic catalysed hydrolysis of propylene carbonate was proposed by the group of Novak<sup>113</sup>. They proposed the reaction of propylene carbonate with aqueous solution  $\text{HClO}_4$  leading to the formation of allylic alcohol and propane-1,2-diol:

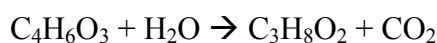


Finally, for both mechanisms, the final products are only carbon dioxide as a gas phase and propylene glycol in the solution. The conversion of propylene carbonate to propylene glycol gives us the opportunity to remove water as the hydrolysis of ester is progressing. Another reason for selecting those two solvents is the relatively high difference in viscosity. The propylene carbonate and propylene glycol at  $25^\circ\text{C}$  have a viscosity respectively of 2.39 cP and 44.44 cP<sup>114</sup>. Such a difference between reactant and product allows adjusting viscosity of the final colloidal solution by controlling the conversion degree. The requirements for ink jet printing impose the choice of a solvent whose viscosity lies between 8-15 cP at the printing temperature.

The stoichiometry of hydrolysis propylene carbonate indicates that 2 moles of water are necessary to fully convert 1 mole of propylene carbonate:



However, after decomposition of intermediate products, water is a reactant and a product at the same time, thus the reaction can be simplified to:



During hydrolysis of propylene carbonate the conversion degree is strongly depending on the initial concentrations of both reactants. Insufficiency of water will limit the total conversion of propylene carbonate into 1,2-propanediol. This fact allows holding the reaction up to a desired point where the viscosity of the mixture is suitable for ink jet printing conditions. The Figure 32 shows the evolution of viscosity of the colloidal solutions after autoclaving treatment for various ratios of reactants.



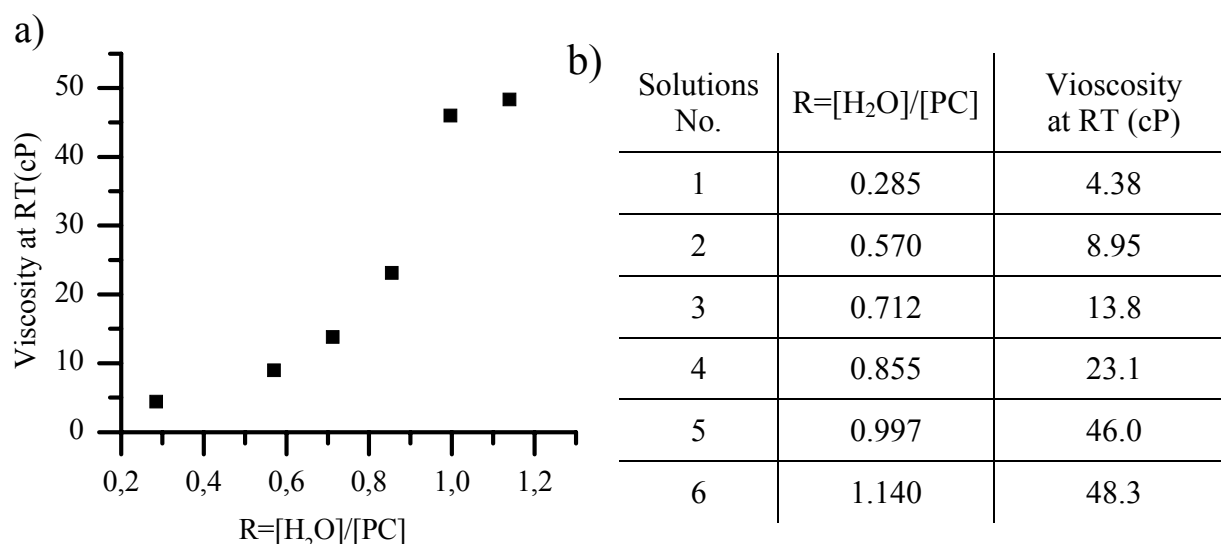


Figure 32. Viscosity of TiO<sub>2</sub> colloidal solutions after 48 h of autoclaving treatment at 120°C for various initial ratio of reactants R=[H<sub>2</sub>O]/[PC]: a) graph, b) table with values.

The viscosity of colloids increases with increasing value of R=[H<sub>2</sub>O]/[PC] indicating that higher concentration of water leads to progressive conversion of propylene carbonate into propylene glycol. For initial composition of R=[H<sub>2</sub>O]/[PC]=0.997, which is close to the stoichiometric value for conversion of PC, the measured viscosity was slightly higher (48.3 cP) than for theoretical for propylene glycol (44.45 cP at 25°C). The possible reason for that can be related to the temperature of measurements and to the presence of TiO<sub>2</sub> nanoparticles. For all colloids the viscosity was measured at room temperature, which could introduce some error with respect to theoretical values at 25°C. However, the error is not significant and measured viscosities indicate on facility of conversion for reactants.

Taking into account that during ester hydrolysis water is fully consumed and that the only remaining components are propylene carbonate and propylene glycol, it is possible to estimate the final composition of the colloidal solutions after autoclaving treatment, by measuring its viscosity. The latter is then compared to the viscosities of reference solutions with different propylene carbonate over propylene glycol ratio. Figure 33a represents the viscosity of colloidal solutions for different molar ratio of reactants (black stars) together with the viscosity of the reference solutions (red dashed curve). The latter data were approximated

using the experimentally fitted equation:  $x = \ln\left(\frac{50.98}{y - 3.788}\right)^{0.14}$ , where x is the molar fraction

of PC and  $\eta$  is the viscosity of colloidal solutions after autoclaving treatment. Then measuring the viscosity after autoclaving allows the determination of the final mole fraction of PC/PG (Figure 33b), in a given preparation.

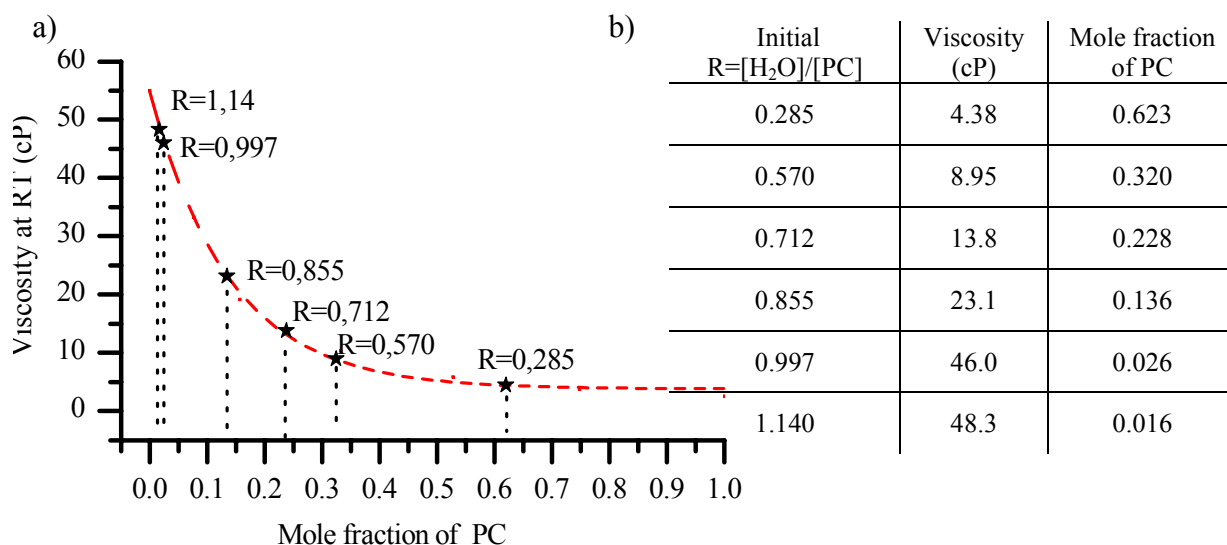


Figure 33. a) Viscosity of colloidal solutions for different molar ratio of reactants (black stars) together with the viscosity of the reference solutions (red dashed curve), b) calculated values I think viscosities are missing in the table.

The acid catalyzed conversion of cyclic alkylene carbonates to alkylene glycols is quite slow in comparison to the same reaction catalyzed by bases or salts<sup>115</sup>. To follow the progress of hydrolysis and to detect its end, measurements of viscosity were carried out at different stages. As a representative for ink-jet printing, the colloidal solution No.3 ( $R=[H_2O]/[PC]=0.712$ ) was chosen because of its lowest aggregation degree of particles (see paragraph II.1.3.d) additionally its viscosity is close to the recommended value. Figure 34a shows the viscosity of one representative colloidal solution (No.3), autoclaved for different time periods at 120°C. The viscosity seems to reach the maximum value after about 40 hours of the reaction.

The ink-jet equipment offers the possibility to process at various temperatures. It is generally preferable to process at temperatures slightly higher than room temperature, in order to obtain reproducible deposition conditions. This allows keeping reliability and avoiding changes in properties of inks in respect to ambient conditions. Additionally manipulation of printing temperature offers the possibility to optimize the physical parameters when needed.

Figure 34b) presents the viscosity of representative colloidal solution for temperature range between 10 and 70°C.

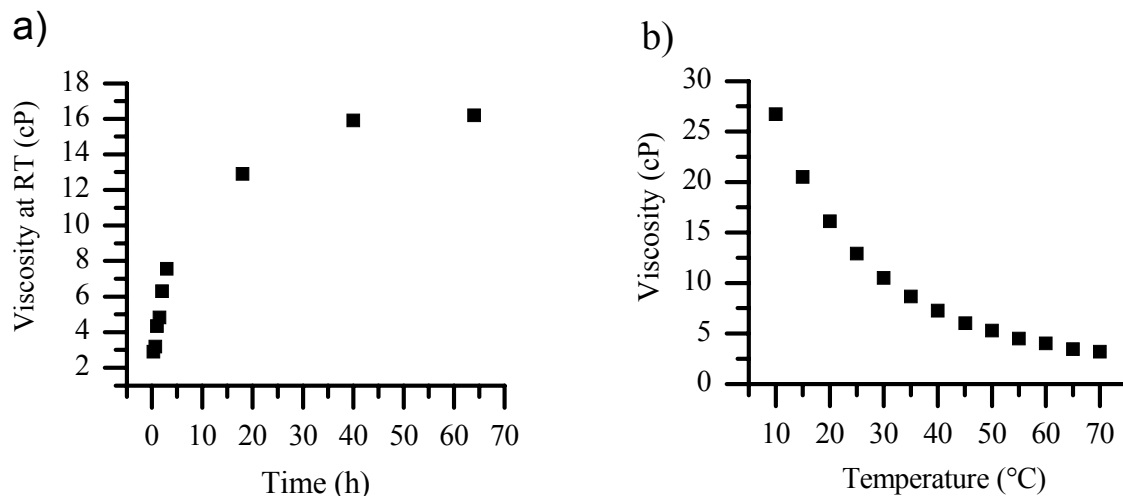


Figure 34. Viscosity of representative colloidal solution No.3 ( $R=[\text{H}_2\text{O}]/[\text{PC}]=0.712$ ): a) autoclaved for different time period, b) measured at various temperatures (after autoclaving for 48 h)

### II.1.3.c). Composition of solvent after autoclaving treatment (FT-IR)

The colloidal solutions No.1 to 6 after autoclaving were examined by Fourier Transform Infrared Spectroscopy (FT-IR). In order to verify the conversion of propylene carbonate and water, the spectra of resulting colloids were compared with reference solvents of pure propylene carbonate, propylene glycol and water. The FT-IR spectra show continuous changes of the spectra for samples prepared at various ratio of reactants  $R=[\text{H}_2\text{O}]/[\text{PC}]$  (Figure 35).

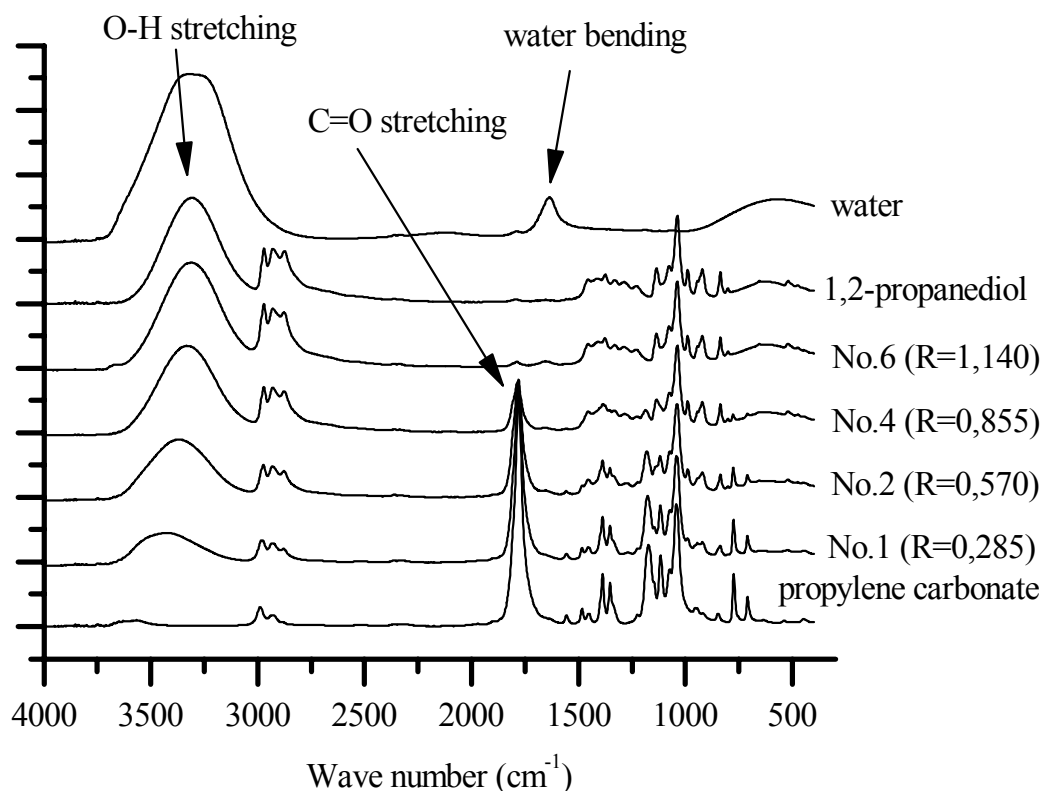


Figure 35. FT-IR of colloidal solutions prepared for various ratio of  $R=[\text{H}_2\text{O}]/[\text{PC}]$  and reference solutions.

The conversion of propylene is proved by distinct changes in the intensities of functional groups characteristic of reactants and resulting products. For samples prepared for increasing value of  $R=[\text{H}_2\text{O}]/[\text{PC}]$ , the intensity of the peak at  $1780\text{ cm}^{-1}$  attributed to the stretching vibration of carbonyl group, subsequently disappears. Consequently, the broad absorption of hydroxyl group centered at  $3305\text{ cm}^{-1}$  increases. The signal of functional hydroxyl group of propylene glycol may overlap with the water O-H stretching mode. Fortunately propylene glycol absorbs light between  $800$  and  $1000\text{ cm}^{-1}$ , which provides a confirmation. Additionally bending vibration of water at  $1650\text{ cm}^{-1}$ , was detected only for sample No.6 ( $R=1,14$ ). For that synthesis the concentration of reactants was higher than the stoichiometry and by the assumption some water was expected in the final solvent mixture. The spectra confirm the conversion of propylene carbonate into propylene glycol, indicating also that water is efficiently removed from the colloidal solutions.

#### II.1.3.d). Photon correlation spectroscopy and zetametry

The samples No.1 to 6 after autoclaving treatment appeared as colloidal solutions. For each synthesis the primary crystallite size of  $\text{TiO}_2$  particles is in the range of 5 nm (see paragraph II.1.3.a) but colloids were ‘milky-turbid’ or highly transparent (Figure 44). The difference in transparency is due to agglomeration or aggregation<sup>116</sup> of individual colloids. The dispersion of resulting particles was found to depend on the initial composition of the solvent mixture noted as  $R=[\text{H}_2\text{O}]/[\text{PC}]$ . In order to determine the size of colloids, the samples were examined by Dynamic Light Scattering. The analysis was performed using a Malvern light scattering unit, Zetasizer Nano series. For each colloidal solutions  $\text{TiO}_2$  (No.1 to 6) the composition of the final solvent was different in the propylene carbonate over propylene glycol ratio. In order to determine the size and size distribution of colloidal particles, the input data regarding a solvent (viscosity and refractive index) were taken from the reference<sup>117</sup> for each particular composition. Figure 36 shows size measurements of as prepared colloids for various ratio  $R=[\text{H}_2\text{O}]/[\text{PC}]$ . The experiments indicate that the minimum of aggregation is achieved for a certain initial composition of solvent at  $R=[\text{H}_2\text{O}]/[\text{PC}]=0.712$  (Figure 36b). For that sample, the measured hydrodynamic diameter of particle is in the range of primary crystallite size, meaning that this system is composed of mono-dispersed  $\text{TiO}_2$  particles with no secondary agglomeration. Samples prepared at lower or higher ratio of solvents result in anatase crystals which assemble as bigger objects creating agglomerates or aggregates. At the low value of  $R=0.285$ , the three population of particles were recorded in the range of 60 to 600 nm. The bad dispersion of particles, for low  $R$  values, is related to the rate of the solvent conversion. The reaction of propylene carbonate is not fast enough to provide sufficient amount of propylene glycol, which is responsible for efficient dispersion of particles. The nucleated crystals tend to form strong agglomerates which cannot be redispersed back when ester conversion reaches the equilibrium. The significant fraction of propylene carbonate in the final solvent composition induces the destabilization of the colloids. For higher values of  $R$ , the particles tend to form bigger agglomerates as  $R$  increases. In that region the ratio of water / propylene carbonate is close to stoichiometry and conversion rate of ester is expected to be fast. The reason for agglomeration is due to the significant amount of water which causes destabilization of nucleated particles at the beginning of the reaction. Nucleated particles in the presence of water create agglomerates which cannot be redispersed in the further stage of the conversion reaction, when the concentration of propylene glycol is increasing.

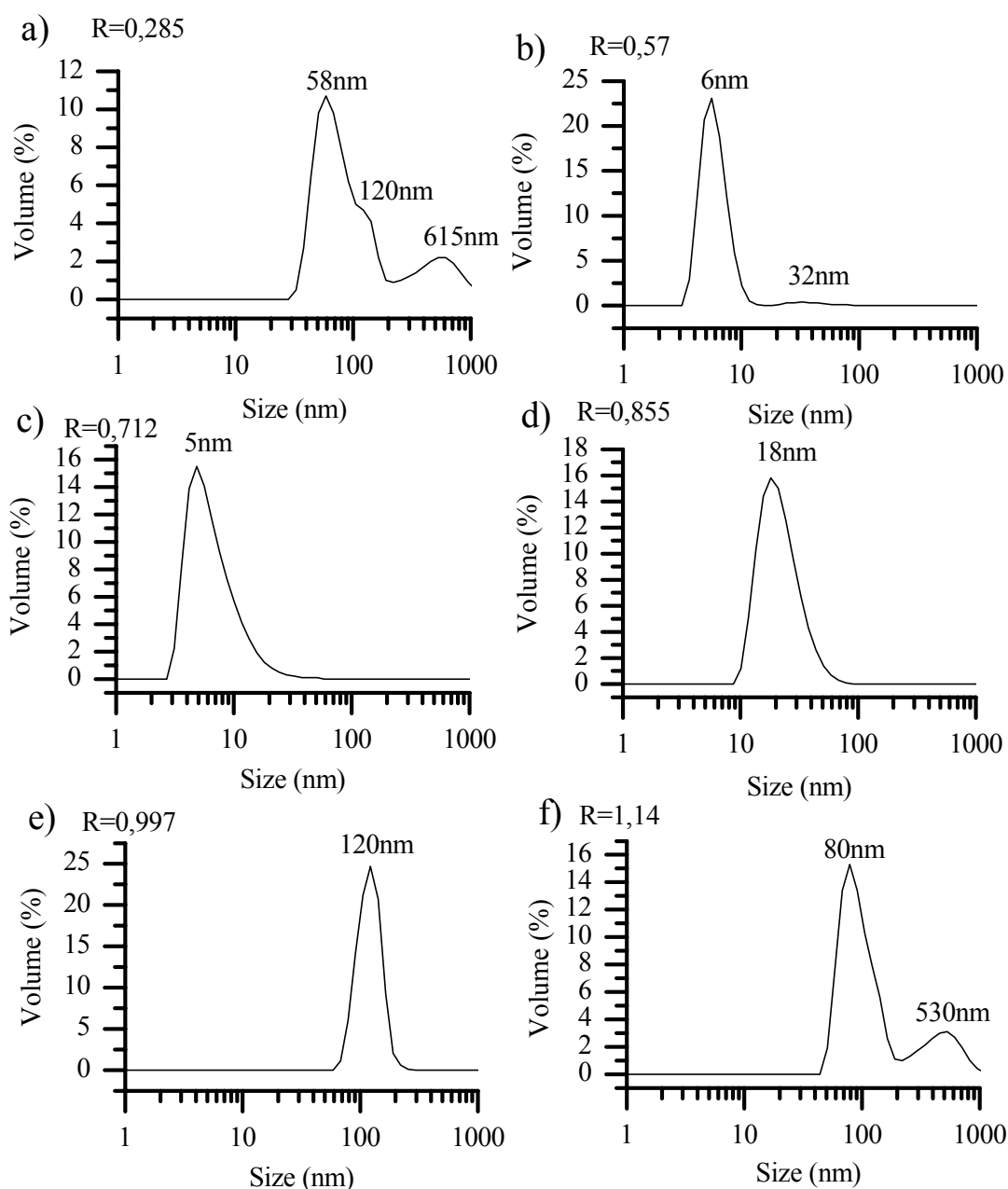


Figure 36. Particle size for colloidal solutions  $\text{TiO}_2$  prepared for various ratio of reactants: a) R=0.285(No.1), b) R=0.57 (No.2), c) R=0.712 (No.3), d) R=0.855 (No.4), e) R=0.997 (No.5), f) R=1.14 (No.6)

The observation indicates that at first the  $\text{TiO}_2$  particles form a flocculated suspension and then they are being peptized during the conversion reaction of solvent. Before the reaction, the reagents create a binary mixture of propylene carbonate and water with limited mutual solubility. During autoclaving, the titanium precursor is hydrolyzed and white precipitates are clearly observed especially when the treatment is processed for less than one

hour. At that stage of the reaction, the concentration of propylene glycol is low and precipitated titanium species are held as flocks. Progressively with time, the white precipitates disappear and the preparation turns to a one phase system due to mutual solubility of PC/H<sub>2</sub>O/PG solution. . Prolonged autoclaving time up to 2 hours, causes that concentration of propylene glycol increases, therefore hydrolyzed titanium species are peptized.

The origin of the dispersion of TiO<sub>2</sub> colloids in surfactant free system can be explained by some specific interaction of solvents with the surface of titanium oxide particles. It is evident that propylene glycol acts as a dispersive agent for presented here synthesis, but the mechanism is not fully understood. By comparison of reported data for homologous polyols, propylene glycol can be regarded as a complexing agent for nucleating particles<sup>108</sup>. Numerous colloidal nanoscale metal oxides and pigments have been successfully prepared by the so-called polyol process. The latter is based on the reaction of hydrolysable metal precursor with or without additives in a polyol medium. In most of the reported syntheses, dipropylene glycol<sup>118, 119</sup> is used as a solvent. A high boiling point of polyols allows carrying out the reaction at relatively high temperatures, causing that the prepared materials are often well crystallized. Affinity of the polyols to the surface of particles prevents the nucleated crystals from growth and aggregation, resulting in nanoscale particles in a colloidal form. Series of homologous polyols (ethylene glycol, glycerin, erythritol, 1,3-propanediol, and 1,4-butanediol) were tested as stabilizers for dispersion of silica particles in high concentrations of electrolytes<sup>120</sup>. The stabilization of colloids was interpreted by the magnitude of hydrophilic character of the polyol molecules. They claimed that alcohol hydroxyl groups interact with siloxyl groups on the particle surface and alter the interactions between colloids. It was concluded that the more hydrophilic the polyol is, the better the colloidal system is stabilized. In contrast, propylene glycol-water mixtures were examined as stabilizer for zirconia dispersions. They found that colloid state of particles in propylene glycol-water system is governed by electrostatic stabilization, predicted by the DLVO theory. The improvement in stability of colloids lies in the reduction of van der Waals interactions between particles. They found that propylene glycol decrease the zirconia Hamaker constant, which is related to the magnitude of van der Waals attractive forces between colloids. Since the attractive interactions between colloids were reduced by addition of propylene glycol, the electrostatic potential barrier necessary to prevent the particles from aggregation is lower. It means that the zeta potential necessary for stabilization of colloids in propylene glycol is lower than in the case of water solvent<sup>121</sup>.

The Zeta potential for as-prepared colloids in an organic solvent was not measurable, probably due to the low conductivities of the solutions. However when diluted 10 times in ultrapure water, the measurements could be performed. Table 3 shows the zeta potential obtained using Smoluchowski equation and pH of colloidal solutions prepared for various  $R=[\text{H}_2\text{O}]/[\text{PC}]$ .

Table 3. Zeta potential and pH of colloidal solutions  $\text{TiO}_2$  diluted 10 times in water

| Solution No. | $R=[\text{H}_2\text{O}]/[\text{PC}]$ | pH   | Zeta potential (mV) |
|--------------|--------------------------------------|------|---------------------|
| 1            | 0.285                                | 3.98 | +32.3               |
| 2            | 0.57                                 | 3.65 | +32.6               |
| 3            | 0.712                                | 3.38 | +35.8               |
| 4            | 0.855                                | 3.25 | +34.2               |
| 5            | 0.997                                | 3.06 | +34.8               |
| 6            | 1.14                                 | 2.87 | +35.6               |

In each case the colloids are acidic with a pH ranging from about 3 to 4. Protons are considered as responsible for charging of particles and their electrostatic repulsion. But the Zeta potential is somehow close to the limit (+ 30 mV) for stabilization of titanium dioxide particles<sup>122</sup>.

The sedimentation of particles could be achieved when the colloidal solution was titrated by potential determining ions:  $\text{H}^+$  and  $\text{OH}^-$ . Figure 37 shows the values of Zeta potential versus pH of the solution. At acidic conditions the colloids were very stable with values of zeta potential up to +70 mV. Changing the pH of colloids towards the isoelectric point resulted in sedimentation.

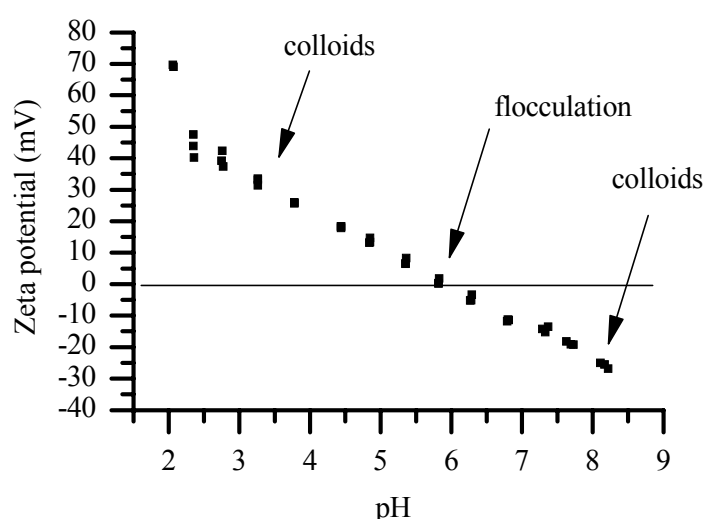


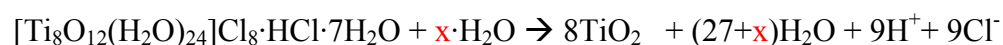
Figure 37. Zeta potential vs pH for colloidal solution  $\text{TiO}_2$  (No.2). Solution was diluted 10 times in ultrapure water and titrated by  $0.25 \text{ molL}^{-1}$  aqueous solutions of HCl and NaOH.



The estimated isoelectric point occurs at pH= 5.9, which is in agreement with the frequently cited values for the point of zero charge for anatase<sup>123</sup>. At pH=8 the particles are stabilized again for negative values of zeta potential of -25 mV. The sedimentation of colloids in the isoelectric point is an evidence for contribution of electrostatic stabilization mechanism. It is believed that the dispersion is achieved by a combined effect of complexation of the particles by propylene glycol which prevents them from formation of strong agglomerates and the electrostatic repulsion governed by protons.

### II.1.3.e). Neutralization reaction - conductivity of colloidal solutions

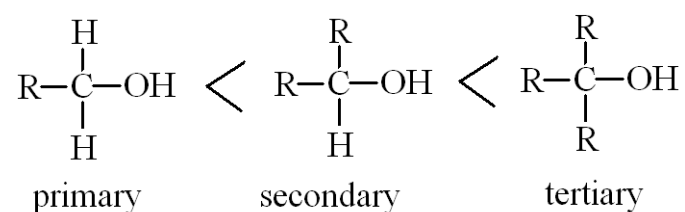
The preparation of colloidal solution takes place in acidic medium. The source of acidic ions is  $\text{Ti}_8\text{O}_{12}$  precursor which during dissolution in water and hydrolysis liberates hydrochloric acid due to the proposed reaction:



One of the restrictions for ink jet printing technique is the non corrosive property of the colloidal solvent. The acidic ions are regarded as a detrimental agent and should be removed from the system. In our case the concentration in hydrochloric acid is reduced by the reaction occurring between HCl and propylene glycol:



Alcohols can exchange hydroxyl group via nucleophilic substitution with hydrogen halides. The products are water and alkyl halides. The reactivity of alcohols with hydrochloric acid depends on the temperature and on their molecular structure. For nucleophilic substitution the reactivity increases with respect to their branching structures:



Tertiary alcohols react with hydrochloric acid at room temperature. For secondary and primary alcohols, the substitution reaction requires elevated temperatures or use of catalyst. For propylene glycol one of hydroxyl group is bonded to primary carbon atom and is considered to have low reactivity towards a substitution reaction. However, for second

hydroxyl group which is connected to secondary carbon atom, the probability of substitution reaction is much higher.

The reactivity of propylene glycol with hydrochloric acid was tested at the reaction temperature of 120°C. Different mixtures of propylene glycol with hydrochloric acid were mixed and autoclaved for 15 hours. The progress of reaction was monitored by measurements of the conductivity, which is proportional to the concentration in hydrochloric acid. Figure 38 shows the conductivity of mixtures measured before and after autoclaving treatment for various concentrations of hydrochloric acid.

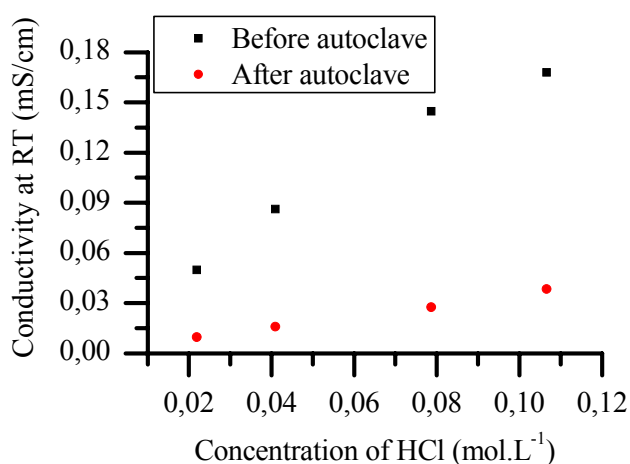


Figure 38. Conductivity of mixture of propylene glycol and concentrated hydrochloric acid

For each concentration of HCl, the conductivity after 15 hours of the reaction is reduced by around 80% in respect to the initial value. The mixtures after the synthesis have a characteristic smell and yellowish colour due to the presence of 2-chloro-1-propanol.

The same procedure was applied for the synthesis of colloidal solutions to follow the neutralization reaction. In case of colloidal solution, simultaneously with the neutralization reaction, the conversion of solvent takes place. Propylene carbonate is converted to propylene glycol and water is consumed. From that reason, the measurements of conductivity cannot be interpreted as a direct values corresponding to concentration of HCl. Since the composition of solvent is changing during the reaction, the values of conductivity will be affected by different mobility of residual ions in respective solvent mixtures.

Figure 39 shows the values of conductivity measured for colloidal solution No.3 ( $R=0,712$ ) for various time of reaction.

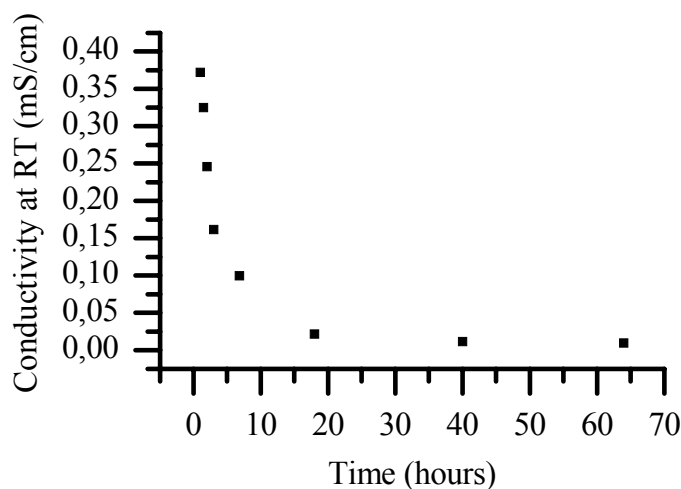


Figure 39. Conductivity of colloidal solution No.3 measured for various time of the reaction.

This graph indicates continuous decrease in conductivity for increasing autoclaving time. The conductivity decreases from 0.37 mS/cm measured at the beginning to 0.0094 mS/cm after 64 hours of autoclaving treatment. The measurements up to first 90 min of reaction can be affected by the error coming from the fact that solvent is composed of binary mixture. The estimation of exact concentration of hydrochloric acid is difficult because of the complexity of the solvent composition. The evolution of the conductivity curve indicates that reaction reaches equilibrium after about 40 hours.

#### II.1.3.f). Chemical composition of colloidal particles (XPS)

The measurement of XPS were performed using Axis Ultra spectrometer commercialized by Kratos with the monochromatic Al K radiation source (1486,6 eV) at the power equal to 150W. For the acquisition the colloidal solution No.3 ( $R=0,712$ ) was dried at 120°C in the air atmosphere for 24 hours. The resulting powder was pressed into pellet in order to obtain a flat surface. The spectra were recalibrated in energy by setting the binding energy of titanium (IV)  $Ti\ 2p^{3/2}$  at 458.7 eV and the data were fitted using Casa XPS software<sup>124</sup> after subtraction of Shirley background. Figure 40 shows the fitting of C1s, Ti 2p and O1s electron processes.

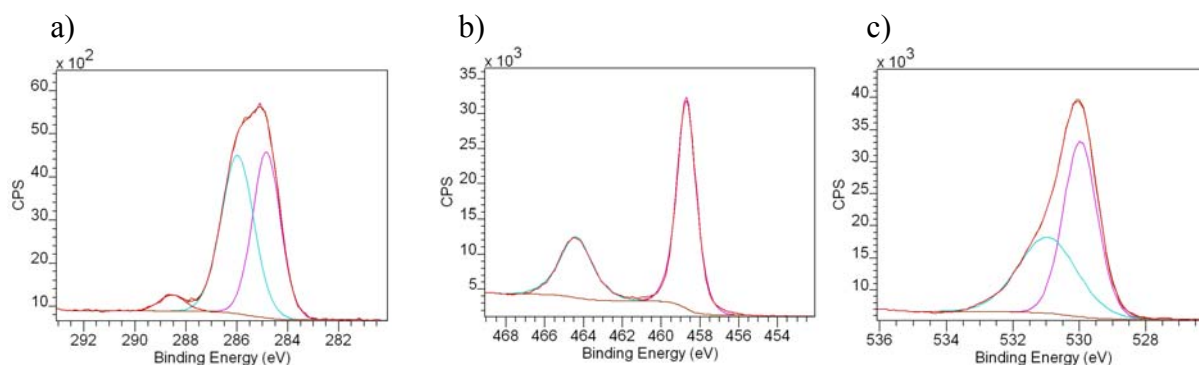


Figure 40. XPS fitting of peaks related to: a) carbon, b) titanium, c) oxygen

The signal of titanium element results in two separated peaks attributed to Ti 2p<sub>3/2</sub> and Ti 2p<sub>1/2</sub> states at the binding energies of 464,4 eV and 458,7 eV respectively. The contribution of oxygen was resolved for a multiplex of two neighbouring peaks. The first type of oxygen was attributed to oxygen ion which is bonded to titanium atom and noted as Ti-O at 530.0 eV. The second one was found at the binding energy of 531,0 eV and identified to oxygen existing as OH<sup>-</sup> species<sup>125</sup>. The contribution of carbon element was considered since the colloidal TiO<sub>2</sub> was synthesized in an organic solvent. The chemical structure of solvent (propylene carbonate and propylene glycol) indicates that in those molecules, carbon atoms exist in four chemical states: H<sub>3</sub>C-C, C-C-O or C- $\overset{\text{C}}{\overset{\text{O}}{\parallel}}\text{-O}$  and O- $\overset{\text{O}}{\overset{\text{C}}{\parallel}}\text{-O}$ . However the best fitting was achieved for three peaks, since the second and third type of carbon sit at very close positions. The first one at 284,8 eV is usually assigned to adventitious elemental carbon<sup>126</sup> and H<sub>3</sub>C-C. The second at 286eV related to -C-O bonds<sup>127</sup>. The third at 288,5eV was considered to the carbon double bonded to oxygen atom (C=O)<sup>128</sup>. The presence of C=O carbon can be related to the carbonyl group coming from contamination of propylene carbonate or surface CO<sub>3</sub><sup>-2</sup> ions, created from atmospheric pollutants. Table 4 shows the parameters for each recorded peaks.

Table 4. Peak parameters for sample No.3 (R=0,712)

| Element | Origin            | Peak position (eV) | FWHM (eV) | Relative % |
|---------|-------------------|--------------------|-----------|------------|
| C 1s    | C-H or C-C        | 284.8              | 1.28      | 12.99      |
|         | -C-O              | 286.0              | 1.50      | 14.55      |
|         | C=O               | 288.5              | 1.23      | 1.22       |
| O 1s    | Ti-O              | 530.0              | 1.20      | 25.68      |
|         | Ti-OH             | 531.0              | 2.07      | 19.29      |
| Ti 2p   | 2p <sup>3/2</sup> | 458.7              | 1.14      | 17.61      |
|         | 2p <sup>1/2</sup> | 464.4              | 1.95      | 8.67       |

The stoichiometry of sample was calculated from spectral analysis. The calculated values indicate that colloidal particles are far from the ideal stoichiometry of TiO<sub>2</sub>. The proposed formula is set as TiO<sub>1,04</sub>(OH)<sub>0,69</sub>(CO<sub>3</sub>)<sub>0,04</sub>(PG)<sub>~0,5</sub>. Calculation indicates that significant part of oxygen atoms exist as a hydroxyl form. In addition, the presence of carbon pollutants is pronounced. It is suggested that such a large number of carbon is related to propylene glycol, which is absorbed or bounded to the surface of colloidal particles.

#### II.1.4. Influence of ultraviolet light on the stability of colloidal solutions

The first scientific reports regarding photo activity of titanium dioxide were published at the beginning of the XX<sup>th</sup> century when people realized that paints incorporating TiO<sub>2</sub> caused bleaching of dyes under sunlight<sup>129</sup>. Titanium dioxide is chemically stable in the dark but when exposed to the ultraviolet light, undergoes some chemical reactions with surrounding molecules. The photo activity of TiO<sub>2</sub> is regarded as a catalytic effect since it remains chemically stable in the bulk and reactions occurs only on the crystals surface. Currently, the interest in TiO<sub>2</sub> photo activity is focused on degradation of some organic molecules or bacteria, hydrogen production, self cleaning surfaces and energy storage. Since the photo activity is related to the surface of titanium dioxide, the research is focused on the synthesis of nano materials, for which the surface aspect is pronounced<sup>130,131</sup>. Colloidal state of particles gives a rise to enhanced photo activity in contrast to the powder, where particles are connected by grain boundaries. Colloidal nano crystals existing as an isolated or weakly aggregated forms expose to the light most of the surface area and therefore the molecules surrounding them, which leads to performance in photo activity phenomena. For the

presenting here colloidal solutions, the UV light exposure had a significant effect, observable even by a naked eye. The absorption of light and photo generated reactions were used to improve a dispersion degree of particles existing in aggregated form.

#### II.1.4.a). Photo activity of colloidal $\text{TiO}_x$ nanoparticles

All examined colloidal solutions were found to be sensitive to the exposure of ultraviolet light. Irradiation of samples in the absence of atmospheric oxygen caused changes in colouration (Figure 41). As prepared colloids were transparent, but when UV light was applied, the colour turned quickly to reddish. Extended time of irradiation resulted in a deep blue colour. The blue coloration remained stable until the samples were protected from the oxygen contact. The exposure to the atmospheric gases caused the colloidal solution to turn back to the colourless state.

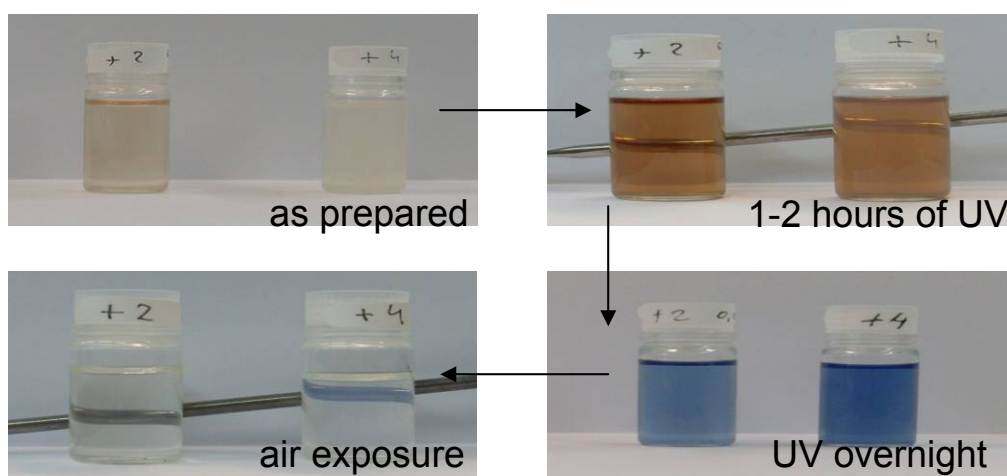


Figure 41. Change of coloration for colloidal solutions  $R=0.712$  (No.3 left) and  $R=1.14$  (No.6 right) after exposition to the light  $\text{UV}=365\text{nm}$  ( $1\text{mW}/\text{cm}^2$ ).

In order to study the coloration of colloidal solutions, the absorption in UV-Visible was realized using a spectrometer *Varian Cary 5G* between 350 and 800 nm. The colloids were placed in a quartz Suprasil<sup>®</sup> cell with the optical path of 1 cm. The contribution of the cell and a reference solvent was subtracted. Figure 42 shows the spectrum of colloidal solution  $\text{TiO}_2$  illuminated for different time periods.

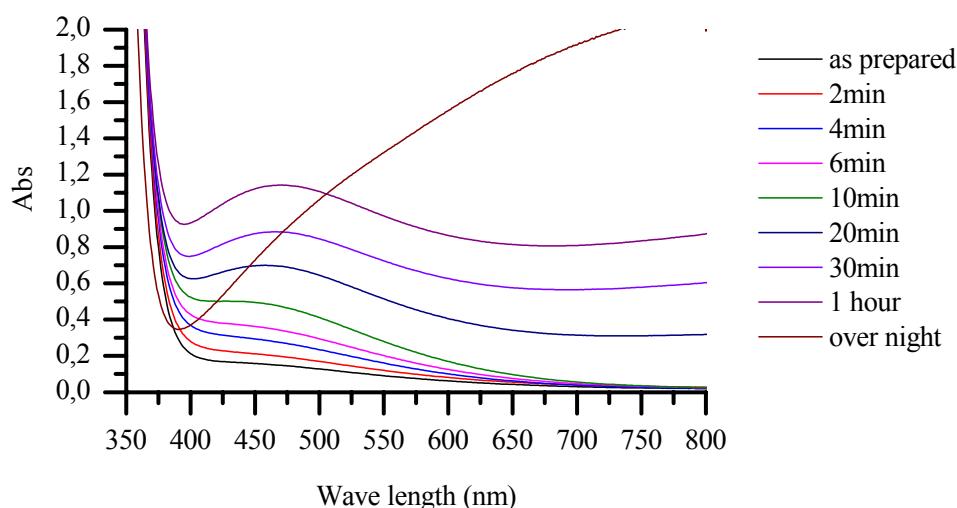


Figure 42. UV-vis spectrum of colloidal solution  $\text{TiO}_2$  irradiated by UV=365nm ( $1 \text{ mW/cm}^2$ ) light for different time periods.

As prepared colloids shows only a strong absorption in the UV domain. Subsequently with prolonged illumination time, a broad band centered at 475 nm start to develop. The minimum of absorption responsible for reddish coloration occurs at around 650-700 nm. The solutions illuminated overnight absorb the light almost in all visible range extended to infrared region. The absorption minimum occurs at 390 nm, leading to a blue colour.

Estimation of the band gap energy for colloidal particles was performed from absorption spectrum. In that case, a thinner cell with the optical path of 0.01 mm (Suprasil<sup>®</sup>) was used in order to avoid the saturation of the detector. The absorption data were fitted to Tauc equation:  $(\alpha \cdot h \cdot \nu)^n = (h\nu)$  for both indirect ( $n=0.5$ ) and direct ( $n=2$ ) bandgap transitions. Applying the Beer-Lambert's law, the absorption coefficient ( $\alpha$ ) can be calculated from the equation:  $\frac{I}{I_0} = e^{(-\alpha \cdot l)}$ , where  $l$  is the optical path. Than  $\frac{I}{I_0} = T = 10^{(-Abs)}$  was taken from the spectrum, where  $T$  is a transmittance and  $Abs$  is absorption. Figure 43 shows the graphs obtained for direct and indirect fitting:

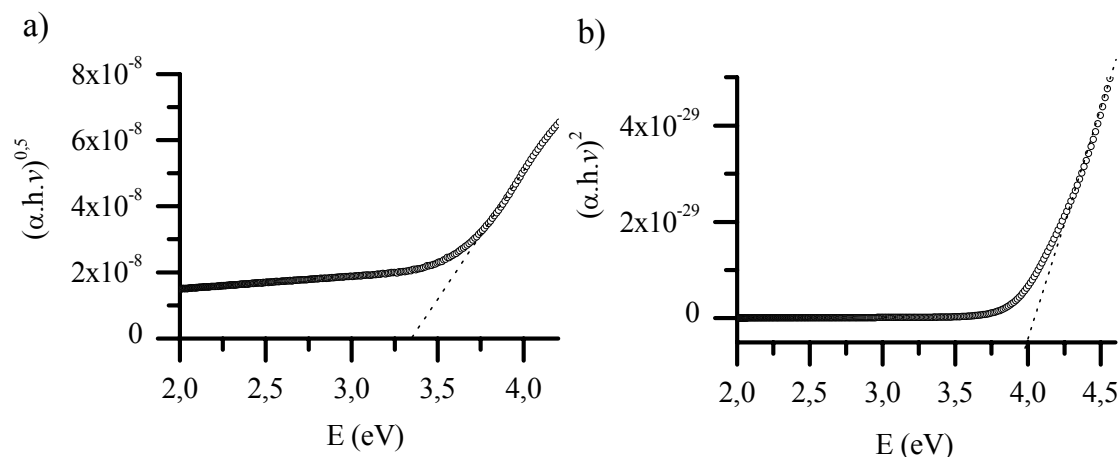


Figure 43. Tauc plots fitted for absorption spectrum of colloidal solution No.3: a) for indirect bandgap ( $n=0.5$ ), b) direct band gap ( $n=2$ ).

The energy band gap was estimated by extrapolation the linear region of the plot above the absorption edge for  $\alpha=0$ . The values indicate on indirect transition occurring at 3.37 eV and direct at 4.01 eV. In both cases, the transitions are higher than those reported in the literature. For anatase there is a consensus that band gap energy is 3.2 eV and is associated to indirect transition<sup>132</sup>. The value for direct fitting is too high and unusual for anatase variety, thus as a correct one the indirect transition was considered. The shift for an indirect transition can be explained by quantum sized effect. For crystals having a size of 5 to 10 nm, the band gap energy can be shifted by 0.1-0.2 eV<sup>133</sup>. The approximation predicts that interband transition for 5 nm anatase can reach an energy equal to 3.4 eV, which is consistent with the results presented here.

The coloration under UV exposure was already reported for titanium gels<sup>134,135,136,137</sup> and colloids<sup>138,139,140,141</sup>. The mechanism of colour changes is due to photo induced charge separation. The absorption of photon with sufficiently high energy ( $h\nu$ ), promotes injection of the electron ( $e^-$ ) to conduction band (CB) and leaving a hole ( $h^+$ ) in the valence band (VB):

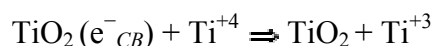


Those photo induced charges undergo fast annihilation unless some organic molecules are present in the system. The organics can react with holes and prevent them from recombination with electrons. The chemistry of holes with organics is rather complex and may lead to creation of radical species or oxidized forms of reacting molecules<sup>142</sup>:

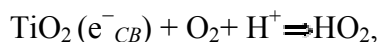


The consumption of holes facilitates accumulation of the electrons and creation of  $\text{Ti}^{+3}$  centres, which are responsible for the blue colouration:





The blue colouration is sustained until the colloids are protected from contact with the atmosphere. The exposure to oxygen results in oxidation of  $\text{Ti}^{+3}$  coloured centers to  $\text{Ti}^{+4}$  and decolouration of the colloidal solution. The origin of temporary reddish colouration, existing at the beginning of illumination is attributable to the formation of peroxo species. The process presumably involves the reduction of residual dissolved di-oxygen traces by photo generated electrons in acidic medium<sup>134</sup>:



#### II.1.4.b). Improvement of dispersion degree by UV irradiation

The irradiation of colloidal solutions  $\text{TiO}_2$  by UV light, except the changes in coloration, leads to the improvement in the dispersion degree of agglomerated particles. As presented in the paragraph II.1.3.d, only the products prepared at  $R=[\text{H}_2\text{O}]/[\text{PC}]=0,712$  is composed of monodispersed colloidal crystals. The rest of samples tend to be agglomerated. Treatment of colloids by UV light allows reducing significantly the size of existing aggregates. Figure 44 shows images of samples prepared for various ratio  $R=[\text{H}_2\text{O}]/[\text{PC}]$  after the synthesis, treated by UV light over night and exposed to the atmospheric gases.



Figure 44. Colloidal solutions  $\text{TiO}_2$  prepared for various ratio  $R=[\text{H}_2\text{O}]/[\text{PC}]$ : a) as prepared, b) irradiated by UV light over night, c) exposed to the air after UV treatment.

The improvement in dispersion degree is observed even by macroscopic observations. It is especially pronounced for samples No.5 and 6 which just after synthesis appears as milky-turbid and turns to transparent after UV exposure. The procedure seems to be not valid for the sample No.1 which probably is composed of strong agglomerates which cannot be “broken down” by illumination. In order to verify the enhancement of particle dispersion, the samples were examined by Dynamic Light Scattering (Figure 45).

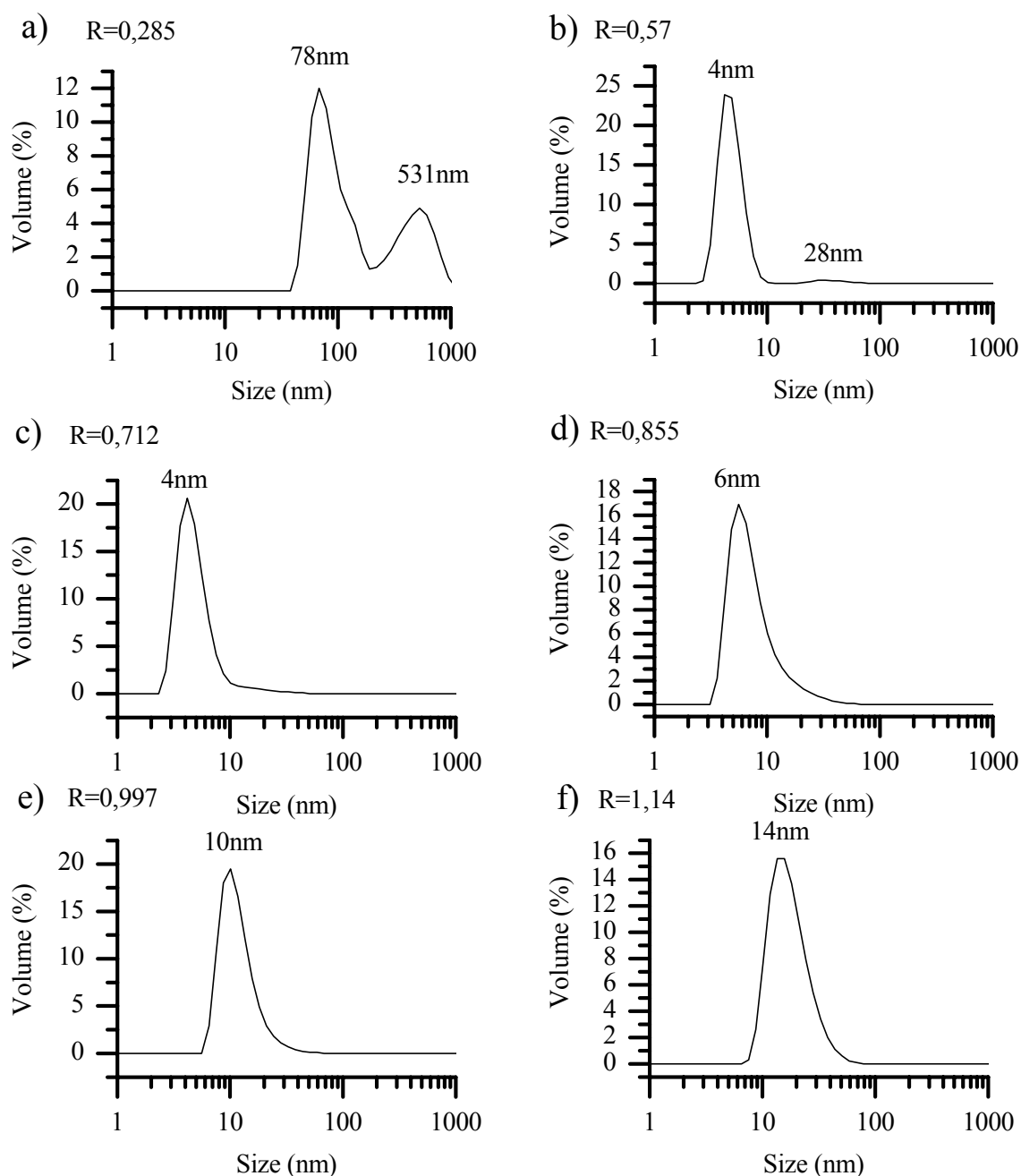


Figure 45. Particle size for colloidal solutions  $\text{TiO}_2$  prepared for various ratio of reactants after ultraviolet treatment: a) R=0.285 (No.1), b) R=0.57 (No.2), c) R=0.712 (No.3), d) R=0.855 (No.4), e) R=0.997 (No.5), f) R=1.14 (No.6)

The measured values were compared with those of as-prepared solutions (see paragraph II.1.3.d). Starting from the sample No.1 ( $R=0.285$ ) there is no particular difference in dispersion degree before and after light treatment. The sample is sensitive for UV irradiation and follows the coloration changes; however the aggregates are still large in range of 80 to 530 nm. Sample No.2 ( $R=0.57$ ) is already well dispersed just after the synthesis and only a slight difference is observed before and after light exposure. The main size of aggregates decreases from 6 to 4 nm, second population of agglomerates seems to be improved from 32 to 28 nm as well. But such a small difference between measured values is rather at the limit of the statistic error and should be interpreted with an attention. The sample No.3 ( $R=0.712$ ) does not show any improvement by the definition, because the solution was composed of monodispersed colloids just after the synthesis. The dispersion degree induced by UV irradiation begins to be significant for the colloids prepared at  $R \geq 0.855$ . For sample No.4 ( $R=0.855$ ) initial agglomerates with a main size of 18 nm are reduced to the 6 nm. The improvement in de-agglomeration becoming more pronounced for No.5 ( $R=0.977$ ) where agglomerates of 120 nm decrease to 10 nm. The sample containing the biggest particles No.6 ( $R=1.14$ ) after UV light treatment changes the agglomerates from 530 nm down to 14 nm. In the last two cases, the de-agglomeration leads to the size of particles which can not be compared to the size of individual colloids. It is expected that the particles exist as a form composed of few primary crystals.

In order to compare the results obtained by Dynamic Light Scattering, the particle dispersion degree was verified by Transmission Electron Microscopy (TEM) as a complementary method. As mentioned in paragraph II.1.3a, the immersion of TEM grid in  $0.05 \text{ mol.L}^{-1} [\text{TiO}_2]$  colloidal solution leads to the formation of a dense layer of particles. To obtain the image showing the size of existing agglomerates, the samples were diluted 100 times in ethanol. The results from TEM images (Figure 46) present the same trend as it was observed by DLS. Sample  $R=0.285$  is clearly composed of aggregated particles, but the size of the biggest objects varies up to 40 nm. The colloids prepared at  $R=0.57$  and  $R=0.712$  show that most of the deposited crystals are not connected and a good dispersion is obtained. Indeed some statistical agglomeration is observed, but it can be related to insufficient dilution and superimposition of individual particles on the TEM grid. For  $R=0.997$  is the colloids are aggregated up to 20 nm as it was observed by DLS. The dispersion of particles observed by TEM is in close agreement with the values obtained by DLS. Only for sample  $R=0.285$  some discrepancy was observed and smaller aggregates were detected by TEM than by DLS. It is

worth to mention that observation of dispersed particles by TEM has some limitations related to the concentration of colloids. Dilution of colloidal particles can affect their dispersion degree. However, both methods provide quantifiable information regarding colloidal state of matter.

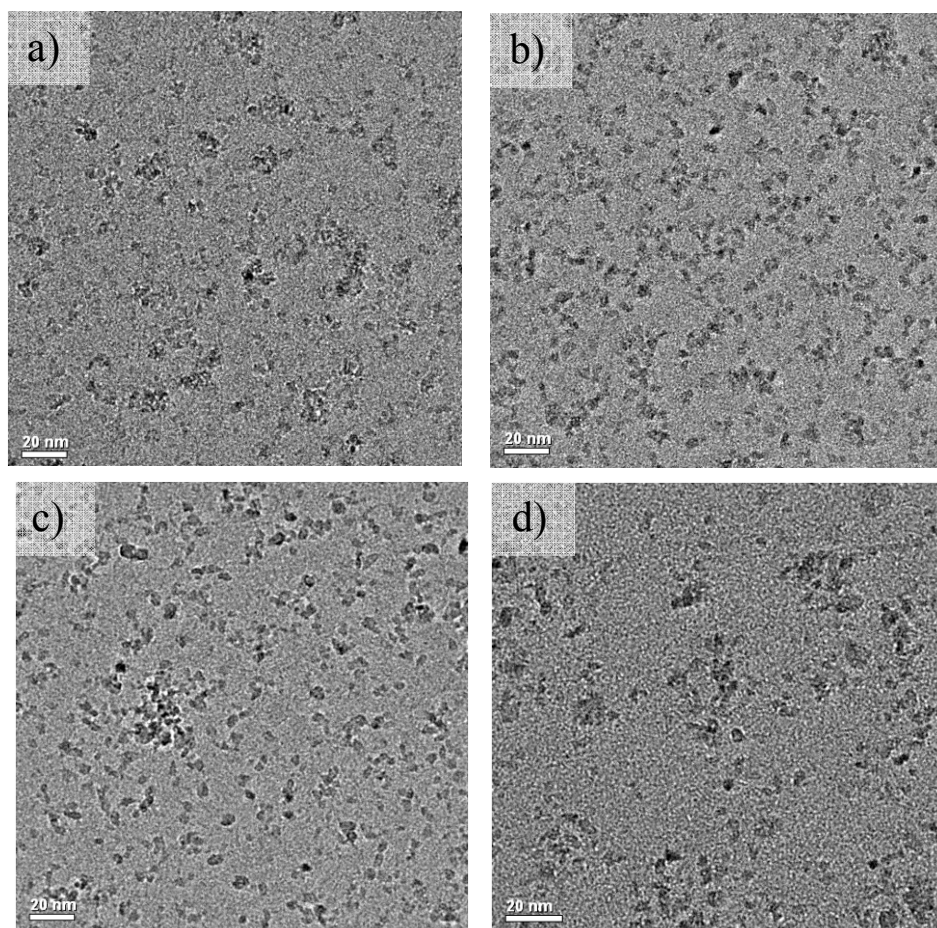


Figure 46. TEM of colloidal solutions UV-illuminated overnight and diluted 100 times in methanol: a)  $R=0.285$ , b)  $R=0.57$ , c)  $R=0.712$ , d)  $R=0.997$

## II.2. Synthesis of colloidal solution in a mixture of propylene carbonate, propylene glycol and water

The paragraph presents a modified version of the synthesis described in the section II.1. The synthesis of colloidal solutions was carried out using  $Ti_8O_{12}$  precursor and the mixture of three solvents. Due to its dispersive abilities, the propylene glycol was added to the

initial mixture of propylene carbonate and water. The products were characterized in terms aggregation of colloids and conversion degree of solvent.

### II.2.1. Protocol of synthesis

The colloidal solutions were prepared using titanium precursor  $[\text{Ti}_8\text{O}_{12}(\text{H}_2\text{O})_{24}]\text{Cl}_8 \cdot 7\text{H}_2\text{O}$ , propylene carbonate (Sigma-Aldrich 99.7%), propylene glycol (Reagent Plus 99% Sigma-Aldrich) and Milli-Q water. Before synthesis the crystals of titanium precursor were eluted several times with ethanol and dried under nitrogen flow. For each synthesis  $\text{Ti}_8\text{O}_{12}$  crystals were dissolved in the appropriate amount of water by vigorous stirring. After crystal dissolution propylene glycol (PG) and propylene carbonate (PC) were added. As prepared reactants, were poured in the teflon vessels (47 mL volume) and autoclaved at  $120^\circ\text{C}$  for 48 hours. The heating rate was approximately  $300^\circ\text{C}/\text{hour}$ . After the synthesis, autoclaves were let to cool down to room temperature and they were opened carefully in order to liberate slowly the carbon dioxide. Table 5 presents the amount of reactants involved for the synthesis.

Table 5. Amount of reactants taken for the synthesis of colloidal  $\text{TiO}_2$

| Sol No. | $\text{Ti}_8\text{O}_{12}$ (g) | $\text{H}_2\text{O}$ (moles) | PC (moles) | PG (moles) | $R=[\text{H}_2\text{O}]/[\text{PC}]$ | Concentration $\text{TiO}_2$ [ $\text{mol.L}^{-1}$ ] |
|---------|--------------------------------|------------------------------|------------|------------|--------------------------------------|------------------------------------------------------|
| 7       | 0.32                           | 0,056                        | 0.195      | 0.039      | 0,285                                | 0,085                                                |
| 8       | 0.32                           | 0,111                        | 0.195      | 0.039      | 0,570                                | 0,081                                                |
| 9       | 0.32                           | 0,167                        | 0.195      | 0.039      | 0,855                                | 0,077                                                |
| 10      | 0.32                           | 0,222                        | 0.195      | 0.039      | 1,140                                | 0,074                                                |
| 11      | 0.64                           | 0,167                        | 0.195      | 0.039      | 0,855                                | 0,155                                                |

The samples were noted by the initial ratio  $R=[\text{H}_2\text{O}]/[\text{PC}]$  of solvents, taken for the synthesis. The molar ratio between propylene glycol and propylene carbonate was kept constant at  $D=[\text{PG}]/[\text{PC}]=0,2$  for each synthesis. The concentrations of resulting colloids refer to the amount of precursor and were established to be in the range of 0,074 to 0,155  $\text{mol.L}^{-1}$  [ $\text{TiO}_2$ ].

## II.2.2. Viscosity of colloidal solutions

The measurements of viscosity were performed in order to verify the reaction degree of propylene carbonate and water. Expecting the complete conversion of the reactants, the viscosity of colloids, where  $R=[H_2O]/[PC] \sim 1$  should be close to the theoretical value of propylene glycol (44.44 cP at 25°). Figure 47 shows the values measured after 48 hours of reaction for colloids prepared at increasing value of  $R=[H_2O]/[PC]$ .

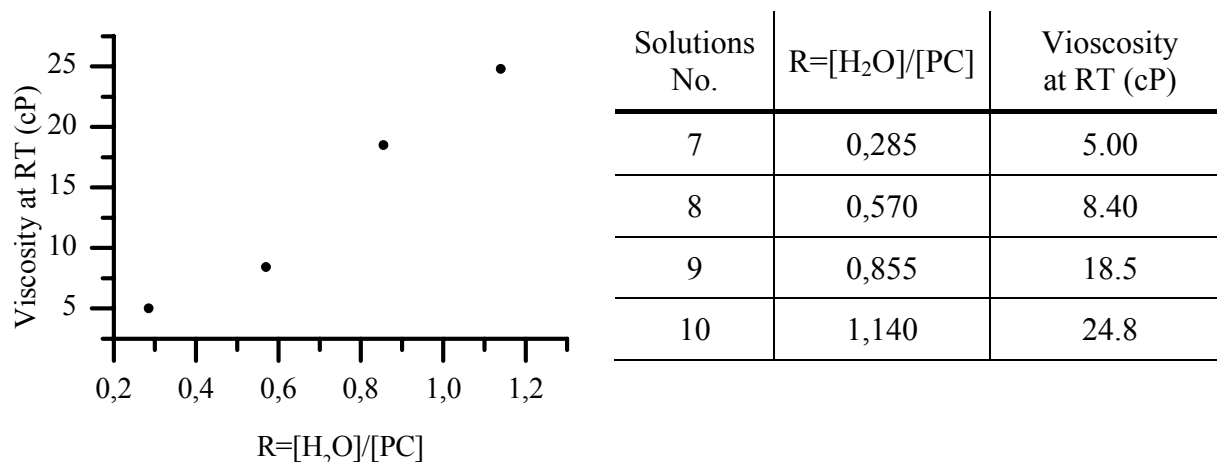


Figure 47. Viscosity of colloidal solutions  $TiO_2$  (No.7-10) after 48 h of autoclaving treatment at 120°C for various initial ratio of reactants  $R=[H_2O]/[PC]$  and addition  $D=[PG]/[PC]=0.2$  : a) graph, b) table with values.

The measured values are far from expected for the complete conversion of propylene carbonate. For solution No.10 ( $R=1.14$ ), the viscosity reaches 24.8 cP, which is almost half of the value recorded for No.6 ( $R=1.14$ ), where only propylene carbonate and water were used for the synthesis. For lower values of  $R$ , the viscosity is also lower than predicted. The addition of propylene glycol into the initial mixture of the reactants shifts the balance of the conversion reaction towards the reactants, which is coherent with the law of mass action. Thus, water and propylene carbonate can not react completely.

One of the main restrictions for the synthesis of colloidal solutions (because of ink-jet printing) was to keep relatively low surface tension of the resulting colloids (see I.2.3.). The colloidal solution which is composed of propylene glycol and propylene carbonate allows keeping the surface tension in the range of 37 to 40 mN/m at 25°C<sup>143,144</sup>. Incomplete conversion of water contributes to physical properties of the mixture.

Figure 48 shows the surface tension of water mixtures with propylene carbonate<sup>143</sup> and water with propylene glycol<sup>144</sup> taken from the reference. In the literature there is a lack of data regarding surface tension of ternary systems for those solvents. However from the graphs one can assume that below 0.2 molar fraction of water in the mixture of PG or PC, the surface tension of the colloidal solution remains below 40 mN/m, at 25°C.

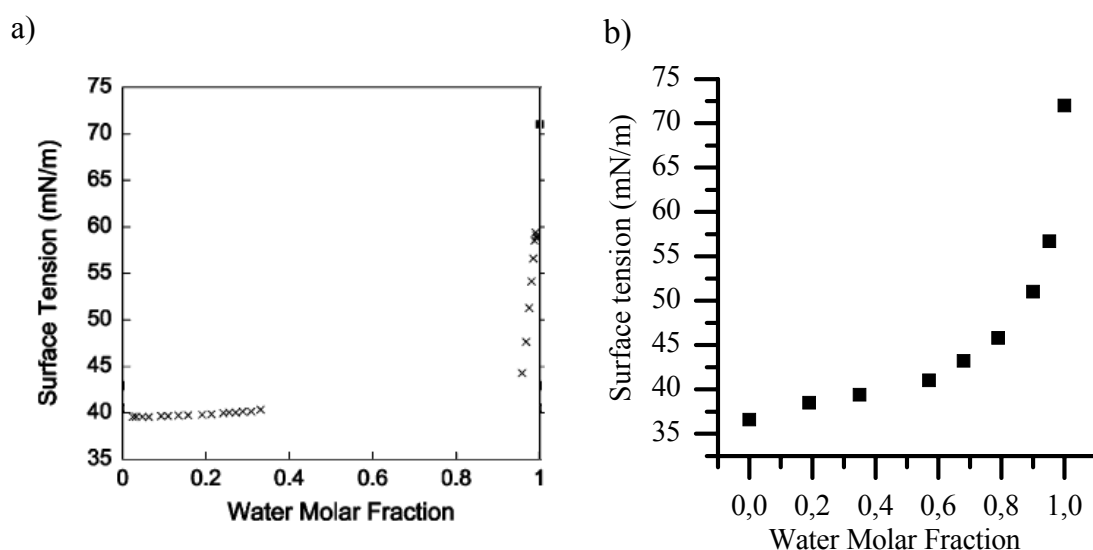


Figure 48. Surface tension of binary mixtures at 25°C: a) propylene carbonate-water<sup>143</sup>, b) propylene glycol-water<sup>144</sup>.

For presented here colloids, the water content is regarded to be below that limit.

### II.2.3. Photon correlation spectroscopy

Incomplete reaction of water for colloidal solutions No.7-10, means that solution is a mixture of three solvents, for which some parameters needed for measurements of particle size distribution (refractive index) can not be precisely known. In order to minimize the error, the colloids were diluted 10 times in ethylene glycol. The physical parameters of ethylene glycol were used as input data for calculation of particle sizes. Figure 49 shows the average

size of aggregates measured by Dynamic Light Scattering for various  $R=[\text{H}_2\text{O}]/[\text{PC}]$ . For increasing values of  $R$ , the size of agglomerates decreases. The minimum of agglomeration occurring in propylene carbonate and water only does not take place in case of the three solvent systems. Addition of propylene glycol to the mixture of propylene carbonate/water, improves the dispersion degree of colloidal particles for higher value of  $R$ . The size of aggregated particles is in the range of crystallite size (5 nm) for  $R=0.855$  and  $R=1.14$ . However at low  $R$ , the particles are composed of larger objects.

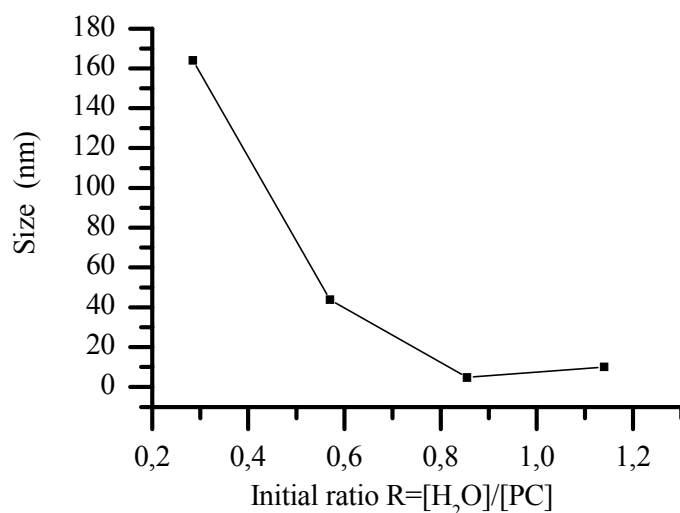


Figure 49. Particle size of colloidal solutions (No.7-10)  $\text{TiO}_2$  for various  $R=[\text{H}_2\text{O}]/[\text{PC}]$ .

The reason for aggregation when  $R=0.285$  and  $0.57$  is suspected to be a consequence of the large amount of propylene carbonate and residual water. The presence of those two solvents, which are not considered as dispersive agents, causes destabilization of the colloidal solutions especially at elevated temperatures ( $120^\circ\text{C}$ ).

### II.3. Synthesis of colloidal solutions in propylene glycol and water

The subchapter presents the synthesis of  $\text{TiO}_2$  colloidal solutions using  $\text{Ti}_8\text{O}_{12}$  precursor, water and propylene glycol. Based on the experience described in sections II.1 and II.2 which provides information about dispersive abilities of propylene glycol, the synthesis has been carried out in solvent containing propylene glycol as the major constituent. The presence of water was necessary to dissolve the titanium precursor and was restricted to the minimum in order to maintain a low surface tension of the prepared colloidal solutions. The



products were characterized in terms of crystallographic structures, dispersion degree and the physical properties of the resulting colloidal solution were estimated.

### II.3.1. Protocol of synthesis

The colloidal solutions were prepared using titanium precursor  $[\text{Ti}_8\text{O}_{12}(\text{H}_2\text{O})_{24}]\text{Cl}_8 \cdot \text{HCl} \cdot 7\text{H}_2\text{O}$ , propylene glycol (Reagent Plus 99% Sigma-Aldrich) and Milli-Q water. Before synthesis the crystals of titanium precursor were eluted several times by ethanol and dried under nitrogen flow. For each synthesis  $\text{Ti}_8\text{O}_{12}$  crystals were dissolved in the appropriate amount of water by vigorous stirring. After crystal dissolution the propylene glycol (PG) was added. As prepared reactants, were closed in the teflon vessels (47mL volume) and autoclaved at  $120^\circ\text{C}$  for 48 hours. The heating rate was approximately  $300^\circ\text{C}/\text{hour}$ . After the synthesis autoclaves were let to cool down to room temperature. Table 6 presents the amount of reactants taken for the synthesis. The samples were noted by the initial ratio  $R=[\text{H}_2\text{O}]/[\text{PG}]$  of solvents, taken for the synthesis. The concentrations of resulting colloids refer to the amount of precursor.

Table 6. Amount of reactants taken for the synthesis of colloidal  $\text{TiO}_2$

| Sol No. | $\text{Ti}_8\text{O}_{12}$ (g) | $\text{H}_2\text{O}$ (moles) | PG (moles) | $R=[\text{H}_2\text{O}]/[\text{PG}]$ | Concentration $\text{TiO}_2$ ( $\text{mol.L}^{-1}$ ) |
|---------|--------------------------------|------------------------------|------------|--------------------------------------|------------------------------------------------------|
| 12      | 0.18                           | 0,056                        | 0.327      | 0,171                                | 0,04                                                 |
| 13      | 0.18                           | 0,166                        | 0.299      | 0,555                                | 0,04                                                 |

### II.3.2. X-ray diffraction, transmission electron microscopy

The crystallographic structure of as-prepared TiO<sub>2</sub> particles was characterized after evaporation of the solvent from colloidal solutions at 120°C under air for 24 hours. Figure 50 shows the X-ray diffraction patterns for products prepared for two particular compositions of solvent mixture of  $R=[\text{H}_2\text{O}]/[\text{PG}]$ .

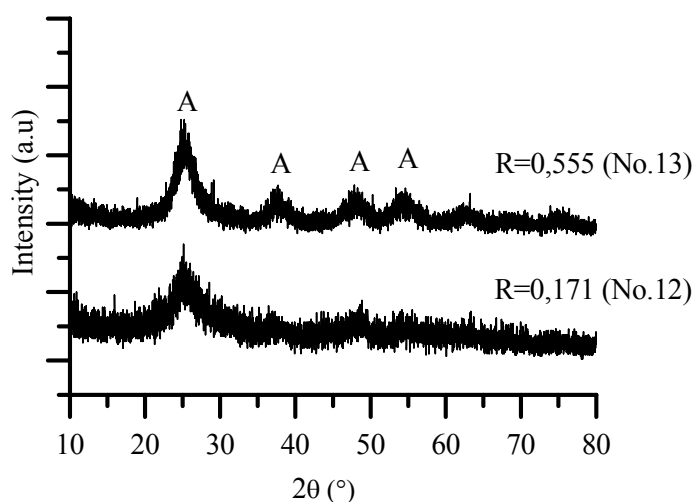


Figure 50. X-ray diffraction patterns for powders obtained by drying colloidal solutions (No.11 and 12).

The obtained diffraction patterns for both colloidal solutions shows the intensity lines attributed to anatase. For sample No.12 prepared at slightly low amount of water, the diffraction peaks are broader. Only the main peak of anatase (101) is clearly detected. The weak signal of diffraction indicates on low crystallite size for the prepared particles. The sample No.13 synthesized at slightly higher amount of water, shows also diffraction peaks related to anatase, however the peaks are more pronounced. In order to confirm the size of colloidal particles the samples were characterized by Transmission Electron Microscopy.

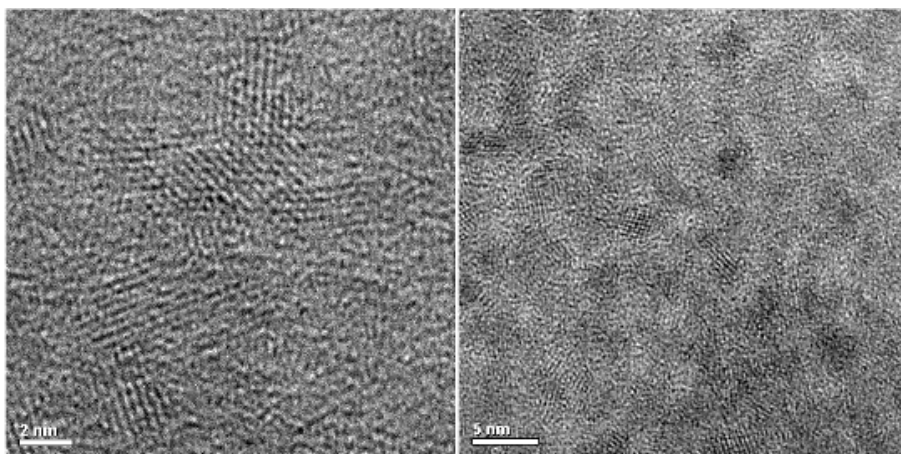


Figure 51. TEM images of solution No.12

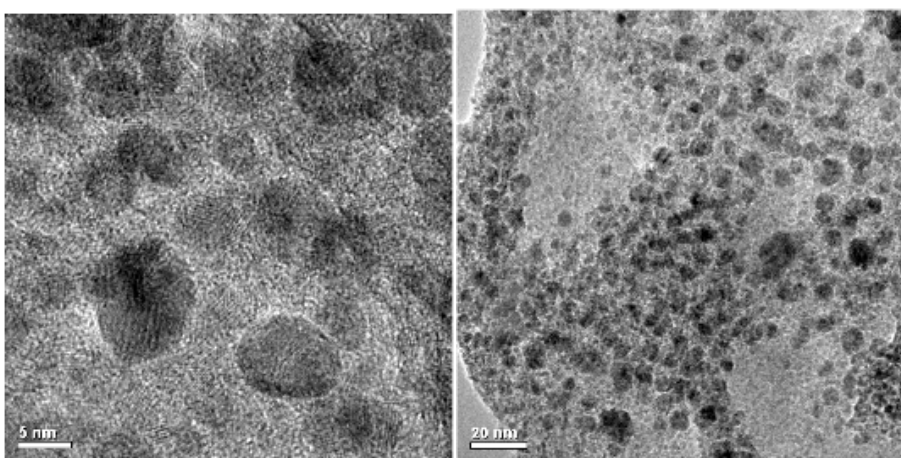


Figure 52. TEM image of solution No.13

Sample No.12 is composed of small crystallized particles with a size not exceeding 2 nm (Figure 51). The colloidal solution Nr.13 (Figure 52) is composed of slightly larger particles. The observed grains are not homogeneous in size and distribute between 4-10 nm. For both syntheses the shape of particles is close to spherical. The size of primary particles was found to depend on the ratio of used reactants  $[H_2O]/[PG]$ . The experiments indicate that the amount of water used for the synthesis has a consequence in the crystal growth phenomena.

### II.3.3. Photon correlation spectroscopy

The obtained solutions No.12 and 13 were optically highly transparent indicating on good dispersion of colloidal particles. The size distribution of agglomerates was examined by Dynamic Light Scattering. The input data for DLS measurements were taken from the reference (viscosity -  $\eta^{145}$ , refractive index -  $n_D^{146}$ ) by estimation of the solvent composition. Figure 53 shows the size distribution of colloidal particles for samples No.12 and 13.

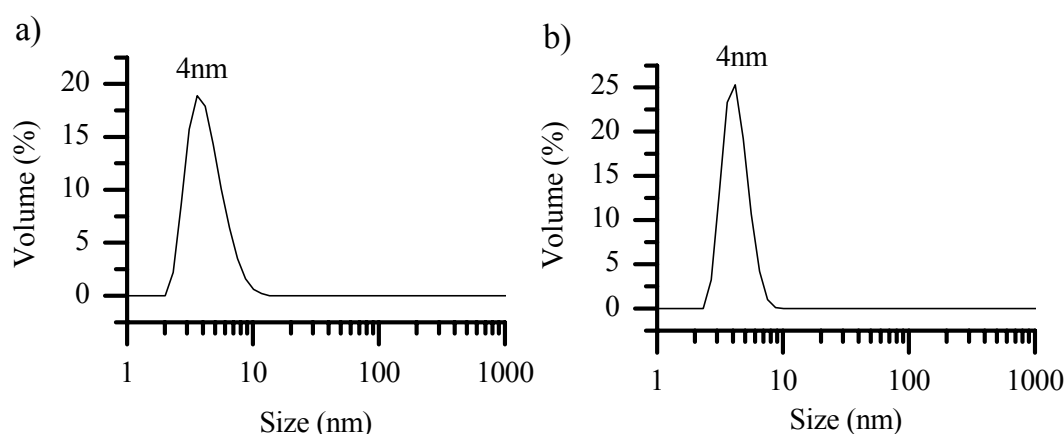


Figure 53. Particle size for colloidal solutions TiO<sub>2</sub>: a) No.12 ( $\eta=36,1\text{cP}$ ,  $n_D=1,432$  , b) No.13 ( $\eta=24,9\text{cP}$ ,  $n_D=1,424$ )

For both colloidal solutions, the main particle size was found at 4 nm. Colloidal solution No.12 for which the primary crystallite size was 2 nm shows broad size distribution in range of 2 to 12 nm. That indicates on slight agglomeration of colloidal crystals. For sample No.13, the size distribution is in range of 3 to 9 nm which is in agreement with the primary grain size detected by TEM (Figure 52).

### II.3.4. Physical properties of colloidal solutions

The physical parameters of the colloids were estimated in order to verify the suitability for the ink-jet printing technique. Table 7 gathers up the calculated values of viscosity, surface tension and boiling points of both colloidal solutions. In both cases, the water present in the solvent mixture is low and allows keeping the surface tension below 40 mN/m. The boiling points are above 120°C as recommended. However, the viscosity for both colloids is

definitely too high (recommended 8-15 cP) and has to be optimized by addition of suitable solvents. In fact for all the presented here colloidal solutions the physical parameters are rather rough approximations. In order to assure jettability, the exact formulation has to be done for each particular printing equipment. The idea to control the physico-chemical parameters at the beginning of the synthesis is to assure flexibility of colloids for further formulations.

Table 7. Physical properties of colloidal solutions

| Sol No. | Mole fraction of H <sub>2</sub> O | Viscosity at 25°C <sup>145</sup> (cP) | Surface tension at 25°C <sup>144</sup> (mN/m) | Boiling point at 600mmHg <sup>147</sup> |
|---------|-----------------------------------|---------------------------------------|-----------------------------------------------|-----------------------------------------|
| 12      | 0.146                             | 36.1                                  | 37.7                                          | 155°C                                   |
| 13      | 0.357                             | 24.9                                  | 39.1                                          | 120°C                                   |

## II.4. Deposition of colloids on conductive glass substrates

The paragraph presents the microscopic images of thin films TiO<sub>2</sub> deposited from colloidal solutions onto conductive glass substrates. The representative samples were deposited by spin coating and ink-jet printing technique. The homogeneity of the deposits was verified.

### II.4.1. Spin coating– Atomic force microscopy

The colloidal solution No.11 was deposited on the conductive glass substrate ASAHI 100 by spin coating. Before deposition, the substrate was eluted with ethanol and dried under compressed air in order to remove dusts. The colloidal solution was spin coated by setting three rotation speeds at: 300-1500-500 r.p.m., for 30 seconds each. After the deposition, the sample was dried in air at 120°C. The AFM image was performed using tapping mode for a substrate before and after deposition (Figure 54).

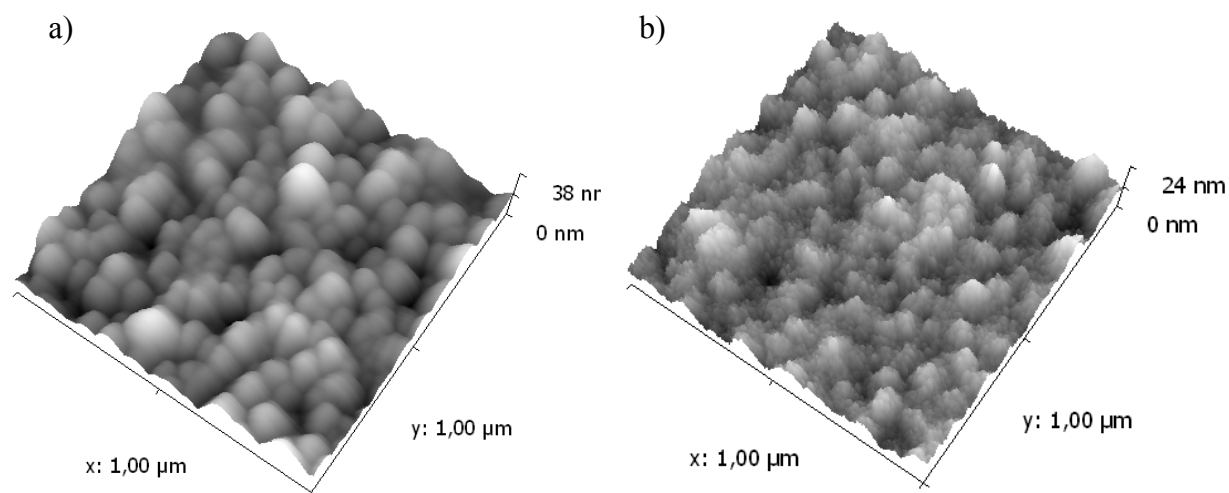


Figure 54. AFM image of conductive glass substrate ASAHI 100: a) bare substrate, b) after deposition of colloidal solution

The surface of conductive glass substrate is composed of nearly spherical grains with a size up to 100 nm. After deposition of colloids, the characteristic topography of the substrate is affected by the coverage of smaller objects. The colloidal particles homogeneously cover the entire surface including peaks and valleys. The deposited film is not thick enough to mask completely the initial roughness of the glass substrate. The measured Root Mean Square (RMS) roughness decreases from 5.34 nm to 3.13 nm after deposition of colloids, meaning that the magnitude between peak and valleys is less pronounced. The skewness,  $R_{sk}$ , for both images is positive meaning that asymmetry of the surface features go towards heels after deposition of colloids. For bare substrate  $R_{sk}$  is equal to 0.478 and decreases to  $R_{sk} = 0.31$  for coated substrate, meaning that surfaces become flatter.

#### II.4.2. SEM – ink jet printing

The representative colloidal solution No.3 was deposited on ITO substrate by ink-jet printing by the industrial partnership unit of the ANR Solhypin project: ARDEJE. Before deposition, the colloids were diluted 1/4 by a solvent (the composition protected by ARDEJE) and optimized by Jerome Mourao. After deposition, the substrate was dried to remove the excess of solution. The printing has been done in two modes in order to deposit different volume of colloidal solution on the substrate. The homogeneity of deposits was verified using Scanning Electron Microscopy (SEM) Jeol 7600F by imaging (topography) and EDX mode

(chemical analysis). Figure 55 shows the deposits for which different contents of colloidal ink were deposited.

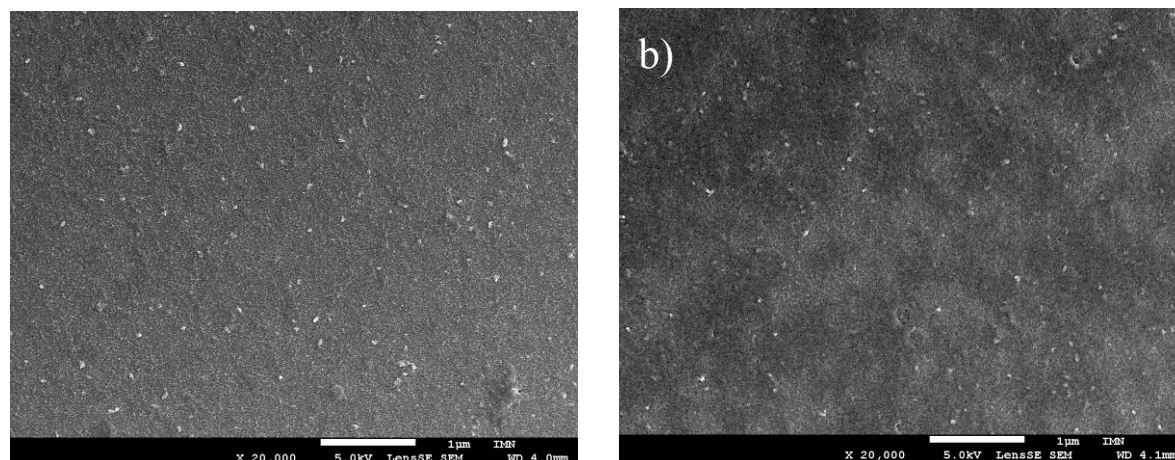


Figure 55. SEM image of  $\text{TiO}_2$  layers on ITO deposited by ink-jet printing: a) with the amount of colloidal ink  $x \text{ mL/cm}^2$ , b) with the amount of colloidal ink  $1.5x \text{ mL/cm}^2$ . The optimal amount of printed material is denoted as 'x'.

The deposition of colloids for which  $x \text{ mL/cm}^2$  of colloidal solution was printed, results in a homogeneously distributed  $\text{TiO}_2$  layers. The surface is uniformly covered by particles but some statistical bigger particles were observed. The deposition for which  $1.5x \text{ mL/cm}^2$  was printed leads to  $\text{TiO}_2$  layers where colloidal particles create a gradient of deposited matter. The SEM image shows the grey shaded domains, meaning that the colloidal solution tend to accumulate and is not distributed homogeneously on the substrate. For that deposition, the amount of printed solution is too high and the excess solvent shrinks due to surface tension.

The deposit for which  $x \text{ mL/cm}^2$  of colloidal solution was printed on the surface is shown for different magnifications in Figure 56. The small size of colloidal particles and homogenous distribution leads to difficulties related with SEM imaging. In order to capture the quality of  $\text{TiO}_2$  layer, the image was focused on the domain where thin film was mechanically scratched during sample preparation. The defect in the form of cross at magnification of 2000 is shown (Figure 56a). Except this defect, the surface is homogeneously covered by the colloidal particles. The morphology of deposited particles is more pronounced for higher magnifications. For figure 56d at zoom of 40 000, the contrast between  $\text{TiO}_2$  layer and the substrate surface is clearly observed. The thickness of thin film was not possible to analyze from cross-section images because of small thickness and charging effects. However, the rough approximation can be deduced from the scratched defect domain. The defaulted place indicates on a layer of about 20 nm (Figure 56d).

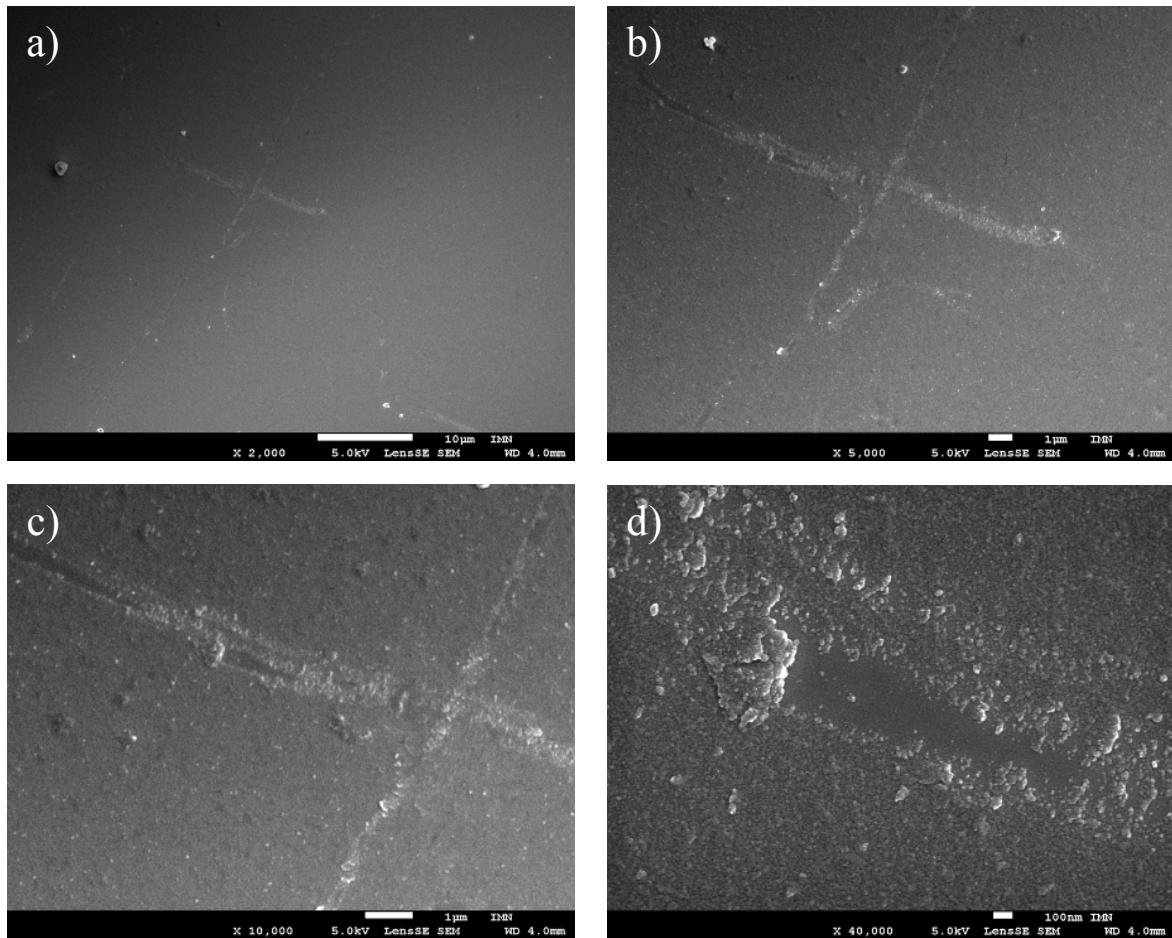


Figure 56. Deposition of colloidal solution  $\text{TiO}_2$  No.3 on TCO by ink-jet printing at magnification: a) 2 000, b) 5 000, c) 10 000, d) 40 000.

The presence of  $\text{TiO}_2$  particles on the all entire surface was confirmed by EDX mapping of elements. The analysis was carried out for a surface area of  $11 \times 8 \mu\text{m}^2$  and 10 keV accelerating voltage. Figure 57 shows the spectra and the distribution of the expected elements. Green colour represents the indium coming from the conductive glass substrate and red colour the titanium element. The indium signal is much more pronounced in comparison to titanium element because of the relative thicknesses of both layers ( $\sim 100 \text{ nm}$  ITO,  $\sim 20 \text{ nm}$   $\text{TiO}_2$ ). Additionally, the electrons, accelerated at a voltage of 10 keV, penetrate 400 nm deep in the sample a, thus the elements related to the glass substrate were also detected: K, Na, Mg, Al, Si, Ca. The spectrum (Figure 57c) shows the elements detected by EDX analysis.



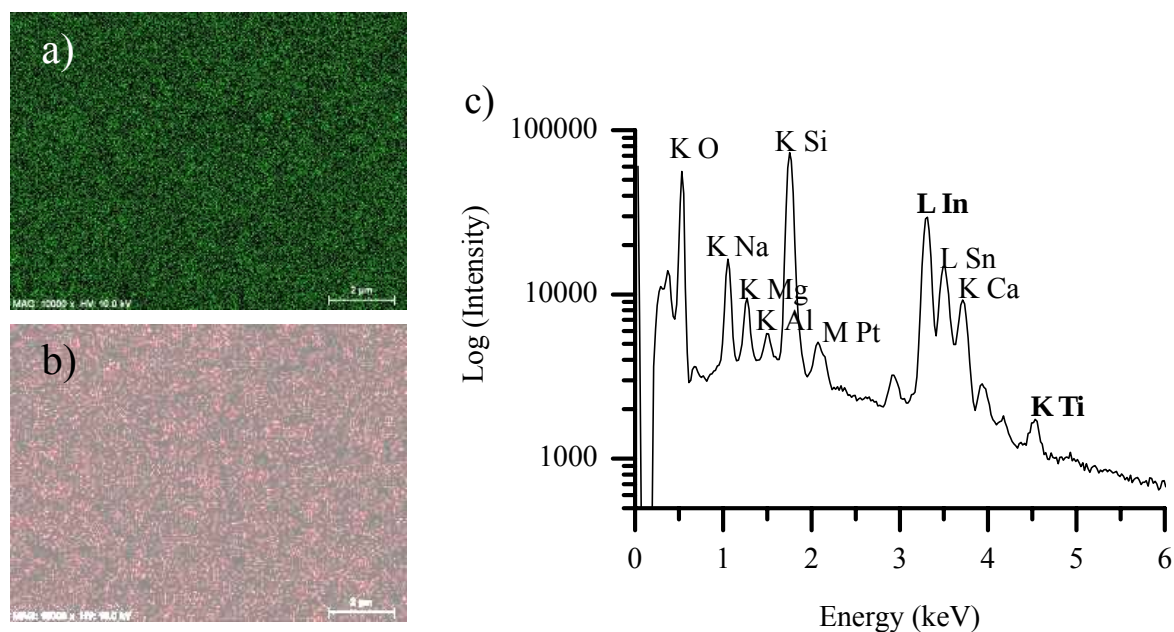


Figure 57. EDX mapping of elements: a) indium element, b) titanium element, c) corresponding spectra.

The deposits of  $\text{TiO}_2$  by ink-jet printing can be preliminary verified by macroscopic observations. The deposits are highly transparent and almost invisible for the naked eye. However it can be observed when the light is reflected from the substrate with a certain angle. Figure 58 shows image of solution No.3 printed on ITO glass substrate in the square shape and dimensions of  $5 \times 5 \text{ cm}^2$ . The deposits are homogenous and the edges can be printed with precision for optimal amount of printed solution.

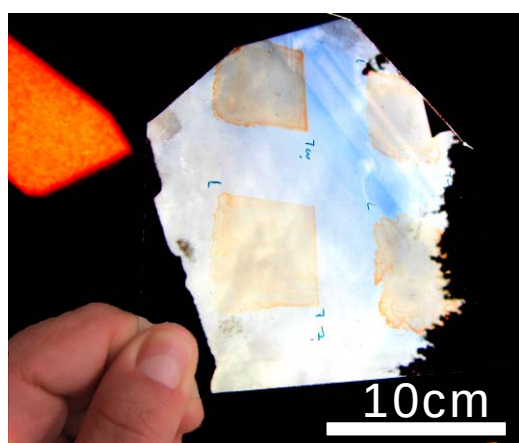


Figure 58. Image of deposits  $\text{TiO}_2$  printed on ITO glass substrate by ARDEJE.

## II.5. Tests of deposited TiO<sub>2</sub> layers in hybrid device

Thin films of TiO<sub>2</sub> were deposited by spin coating on conductive glass (ITO) and assembled in photovoltaic devices. The tests and cells assembly were done at the partnership unit (CEA-INES) by Solenn Berson. The results presented here were recorded for inversed structure: glass / ITO/ **TiO<sub>2</sub>** / P3HT:PCBM / HTL /Ag . The 0.28 cm<sup>2</sup> cells were tested under standard AM1.5 illumination at 40°C.

Before deposition, the colloidal solutions were illuminated by UV light (365 nm) in order to eliminate statistically agglomerated particles. Table 8 presents the representative results for the solar cells involving colloidal solutions of TiO<sub>2</sub> with different particle sizes as n-type layers.

Table 8. Initial performance of solar cells using TiO<sub>2</sub>

| Solution No. | Crystallite size of TiO <sub>2</sub> (nm) | Voc (mV) | Jsc (mA/cm <sup>2</sup> ) | FF (%) | PCE (%) |
|--------------|-------------------------------------------|----------|---------------------------|--------|---------|
| 3            | 5                                         | 600      | 11.2                      | 55.2   | 3.7     |
| 12           | 2                                         | 589      | 10.2                      | 52.3   | 3.15    |
| 13           | 4-10                                      | 581      | 11.0                      | 53.4   | 3.4     |

Among the results presented here, the best performance for organic solar cells was achieved for colloidal solution No.3, reaching a power conversion efficiency of 3.7%. For that solution the mean crystallite size is equal to 5 nm and the particles are mono-dispersed. The solutions having smaller (2 nm) and bigger (4-10 nm) crystallite diameters show slightly lower cell performance. In order to explain the origin of cell performance for those three cases, a few aspects should be considered. First, the mean size of building units of thin film is different for those three cases, which leads to modification of the electronic structure of TiO<sub>2</sub><sup>148</sup>. The changes in electronic structure may result in some mismatch between electronic configuration of organic absorber and TiO<sub>2</sub>. The mean crystallite size also affects the number of crystal inter connections within the bulk of the film. Despite that, the packing arrangement of particles should be considered, especially for the case of solution No.13, where crystals were not homogenous in size. Additionally, the solvent for each of those three solutions was different. Solution No.3 was composed of mixture propylene carbonate and 1,2-propanediol. Solutions No.12 and 13 were mixture of water and 1,2-propanediol. The properties of solvent may affect the stability of colloidal particles and their arrangement during the different stages

of evaporation. Thus, bearing in mind the above considerations, it is not easy to select one parameter which is responsible for the performance of thin film layers.

The layers deposited from colloidal solution No.3 were tested for long term stability. Figure 59 shows the variation of power conversion efficiency of the cells for the time period of 6500 hours of continuous illumination. In the graph, the red line corresponds to the results of the layers prepared from the colloidal solution UV illuminated overnight and the blue line represents those associated to the colloids illuminated for one hour.

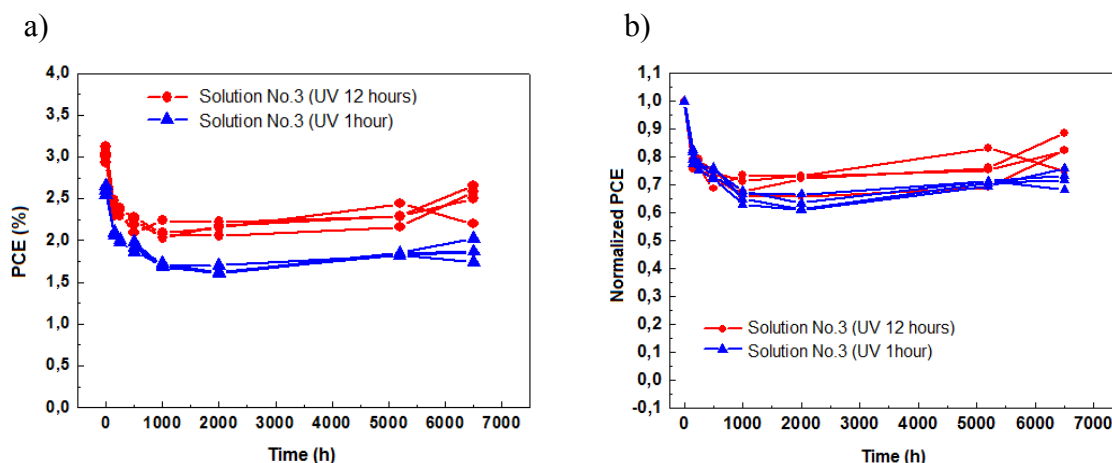


Figure 59. Power conversion efficiency of organic solar cells having  $\text{TiO}_2$  charge transporting layer: a) nominal value of PCE, b) normalized values.

The solar cell for which the colloidal solution was illuminated for 12 hours shows better performance, than the one for which colloids were illuminated for 1 hour. The difference in power conversion efficiency between those two experiments is around 0,5%. This behaviour is not well understood. One of the possible explanations can be due to statistically agglomerated particles. The solution which was used for the experiment is considered to be well dispersed, however some statistical aggregates might be formed. The illumination by UV light was found to improve the dispersion of strongly aggregated colloids, thus it might also eliminate statistical aggregates. Another explanation can be related to surface chemistry of illuminated particles. The UV treatment, followed by oxygen contact, induce the reversible change in oxidation state of titanium atoms ( $\text{Ti}^{+4} \leftrightarrow \text{Ti}^{+3}$ ). It is suspected that this process might modify the surface of colloidal particles before deposition and improves the semiconductive properties of  $\text{TiO}_2$  thin films.

For tested solar cells the power conversion efficiency drops down during the first 1000 hours of AM1.5 illumination to about 70 % of the initial value. When the illumination time is

extended the PCE surprisingly increases slowly. For the best solar cell (prepared using colloids illuminated by UV for 12 hours) the PCE loss is limited to 17 % after 6500 hours.

## Conclusions of chapter II

Colloidal solutions of  $\text{TiO}_2$  were prepared by hydrolysis reaction of ' $\text{Ti}_8\text{O}_{12}$ ' precursor and organic solvents in solvothermal conditions at  $120^\circ\text{C}$ . Three formulations were tested. The first formulation involved the use of solvent mixture of water and propylene carbonate. Those solvents mixed with different molar ratio of  $R=[\text{H}_2\text{O}]/[\text{PC}]$  react with each other to form 1,2-propanediol. The progress of that reaction affects the colloidal stability of particles which are formed during hydrolysis of ' $\text{Ti}_8\text{O}_{12}$ ' precursor. The examined range of  $R=[\text{H}_2\text{O}]/[\text{PC}]$  results in synthesis of anatase particles with the size of primary crystals in range of 5 nm. For low and high values of  $R=[\text{H}_2\text{O}]/[\text{PC}]$  the particles were strongly agglomerated. The optimal conditions to synthesize the monodispersed colloids were found at  $R=[\text{H}_2\text{O}]/[\text{PC}]=0,712$ . The water, which is introduced as a reactant, is fully consumed during the reaction within 48 hours. The large difference of viscosity between reactants and products allows controlling the viscosity of final colloidal solutions and adjusting to the value dedicated for ink-jet equipment. All examined colloids were photosensitive to exposure of ultraviolet light. The illumination of samples in airtight conditions caused improvement of dispersion degree for agglomerated colloids and this procedure was applied before each deposition on the substrates. The colloids were tested in terms of compatibility with industrial ink-jet equipment and deposits were studied by SEM. For the optimally adjusted amount of printed material, deposited colloids resulted in homogeneously distributed  $\text{TiO}_2$  layers on conductive glass substrates.

The second chemical formulation for synthesis of colloidal solution  $\text{TiO}_2$  employed the propylene carbonate, 1,2-propanediol and water as solvents. In this formulation the propylene carbonate reacts with water. The presence of 1,2-propanediol allows to obtain well dispersed and more concentrated colloids in a wider range of  $R=[\text{H}_2\text{O}]/[\text{PC}]$  as compared to the first formulation of the synthesis. However, addition of 1,2-propanediol causes incomplete reaction between propylene carbonate and water. The residual water is undesired, because of its high impact on surface tension, which causes dewetting of colloidal solutions on the substrates.

The third formulation of colloidal solutions employ the use of water and 1,2-propanediol as a solvents for the hydrolysis of 'Ti<sub>8</sub>O<sub>12</sub>' precursor. The amount of water was limited in order to obtain the colloidal solutions with the surface tension below 40mN/m. The synthesis results in highly dispersed particles for two examined ratio of  $R=[\text{H}_2\text{O}]/[\text{PG}]$ . The ratio of solvent mixture affected also the size of anatase crystals. For  $R=[\text{H}_2\text{O}]/[\text{PC}]=0,171$ , the crystallite size was in range of 2 nm. The synthesis at  $R=[\text{H}_2\text{O}]/[\text{PC}]=0,555$  resulted in anatase crystals with the size distribution in range of 4 to 10 nm. However, for this formulation, the viscosity of colloidal solutions is too high in respect to the recommended by ink-jet printing.

The three formulations of the synthesis presented in the chapter give an opportunity to synthesize the stable monodispersed colloidal solutions of TiO<sub>2</sub> (anatase) with the crystallite size in range of 2 to 8 nm. The use of propylene glycol, propylene carbonate and water as a medium for hydrolysis of Ti<sub>8</sub>O<sub>12</sub> precursor, gives the opportunity for controlling the physical parameters of colloidal solutions in respect to the values recommended by ink-jet printing. The colloidal solutions deposited on conductive glass substrates were used as a n-type charge transporting layer for organic solar cell. As prepared photovoltaic devices shows the power conversion efficiencies as high as 3.7% and durability over 6500 hours with a decrease in PCE limited to 17 %. The concept of employing TiO<sub>2</sub> as a protective layer validated the concept of stable organic solar cells.

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# Chapter III: Synthesis and characterization of colloidal solutions of nickel hydroxide and nickel oxide thin films

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## Introduction

This chapter describes a method for the synthesis of colloidal nickel hydroxide in propylene glycol. Resulting colloids were used as precursor for deposition of nickel oxide thin films and were tested as a p-type conducting layers in hybrid organic solar cells. The colloids were prepared in three steps in order to carry out the synthesis and purify the nickel hydroxide from by-products. The first step involves hydrolysis of nickel salt (nickel chloride and nickel nitrate) by organic base (tetramethyl ammonium hydroxide) using controlled titration method. In that step nickel hydroxide species were synthesized via acid-base reaction between nickel salt and organic base. The synthesis was realized at two different temperatures in order to modify the stoichiometry of the resulting hydroxide. The second step of the synthesis involves the flocculation of nickel hydroxide species by addition of selected solvent and separation of products by centrifugation. In the last third step, nickel hydroxide is peptized in propylene glycol in order to obtain colloidal solutions with fine particles. The nickel oxide thin films were obtained by deposition of colloidal nickel hydroxide by spin coating and followed by heat treatment procedures. The products were characterized at each stage of preparation in order to verify the crystallographic structures, stoichiometry and control dispersion abilities of the products. The resulting thin films were characterized by electron microscopy techniques and homogeneity of deposited layers was discussed. Finally the films of nickel oxide were tested as a hole transporting layers in hybrid organic device and the cells performance was presented.

### III.1. The synthesis of colloidal nickel hydroxide and nickel oxide

#### III.1.1. Protocol of synthesis

The colloidal solutions of nickel hydroxides were prepared using the following precursors:  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (99.9%, Sigma-Aldrich) or  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Merck for analysis EMSURE), as nickel salts, tetramethylammonium hydroxide pentahydrate (97%, Sigma-Aldrich) as precipitating base agents and different solvents such as ethylene glycol ( $\geq 99\%$  Sigma-Aldrich), propylene glycol ( $\geq 99.7\%$ , Sigma-Aldrich), acetone ( $\geq 99.5\%$ , ReagentPlus, phenol free). The synthesis of nickel hydroxide involves three steps defined in the following manner.

**1<sup>st</sup> step:** The synthesis of the nickel hydroxide was realized by acido-basic reaction between nickel salts and the organic base by controlled titration in organic solvents. For each experiment 20 mL of 0.1 mol.L<sup>-1</sup> [Ni<sup>+2</sup>] were titrated by 5 mL of 0.8 mol.L<sup>-1</sup> [TMAOH] with controlled speed of 0.2 mL/min and vigorous stirring to avoid local changes in pH. The synthesis was performed at two different temperatures in ethylene glycol at RT and propylene glycol at 70°C:

- for the synthesis at room temperature nickel chloride and nickel nitrate were prepared in ethylene glycol at the concentration of 0.1 mol.L<sup>-1</sup> [Ni<sup>+2</sup>]. In order to dissolve the nickel salts the solution was vigorously stirred at 60°C. Tetramethylammonium hydroxide (TMAOH) solutions were prepared at concentration of 0.8 mol.L<sup>-1</sup> [TMAOH] in ethylene glycol by dissolution of crystals under vigorous magnetic stirring at room temperature.

-For the synthesis carried out at 70°C, the precursor Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O was dissolved in propylene glycol at the concentration of 0.1 mol.L<sup>-1</sup> [Ni<sup>+2</sup>] by vigorous stirring at 60°C. The TMAOH solution was dissolved in propylene glycol at concentration of 0.8 mol.L<sup>-1</sup> [TMAOH] at room temperature.

**2<sup>nd</sup> step:** Immediately after titration, as-prepared solutions were flocculated by addition of 50 mL acetone and stirred for 5min. The flocculated solids were separated from the liquid phase by centrifugation (10 min with 12 000 r.p.m.).

**3<sup>rd</sup> step:** Freshly obtained green jelly sediments were peptized in 20mL of propylene glycol by vigorous stirring in a closed vessel at 70°C for 24 hours in a heated bath. The pH of as-prepared solutions is listed in the Table 9.

The nickel oxides were prepared from the nickel hydroxide precursors by two thermal treatments in air. The first heat treatment was performed at 120°C for 24 hours. The second heat treatment was realized at 400°C for 2 hours with a temperature ramp of 200°C/h. The general scheme of the synthesis is presented in Figure 60.

Table 9. Supporting information for the synthesis of colloidal hydroxides

| Nickel salt                                          | Titration temperature | Solvent for titration reaction | pH of the colloidal solution after redispersion |
|------------------------------------------------------|-----------------------|--------------------------------|-------------------------------------------------|
| NiCl <sub>2</sub> ·6H <sub>2</sub> O                 | ambient               | Ethylene glycol                | 10.65                                           |
| Ni(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O | ambient               | Ethylene glycol                | 10.13                                           |
| Ni(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O | 70°C                  | Propylene glycol               | 9.00                                            |

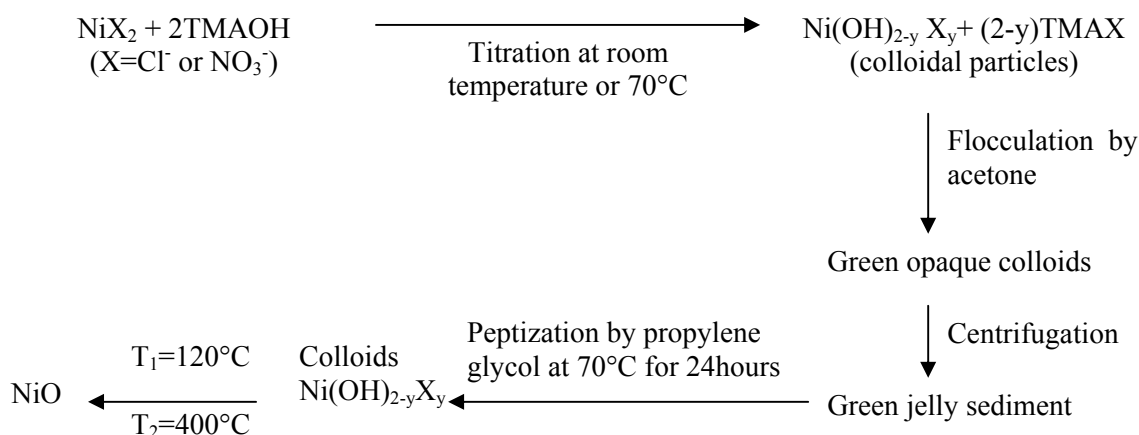


Figure 60. Scheme of the synthesis

### III.1.2 Titration-controlled hydrolysis of nickel salts

The first step for synthesis of nickel hydroxide was carried out by pH-metric titration using Titrand 809 titrator with Tiamo software (Metrohm). The procedure was realized by constant rate addition of tetramethylammonium hydroxide to the nickel salts. The pH of the solutions was monitored during addition of the base for increasing ratio of reactants, noted as  $R = [\text{OH}^-]/[\text{Ni}^{+2}]$ . The pH measurements provide the information about the rate of acid-basic reaction between nickel and hydroxyl ions. Figure 61 shows the typical curves obtained for titration of nickel chloride and nickel nitrate salts. In the case of titration nickel salts at room temperature (Figure 61a and b), the addition of base results in gradual increase of pH until the ratio of the reactants reaches value of  $R = [\text{OH}^-]/[\text{Ni}^{+2}] = 1.5$ . Above that value the abrupt increase of pH is observed. In the case of titration of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  at  $70^\circ\text{C}$  (Figure 61c), the addition of the base results in rather constant  $\text{pH} = 6$  until the ratio of reactants reaches the value of  $R = [\text{OH}^-]/[\text{Ni}^{+2}] = 1.75$  and above that value the sharp increase in pH takes place.

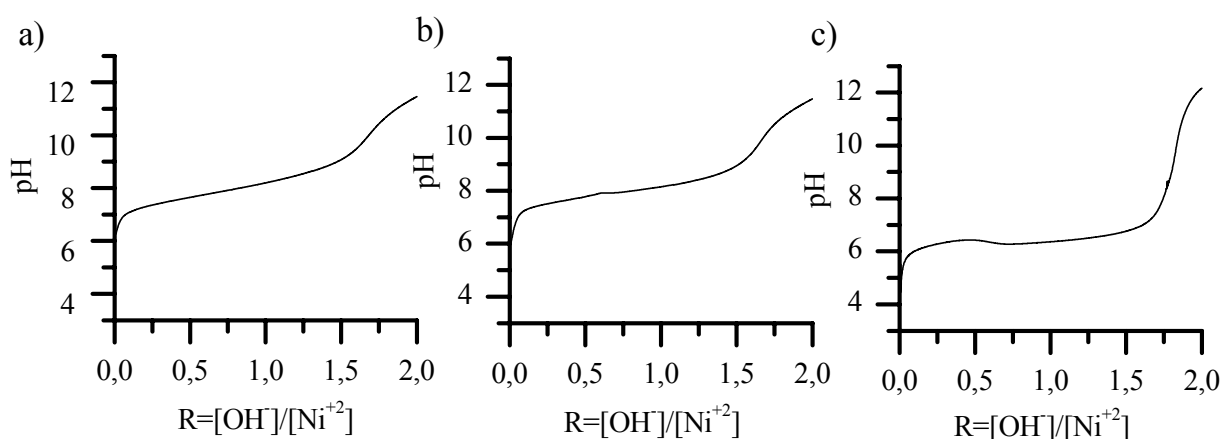


Figure 61. Titration of nickel salts by TMAOH: a)  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  at room temperature, b)  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  at room temperature, c)  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  at  $70^\circ\text{C}$ .

At the beginning of the titration where addition of the base causes only gradual changes in the pH, the solution acts as a buffer for addition of hydroxyl ions. In that region nickel ions are suspected to be hydrolyzed by the base and to form nickel hydroxylated species. Finally where addition of a base causes an abrupt increase in pH, the capacity of buffer solution is saturated, meaning that the hydrolysis reaches equilibrium and further addition of the base causes only increase of concentration of hydroxyl ions in the solution.

The shape of titration curves provides the information about the stoichiometry of the nickel hydroxyl species. For all three titrations the abrupt increase in pH values takes place below the theoretical value predicted for divalent nickel ions. The stoichiometry of formed products was assumed to be related to equilibrium of hydrolysis reaction and was estimated from the end point of the titration curve. The end point was evaluated from the first derivate of “S” shaped curve. The calculated values indicate the formation of  $\text{Ni}(\text{OH})_{1.7}\text{Cl}_{0.3}$  in case nickel chloride and  $\text{Ni}(\text{OH})_{1.67}(\text{NO}_3)_{0.33}$  for nickel nitrate titrated at room temperatures. For the titration of nickel nitrate at  $70^\circ\text{C}$ , the end point of titration suggest the formation of  $\text{Ni}(\text{OH})_{1.82}(\text{NO}_3)_{0.18}$ . In proposed formulas the chloride and nitrate counter ions were added to balance the charge of divalent nickel ion.

## III.2. Characterization of products

### III.2.1. Photon correlation spectroscopy

The synthesis of nickel hydroxides results in green precipitated particles in the case of titration at 70°C. However, at the end of titration experiments at room temperature, the precipitation of nickel hydroxide was not observed and the solution remained translucent. The particle growth and formation of jelly-like solution was visible after few hours of titration experiment. The Figure 62 shows the particle size evolution during ageing at 30°C of as-prepared  $\text{Ni}(\text{OH})_{1,67}(\text{NO}_3)_{0,33}$ . For freshly prepared solution, the particle size measured by Dynamic Light Scattering indicates two populations of particles in the range of 8–24 nm. After one hour, the size of particles grows up to 28 nm with a small fraction of particles 1  $\mu\text{m}$  in size. Ageing for 4 hours results in colloidal particles having a mean diameter of about 1.3  $\mu\text{m}$ . After 7 hours of treatment, the solution is not any longer transparent with the size of particles of about 3  $\mu\text{m}$ .

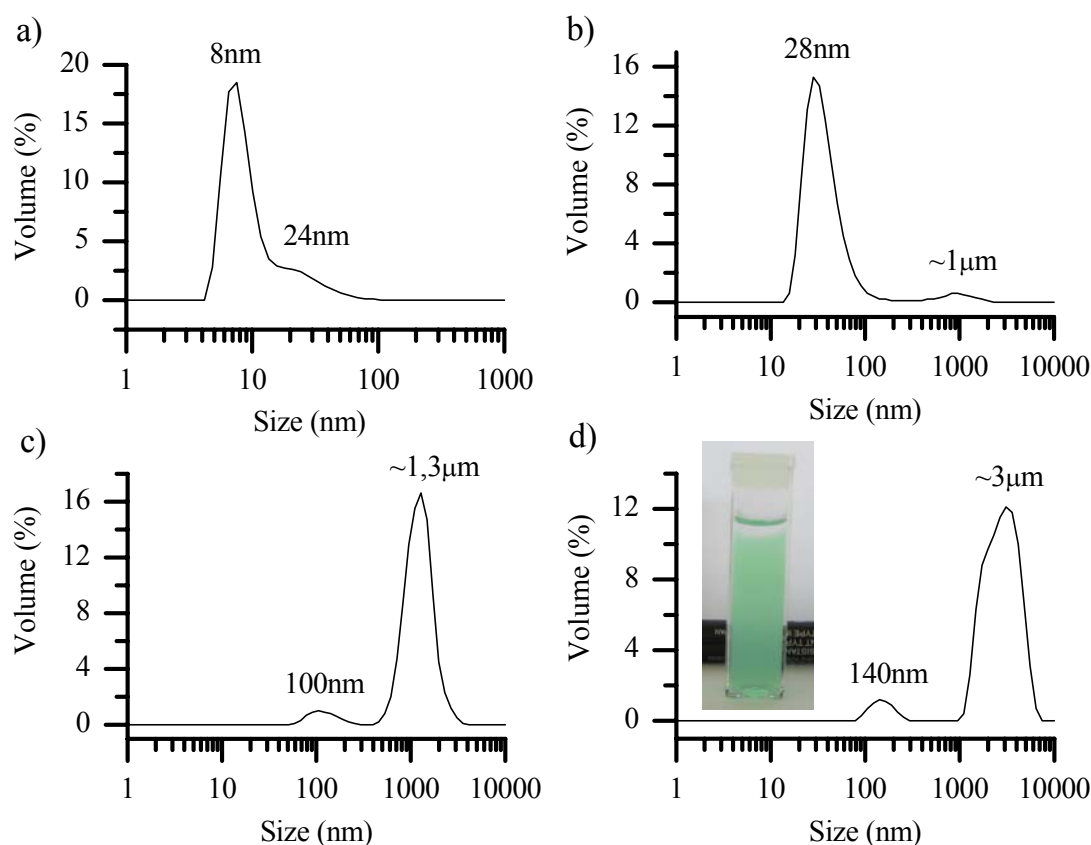


Figure 62. Particle size during ageing at 30°C, of as-prepared colloidal  $\text{Ni}(\text{OH})_{1,67}(\text{NO}_3)_{0,33}$  at 30°C: a) 30min, b) 1h, c) 4h, d) 7h

It is suspected that ethylene glycol acts as a strong complexing agent for nickel anions<sup>149</sup>. The complexation might lower the hydrolysis rate and condensation of hydrolyzed species. During addition of the base to solution containing nickel ions, the ethylene glycol molecules rapidly act as chelating agent of the nickel hydroxylated species as they are formed; the effect is to stabilize them as small building units and to prevent from a fast growth. The growth of hydroxide particles after several hours of ageing causes redispersion problems. For that reason, sedimentation of particles by acetone and redispersion are applied just after titration.

The peptization of hydroxide particles was realized in propylene glycol to obtain the concentration of  $0.1 \text{ mol. L}^{-1} [\text{Ni}(\text{OH})_{2-y}\text{X}_y]$ . The ethylene glycol was not suitable to stabilize colloidal particles. Considering the electrostatic stabilization effect the curtail factor is related to dielectric properties of the solvents ( $\epsilon$  – dielectric constant). Generally the solvents are divided in a high polar media ( $\epsilon > 11$ ) or semipolar ( $5 < \epsilon < 11$ ). The electrostatic stabilization in non aqueous media can occurs rapidly in a high polar media and occurs under certain circumstances in semipolar media<sup>150</sup>. The static dielectric constants for ethylene glycol<sup>150</sup> ( $\epsilon = 37.0$ ) and propylene glycol<sup>151</sup> ( $\epsilon = 28.36$ ) suggests that ethylene glycol should be better solvent for electrostatic stabilization. The opposite behavior suggests that other mechanism than electrostatic is responsible for particle dispersion. It is believed that glycols may stabilize the colloids by formation of solvation layer on the particle surface. In this concept the glycol molecules are bonded to the particle surface by hydrogen bonding<sup>150</sup>. It is believed that both ethylene glycol and propylene glycol might create a solvation layer on the surface of nickel hydroxide. However solvation by propylene glycol introduces stronger steric effects in comparison to ethylene glycol, because of more bulky structure.



Figure 63 shows the particle size measured by Dynamic Light Scattering for precursors:  $\text{Ni(OH)}_{1.7}\text{Cl}_{0.3}$ ,  $\text{Ni(OH)}_{1.67}(\text{NO}_3)_{0.33}$ ,  $\text{Ni(OH)}_{1.82}(\text{NO}_3)_{0.18}$  redispersed in propylene glycol.

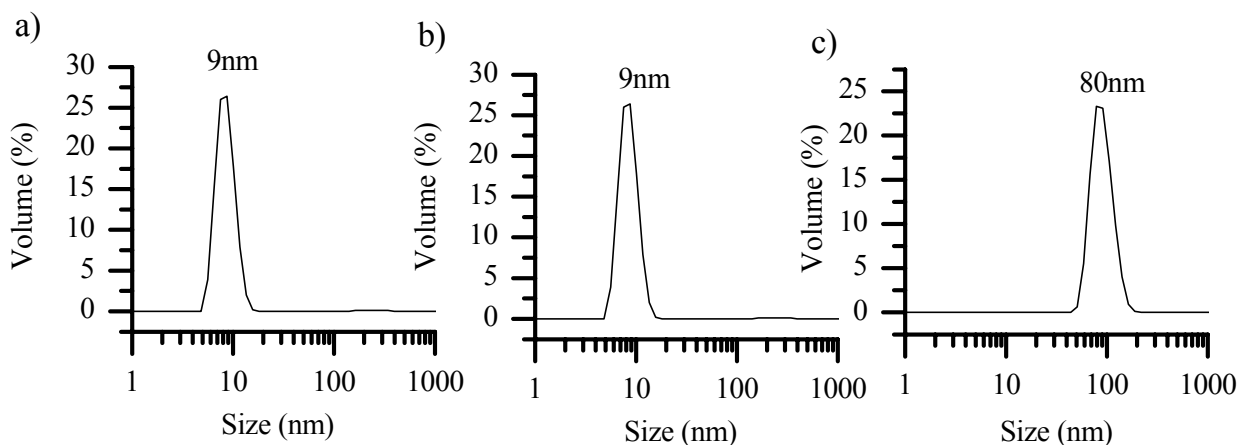


Figure 63. Particle size of colloidal solutions: a)  $\text{Ni(OH)}_{1.7}\text{Cl}_{0.3}$ , b)  $\text{Ni(OH)}_{1.67}(\text{NO}_3)_{0.33}$ , c)  $\text{Ni(OH)}_{1.82}(\text{NO}_3)_{0.18}$

In the case of  $\text{Ni(OH)}_{1.7}\text{Cl}_{0.3}$  and  $\text{Ni(OH)}_{1.67}(\text{NO}_3)_{0.33}$ , which were initially prepared at room temperature, redispersion leads to particles with mean diameter of 9 nm. The hydroxide prepared at 70°C was stabilized with larger particles having size of 80 nm. It seems that synthesis of nickel hydroxide at higher temperatures leads to the formation of agglomerates which can not be easily redispersed-back in peptization process and/or composed from bigger primary particles. The measurements of particle size were in agreement with macroscopic observation (Figure 64). The colloids having mean diameter of 9 nm were greenish and highly transparent. The solution of 80 nm particles was still translucent but with significant effect of light scattering.

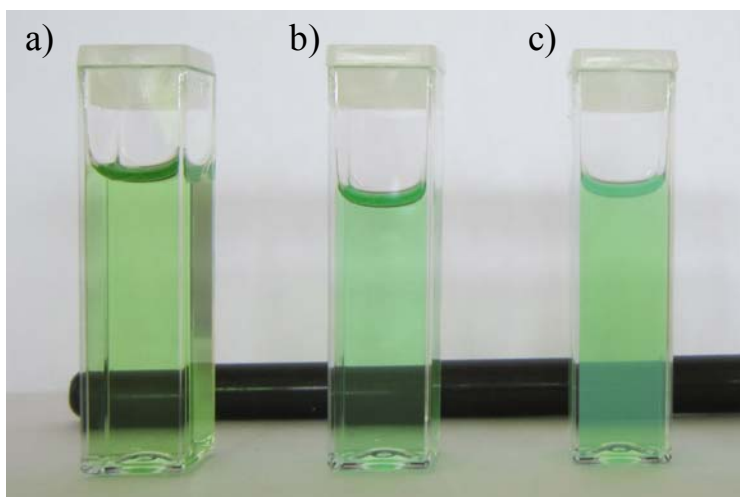


Figure 64 .Image of colloidal particles redispersed in propylene glycol: a)  $\text{Ni}(\text{OH})_{1.7}\text{Cl}_{0.3}$ , b)  $\text{Ni}(\text{OH})_{1.67}(\text{NO}_3)_{0.33}$ , c)  $\text{Ni}(\text{OH})_{1.82}(\text{NO}_3)_{0.18}$

### III.2.2. X-ray diffraction of nickel hydroxides

Crystallographic structure of nickel hydroxylated species was verified after sedimentation and redispersion procedure. X-ray diagrams were recorded using a SIEMENS D 5000 diffractometer operating in Bragg Brentano mode. The colloidal solutions of established nickel hydroxides:  $\text{Ni}(\text{OH})_{1.7}\text{Cl}_{0.3}$ ,  $\text{Ni}(\text{OH})_{1.67}(\text{NO}_3)_{0.33}$  and  $\text{Ni}(\text{OH})_{1.82}(\text{NO}_3)_{0.18}$  were dried for 24 hours at  $120^\circ\text{C}$  in order to remove the solvent. For resulting powders, the X-ray diagrams are shown in Figure 65.

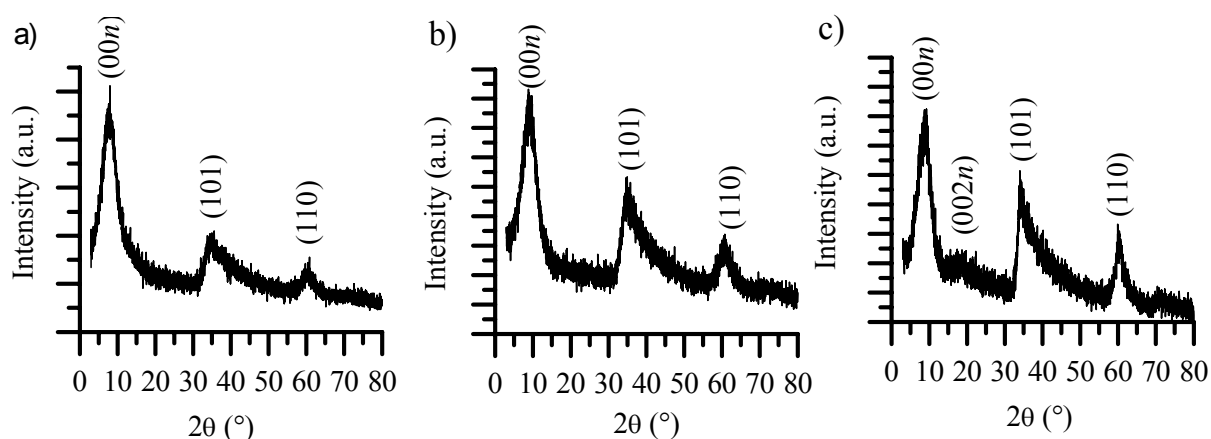


Figure 65. X-ray diagrams of hydroxides obtained after drying the colloidal solutions: a)  $\text{Ni}(\text{OH})_{1.7}\text{Cl}_{0.3}$ , b)  $\text{Ni}(\text{OH})_{1.67}(\text{NO}_3)_{0.33}$ , c)  $\text{Ni}(\text{OH})_{1.82}(\text{NO}_3)_{0.18}$

Nickel hydroxide crystallizes in two polymorphic forms namely called  $\alpha$ -Ni(OH)<sub>2</sub>,  $\beta$ -Ni(OH)<sub>2</sub>. Both varieties crystallize in hexagonal system with the brucite-type structure and the layers Ni(OH)<sub>2</sub> stacked along c-axis (Figure 66). Each layer is composed of hexagonally arranged octahedrally oxygen-coordinated Ni (II) ions<sup>152</sup>. The difference between those two polymorphs lies in the relative arrangement of stacking units. The  $\beta$ -Ni(OH)<sub>2</sub> is composed of perfectly stacked Ni(OH)<sub>2</sub> layers along the c-direction with the interlamellar distance of 4.5 Å. The  $\alpha$ -Ni(OH)<sub>2</sub> phase is characterized by the interlamellar distance higher than 7.5 Å<sup>153</sup>.

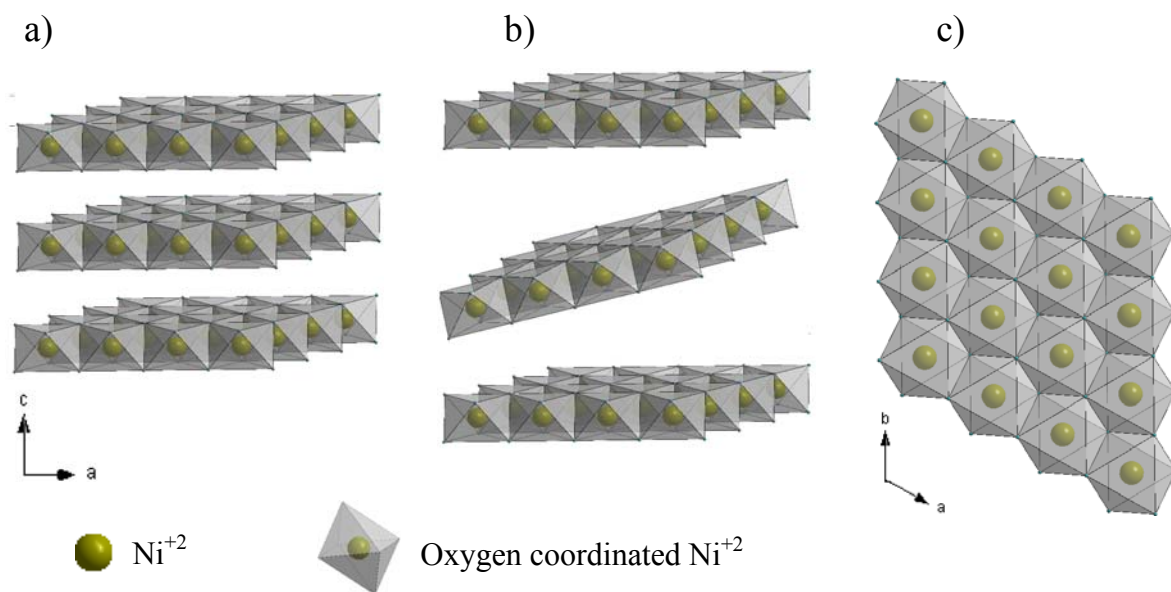


Figure 66. The structural arrangement of atoms in Ni(OH)<sub>2</sub>: a) in  $\beta$ -Ni(OH)<sub>2</sub>, b) in  $\alpha$ -Ni(OH)<sub>2</sub>, c) planar arrangement of octahedrally oxygen coordinated nickel ions, sharing edges and corners.

For presented here hydroxides the diffraction patterns were identified with poorly crystallized  $\alpha$ -Ni(OH)<sub>2</sub> variety. In alpha nickel hydroxide the layers are misoriented relatively to each other and create so-called turbostatic disorder. The X-ray diagrams shows a typical asymmetry of the (101) reflections, indicating on characteristic turbostatic disorder between interlayer sheets<sup>154</sup>.

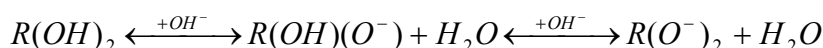
The  $\alpha$ -Ni(OH)<sub>2</sub> is characterized by deficiency of hydroxyl anions in the stacking units. The counter ions which restore the charge neutrality are inserted between positively charged Ni(OH)<sub>2-y</sub> stacking layers together with water molecules. The amount and size of intercalated anions causes the interlamellar distance to vary as a function of the nature of the inserted molecules. There is an evidence on insertion of monovalent (Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup>)<sup>155, 156</sup> or divalent (SO<sub>4</sub><sup>-2</sup>, CO<sub>3</sub><sup>-2</sup>)<sup>157</sup> anions, as well as long chain organic molecules (C<sub>n</sub>H<sub>2n+1</sub>SO<sub>3</sub><sup>-</sup>, n=10,

14, 18)<sup>158</sup>. Occasionally carbonates can be found in the chemical composition of hydroxides independently from the type of anions used for the synthesis. The presence of carbonates arises from spontaneous anionic exchange during washing and drying operations<sup>159</sup>. The facility of anions insertion between Ni(OH)<sub>2</sub> sheets causes that reported basal distance may vary between 7.5 Å to 31.7 Å.

The basal distance calculated from (00*n*) reflections was found to be 11.3 Å for Ni(OH)<sub>1.7</sub>Cl<sub>0.3</sub>, 9.78 Å for Ni(OH)<sub>1.67</sub>(NO<sub>3</sub>)<sub>0.33</sub> and 10.26 Å for Ni(OH)<sub>1.82</sub>(NO<sub>3</sub>)<sub>0.18</sub>. Those values are a bit higher than expected due to insertion of chloride, nitrate or eventually carbonate anions (~7.5 Å). The reason for that can be explained by incorporation of additional glycol molecules between the nickel hydroxide sheets. The synthesis and redispersion of hydroxides takes place in ethylene glycol and propylene glycol respectively in the case of synthesis at room temperature and in propylene glycol only in case of synthesis at 70°C. The glycol rich environment may give rise to intercalation of polyol molecules.

Among the data reported for isostructural nickel hydroxides synthesized in glycols, the available data describe the nickel hydroxyl acetate compounds. The reported interlamellar distance was found at 10.2 Å when nickel acetate was precipitated by NaOH in presence of propylene glycol as a solvent<sup>160</sup>. For hydrolysis of nickel acetate by addition of water in propylene glycol or diethylene glycol, the interlayer distance was found at 10.5 Å<sup>161</sup>. For those references, the basal spacing was justified by insertion of acetate ions and water molecules. The incorporation of glycol molecules between basal planes was excluded, implying that glycols might only be physically absorbed to the surface. On another hand, one report proposes the existence of glycols between nickel hydroxide layered structures. In that case, nickel acetate was hydrolyzed by sodium carbonate in the presence of ethylene glycol. The evidence for interlayered glycols between stacking sheets was confirmed by FT-IR and thermogravimetric studies, however the interlayer distance was found at 7.4 Å<sup>162</sup>.

In the work presented here, it is quite difficult to justify the basal spacing at the range of 9.8-11.3 Å, just by nitrate or chloride insertion since no other counter ions are present in the system. Thus one proposed hypothesis is that neutral glycol molecules might also be incorporated between the interlayer structures. Another possible solution may be explained by the presence of deprotonated polyols in a form of alcoholate anions. The alcoholate anions may be formed in a presence of strong alkali resulting in acid-base equilibrium<sup>163</sup>:



Thus alcoholate, having a negative charge might be more easily incorporated between the sheets of the hydroxide, than the neutral alcohols.

### III.2.3. X-ray diffraction of nickel oxides

Nickel oxide was obtained by thermal decomposition of nickel hydroxide precursors. Figure 67 shows the X-ray diagrams for products prepared by heating of  $\text{Ni}(\text{OH})_{1.7}\text{Cl}_{0.3}$ ,  $\text{Ni}(\text{OH})_{1.67}(\text{NO}_3)_{0.33}$  and  $\text{Ni}(\text{OH})_{1.82}(\text{NO}_3)_{0.18}$  at  $400^\circ\text{C}$  in air.

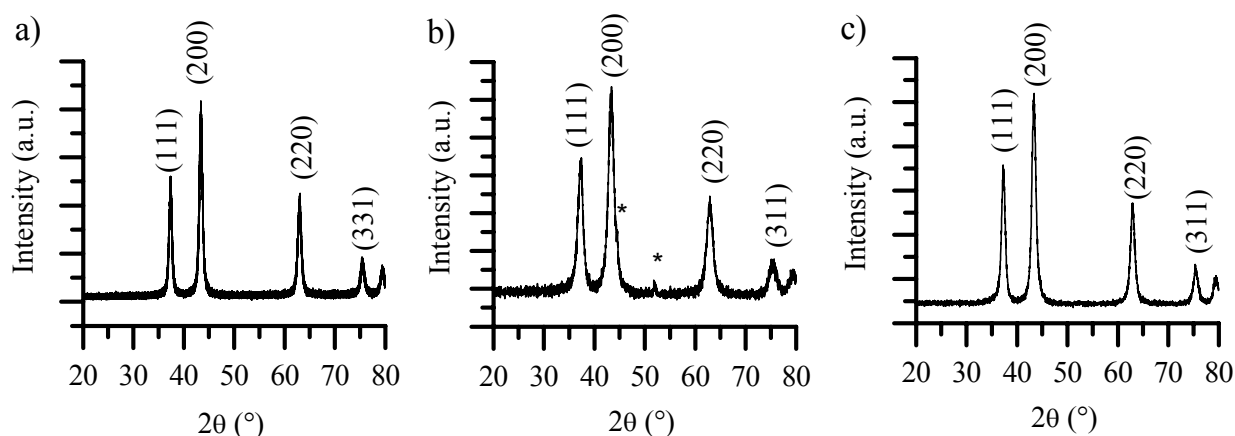


Figure 67. XRD diagrams of products obtained from decomposition of precursors: a)  $\text{Ni}(\text{OH})_{1.7}\text{Cl}_{0.3}$ , b)  $\text{Ni}(\text{OH})_{1.67}(\text{NO}_3)_{0.33}$ , c)  $\text{Ni}(\text{OH})_{1.82}(\text{NO}_3)_{0.18}$ . The peaks of metallic nickel are marked by an asterisk (\*)

The diagrams for each sample show sharp reflections typical for nickel oxide phase. However decomposition of  $\text{Ni}(\text{OH})_{1.67}(\text{NO}_3)_{0.33}$  results in formation of contaminants. The contaminants are evidently detected at  $2\Theta=51.95^\circ$ , which correspond to (200) peaks of metallic nickel. The contribution of most intense (111) nickel peak is also observed at around  $2\Theta=45^\circ$  causing a shouldering of NiO (200) peak. The formation of metallic nickel might arise from the reductive nature of glycols. The  $\text{NiO}/\text{Ni}(\text{OH})_{2-y}\text{X}_y$  reduction to metallic particles by glycols was extensively studied in the so-called polyol process. On the basis of the polyol reaction, the formation of metallic particles is facilitated at elevated temperatures<sup>164, 165</sup> (usually at boiling point of the polyols). For the syntheses presented here, the heat treatment procedure is divided into two stages. The first step takes place at  $120^\circ\text{C}$  in order to evaporate the solvent, which can act as a reducing agent for colloidal nickel hydroxides. In that stage, the presence of glycol is minimized. The second stage at  $400^\circ\text{C}$  allows transformation of hydroxide into oxide. Despite two heat treatments, the formation of metallic pollutants indicates that glycol is

not totally removed. In addition, glycol molecules might be inserted between interlayer structures of the hydroxide and facilitate reduction of nickel ions.

Comparing the samples prepared from the nickel nitrate precursors, the one synthesized at 70°C was free from metallic contaminations. For that sample, the nickel hydroxide precursor was characterized by higher interlayer distance. Higher interlayer distance of the hydroxide might facilitate the total oxidation of glycol. The smaller stacking periodicity may induce a confinement of the glycol molecules within the structure, leading to reductive conditions during a thermal treatment.

#### III.2.4. Transmission Electron Microscopy

The nickel hydroxide precursors and final nickel oxides were analysed by Transmission Electron Microscopy (TEM). Transmission micrographs were recorded using a copper grid dipped in a solution containing hydroxide or resulting NiO nanoparticles dispersed in ethanol. The samples of nickel hydroxide were very unstable under focus of the electron beam. Figure 68 shows the TEM observation for  $\text{Ni}(\text{OH})_{1.82}(\text{NO}_3)_{0.18}$  precursor.

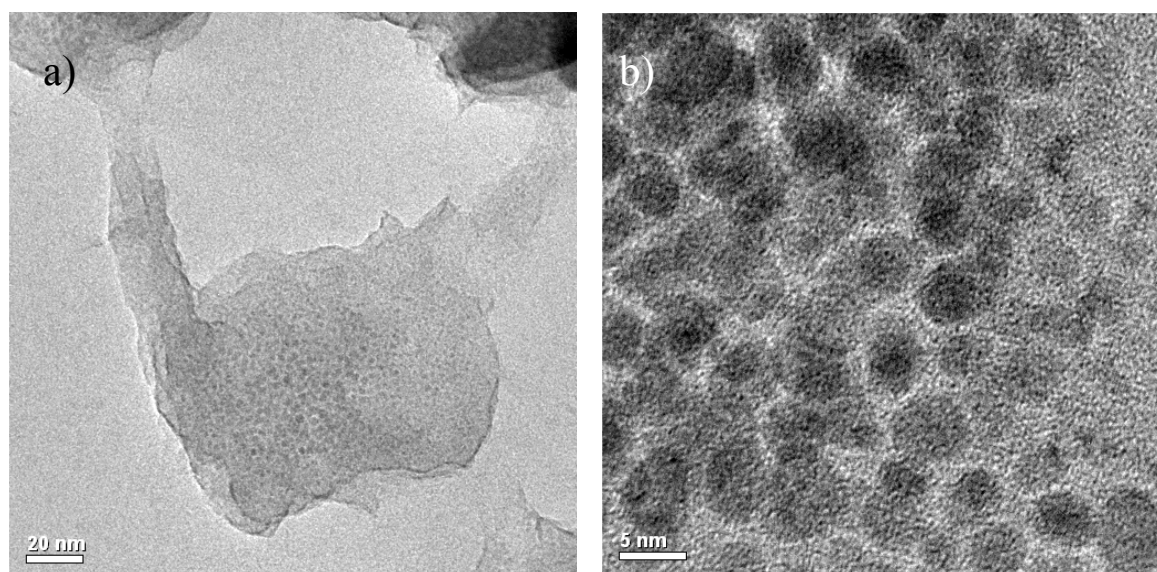


Figure 68. TEM image of  $\text{Ni}(\text{OH})_{1.82}(\text{NO}_3)_{0.18}$  precursor at different magnifications: a) 80 000, b) 400 000.

The recorded image shows unshaped objects of around 100 nm. The degradation of the samples results in rapid formation of round particles with diameter  $\approx 5$  nm. The destruction of the  $\alpha\text{-Ni}(\text{OH})_2$  structures under exposure of electron beam was also reported in the literature.



The instability of the sample was attributed to reduction of hydroxide structures to metallic nickel particles<sup>166</sup>.

The nickel oxides prepared from  $\text{Ni(OH)}_{1.7}\text{Cl}_{0.3}$ ,  $\text{Ni(OH)}_{1.67}(\text{NO}_3)_{0.33}$  and  $\text{Ni(OH)}_{1.82}(\text{NO}_3)_{0.18}$  precursors are shown in Figure 69.

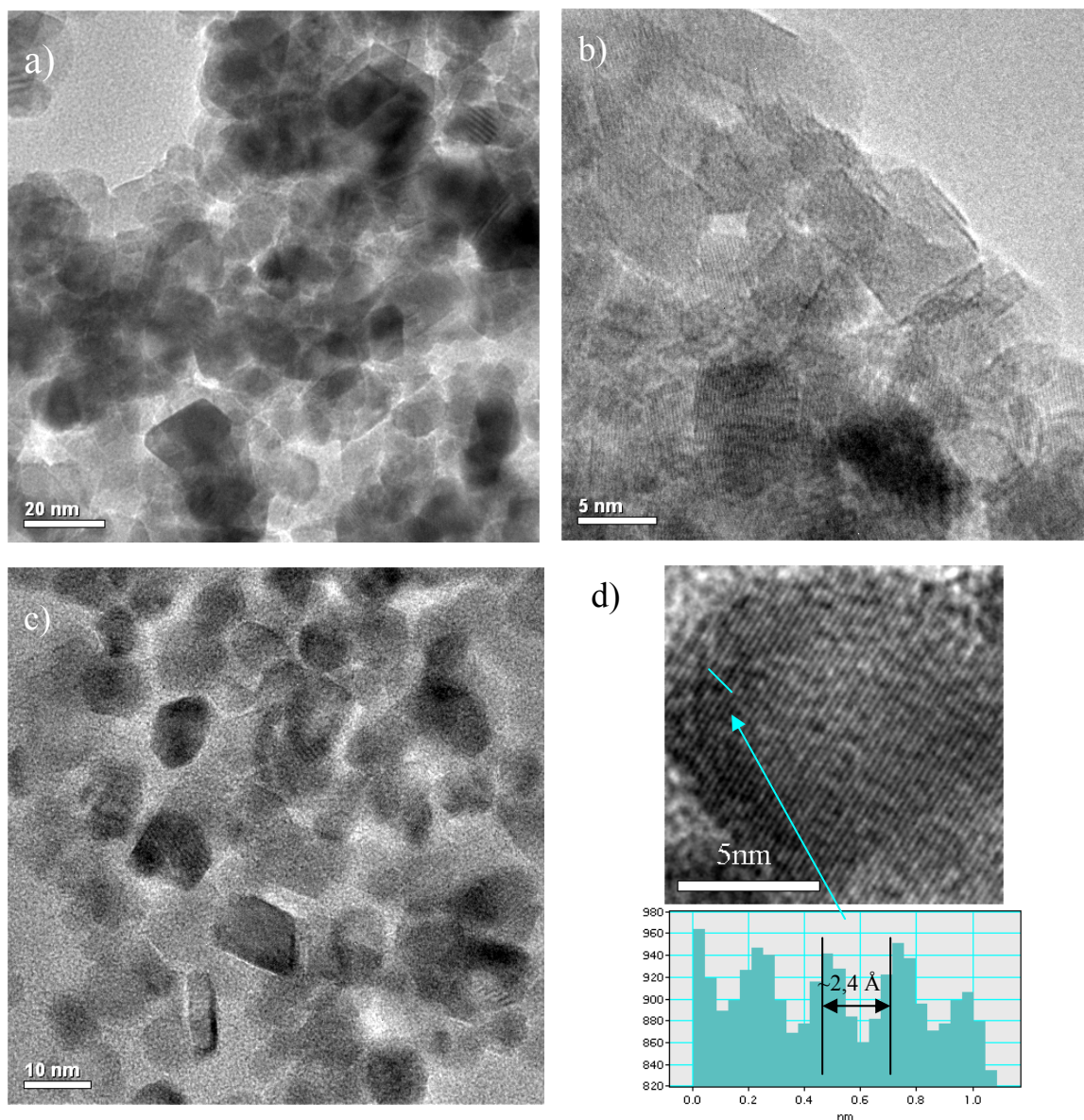


Figure 69. TEM image of nickel oxides obtained from precursors: a)  $\text{Ni(OH)}_{1.7}\text{Cl}_{0.3}$ , b)  $\text{Ni(OH)}_{1.67}(\text{NO}_3)_{0.33}$ , c)  $\text{Ni(OH)}_{1.82}(\text{NO}_3)_{0.18}$ , d) high resolution image and histogram of NiO obtained from  $\text{Ni(OH)}_{1.82}(\text{NO}_3)_{0.18}$ .

For all three precursors, the morphology of the nickel oxide particles is not uniform and their size distribution is not homogenous. The observed objects were roughly spherical or rectangular with the size ranging between 5 to 20 nm. From the micrographs one can

conclude that the smallest particles reveal round shapes. Among the bigger particles the rectangular shape is predominant. The observed particles were always aggregated and the recorded images show superposition of randomly oriented crystals. For some crystals, the high resolution images expose the lattice spacing. Figure 69d shows the lattice planes recorded for NiO prepared from  $\text{Ni(OH)}_{1.82}(\text{NO}_3)_{0.18}$  precursor. The average distance calculated from the histogram is equal to 2.4 Å, which corresponds to the largest (111) spacing of NiO fcc lattice. The lower indexed planes were not observed during samples imaging.

### III.2.5. Thermal analysis: ATG-DSC, MS

The synthesis of nickel oxide is realized by thermal decomposition of colloidal hydroxide precursors. To acquire a better understanding of the decomposition process, the colloidal samples of  $\text{Ni(OH)}_{1.7}\text{Cl}_{0.3}$ ,  $\text{Ni(OH)}_{1.67}(\text{NO}_3)_{0.33}$ ,  $\text{Ni(OH)}_{1.82}(\text{NO}_3)_{0.18}$  were analyzed by Thermogravimetric analysis (TGA) coupled with Differential Scanning Calorimetry (DSC) using NETZSCH STA 449 F3 Jupiter instrument. Complementary the mass spectroscopy (MS) was performed using NETZSCH QMS 403 C Aëolos device. The measurements were performed for powders obtained from colloidal precursors which were dried at 120°C in air for 24h. The analysis was carried out starting from room temperature up to 700°C by increment of 3°C/min in air.

Figure 70 shows the TGA-DSC and MS signals recorded for  $\text{Ni(OH)}_{1.7}\text{Cl}_{0.3}$  precursor. The TGA-DSC profiles indicate that decomposition of the sample occurs in a multi step process. The initial heating up to 120°C results in a mass loss accompanied by an endothermic peak on DSC curve attributed to physically absorbed water. It is worth to mention that sample before the analysis was already heat treated at 120°C to separate the solvent from colloidal particles. The mass loss in that range indicates on hygroscopic nature of the hydroxide, which absorbs the water within the preparation and analysis procedure. The desorption of physically absorbed water was recorded also by MS. The characteristic broad peak of  $m/z=17$ , attributed to  $\text{OH}^-$  ions shows departure of water up to 240°C. Since there is a delay in temperature between TGA and MS, the weight loss associated to this weak bounded water is usually estimated from the middle of the plateau on the TGA trace. At 180°C, this loss was estimated to 11.7% mass of the sample. Since the total weight loss, at 700°C, is 51,3 % and assuming



that, at this temperature, the final product is NiO, the amount of water molecule per Ni atom is 1.0. At 240°C, the small exothermic peak on the DSC curve was observed and accompanied by a mass loss on the TGA profile, and by the beginning of  $m/z=17$  peak on MS signal. Simultaneously, the MS indicate on departure of  $m/z=17$  attributed to structural water and  $\text{CO}_2$  ( $m/z=44$ ) resulting from the decomposition of organic compounds. At 240°C, the hydroxide precursor starts to decompose which is accompanied by removal of water and glycol molecules. Above 240°C, three exothermic peaks are observed on DSC curve, meaning that decomposition of nickel hydroxychloride goes through several steps. According to the literature for the nickel hydroxychloride which is synthesized in aqueous conditions, the decomposition occurs in a stepwise manner independently from the atmosphere (air or nitrogen)<sup>167</sup>. For the hydroxide presented here, four exothermic peaks are recorded on DSC curve within the 200°C and 400°C.

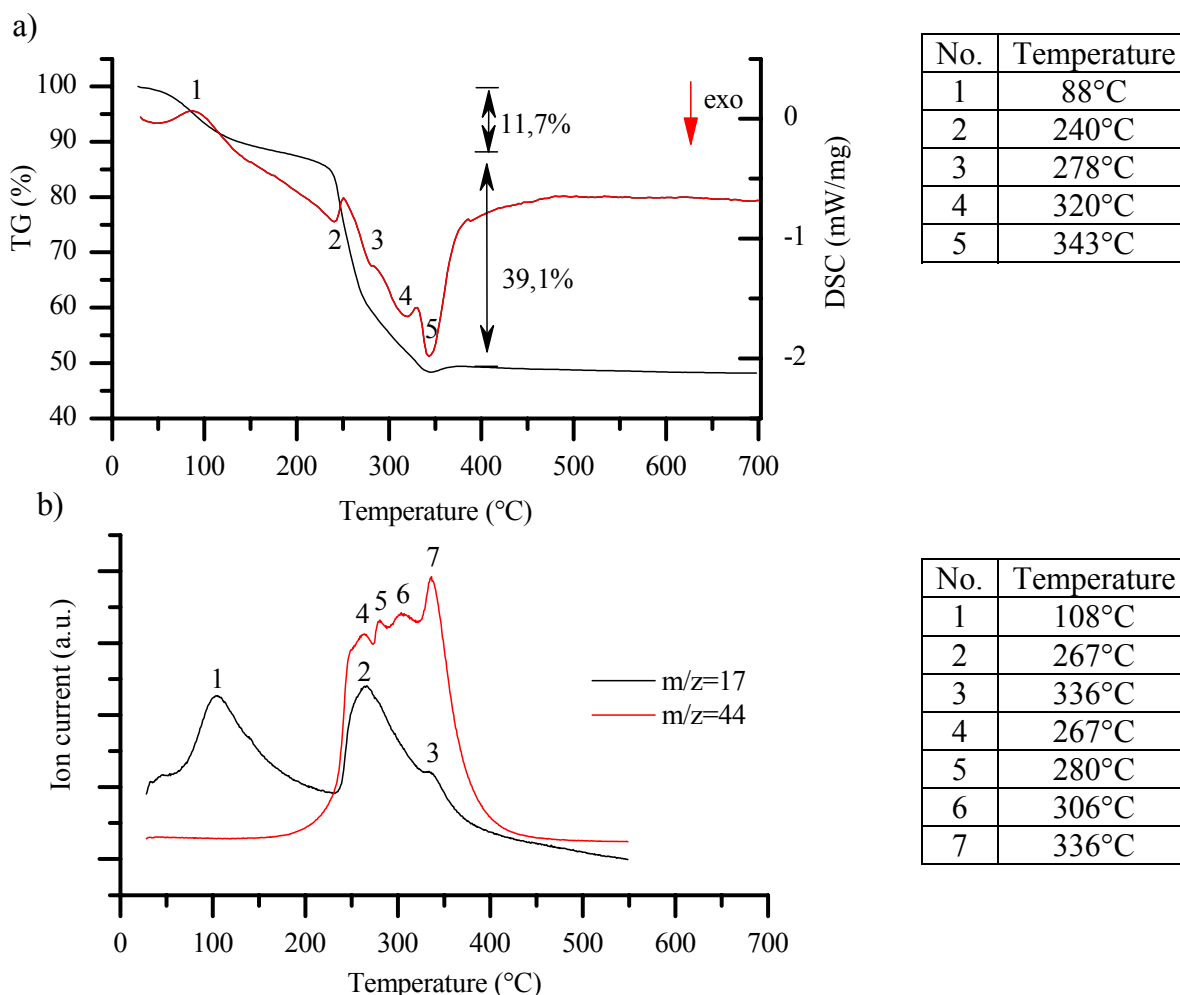


Figure 70. Thermal analysis of the precursor  $\text{Ni}(\text{OH})_{1.7}\text{Cl}_{0.3}$ : a) TGA-DSC, b) mass spectroscopy. The precise values of the peak positions are listed in supporting tables.

Those four DSC peaks are coherent with the four MS peaks of  $m/z=44$  within 200°C and 400°C. The last  $m/z=44$  peak, occurs simultaneously with small signature of  $m/z=17$  and strong exothermic DSC peak at around 343°C. These signals might be explained by combustion of residual glycols in air atmosphere due to exothermic reaction:  $C_2H_4(OH)_2 + 2.5O_2 \longrightarrow 2CO_2 + 3H_2O + heat$ . Taking into account that in this second weight loss is including the departure of  $0.7H_2O$  and  $0.3 HCl$  to form  $NiO$ , (ie 15.35%), the weight loss associated with the organic part of ethylene glycol molecules is 24.3%. The maximum EG molecule included in the hydroxide would be 0.6 per Ni atom. This is a first approximation because additionally to the water release coming from the hydroxide another one can be attributed to some interlayered water molecules.

The thermal analysis done for  $Ni(OH)_{1,67}(NO_3)_{0,33}$  precursor is presented in Figure 71.

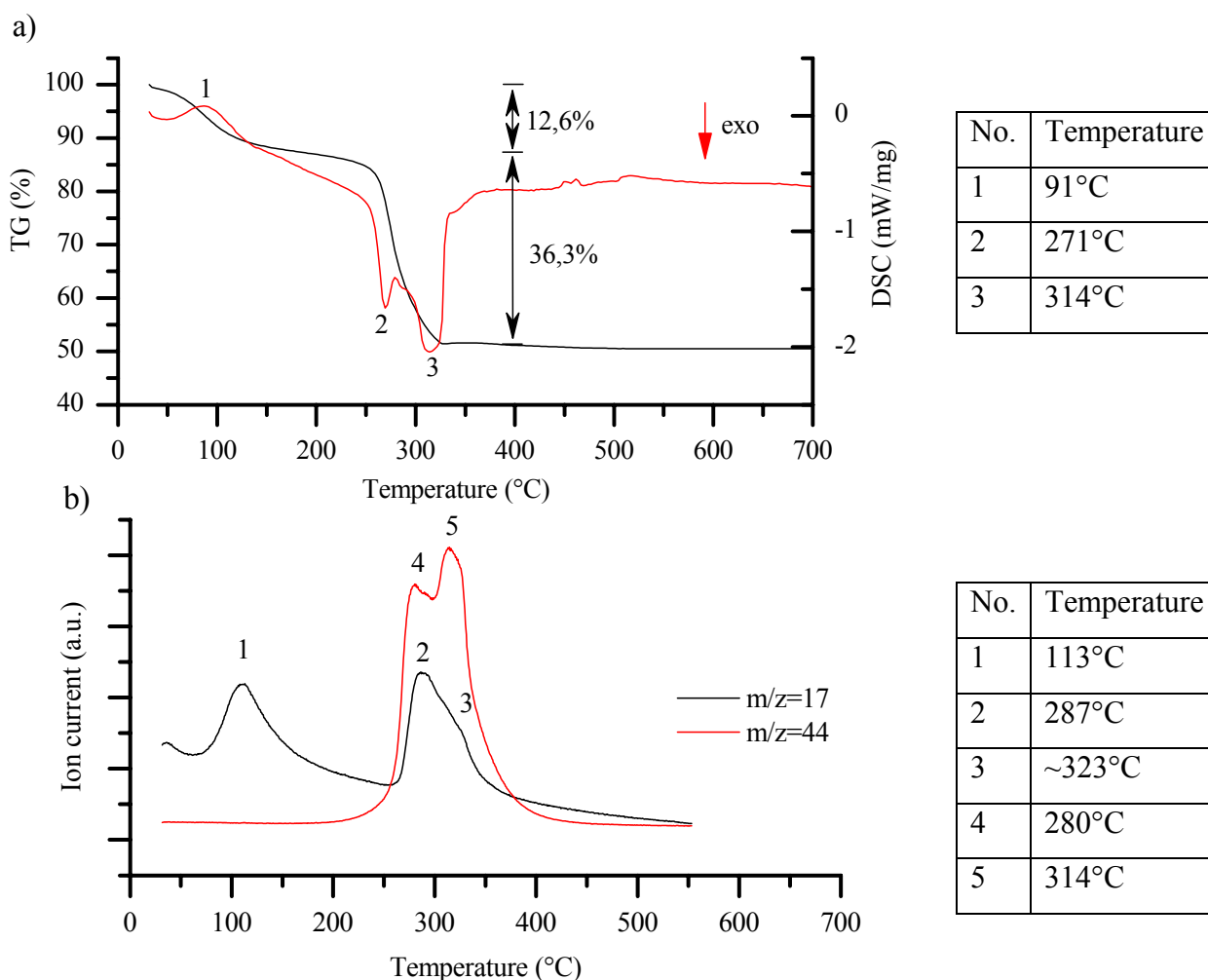


Figure 71. Thermal analysis of the precursor  $Ni(OH)_{1,67}(NO_3)_{0,33}$ : a) TGA-DSC, b) mass spectroscopy. The precise values of the peak positions are listed in supporting tables.

The TGA-DSC profiles show initial mass loss with corresponding endothermic peak and MS  $m/z=17$  related to absorbed water, as it was observed for previous precursor. Estimated absorbed water was about 12.6% of the total mass. This loss corresponds again to 1 water molecule per Ni atom. The second lost of mass, coupled with exothermic peak on DSC curve was found at 271°C. Simultaneously the MS shows the departure of species identified with  $m/z=17$  and  $m/z=44$ , related to structural water and departure of organic molecules. The temperature of 271°C was established as a beginning of decomposition process. The last and the strongest DSC exothermic peak was centered at 314°C. As it was observed for previous precursor, the strongest exothermic peak was also accompanied by MS  $m/z=17$  and  $m/z=44$  departure and was explained as glycol combustion. The total mass loss within a decomposition range of the precursor was estimated on 36.9%. According to the literature, for nickel hydroxynitrate the decomposition occurs in one step process, for the synthesis carried out in water medium<sup>167</sup>. The two exothermic peaks presented here on DSC curve suggest two steps, where one extra peak results from glycol combustion effect. Based on the same type of estimation than the one described above for chloride, the following composition can be proposed:  $\text{Ni}(\text{OH})_{1.67}(\text{NO}_3)_{0.33}, x\text{EG}$  with  $x_{\text{max}} = 0.35$ .

Figure 72 shows thermal analysis performed for  $\text{Ni}(\text{OH})_{1.82}(\text{NO}_3)_{0.18}$ . The mass loss is due to absorbed water and was estimated on 14,6 %, which corresponds to 1,2 water molecule per Ni atom. The decomposition was initiated at 271°C as it was observed for previously described  $\text{Ni}(\text{OH})_{1.67}(\text{NO}_3)_{0.33}$  precursor, having the same counter ions but different stoichiometry.

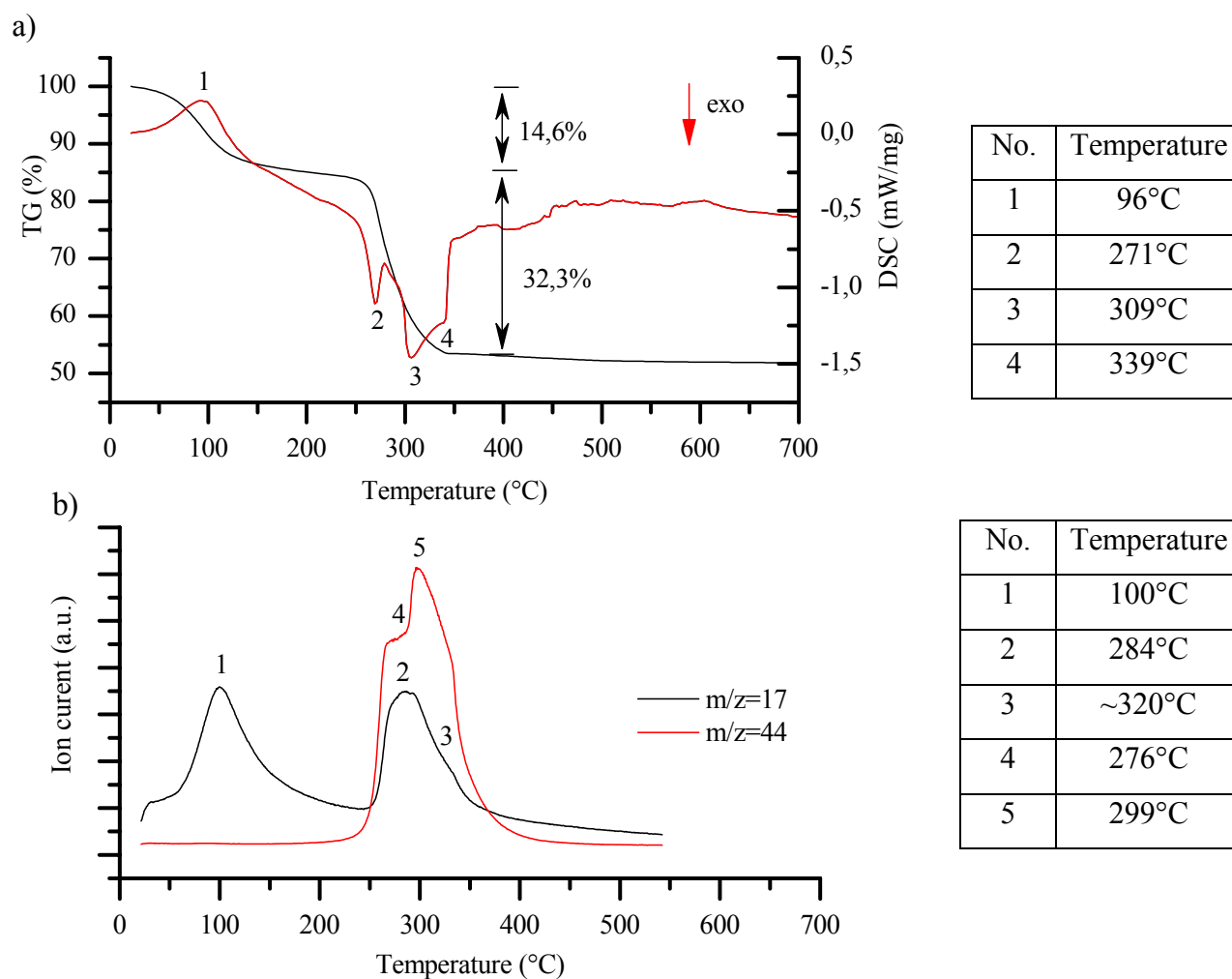


Figure 72. Thermal analysis of the precursor  $\text{Ni}(\text{OH})_{1.82}(\text{NO}_3)_{0.18}$ : a) TGA-DSC, b) mass spectroscopy. The precise values of the peak positions are listed in supporting tables.

However for  $\text{Ni}(\text{OH})_{1.82}(\text{NO}_3)_{0.18}$ , the DSC analysis shows the influence of three peaks during decomposition. Those three DSC peaks have a close signature on MS  $m/z=44$  profile. The origin of additional peak probably is due to some additional reaction related to glycol species. Based on the same type of estimation than the one described above for chloride, the following composition can be proposed:  $\text{Ni}(\text{OH})_{1.82}(\text{NO}_3)_{0.18}, n\text{H}_2\text{O}, x\text{PG}$  with  $x_{\text{max}} = 0.25$ .

The transformation of described here nickel hydroxides to nickel oxides was found to begin at 240°C for nickel hydroxychloride and at 271°C for nickel hydroxynitrate. For all examined hydroxides, the beginning of decomposition process was associated to the appearance of  $m/z=44$  signal. In addition, the position of exothermic peaks on DSC curves, corresponds to MS  $m/z=44$  profiles. The analysis suggests that decomposition of hydroxide is associated with departure of organic molecules. It is possible that glycol molecules which are inserted between the interlayer sheets of the hydroxides are liberated while the structure starts to collapse. Another explanation might be attributed to some catalytic effect generated by decomposition of nickel hydroxide to nickel oxide, inducing glycol combustion.

### III.2.6. XPS of nickel hydroxides

The synthesis of colloidal solutions of nickel hydroxide described here is carried out in the organic solvent. The presence of the glycol molecules, which are probably inserted between the interlayer slabs of the hydroxide, was confirmed by XRD analysis. The diagrams for synthesised hydroxides show higher interlayer distance than expected (from the theory), suggesting that expansion of lattice planes along c-axis is caused by glycol insertion. In addition, the mass spectrometry has shown the departure of organic species during thermal decomposition of the precursors. Both analyses indicate the presence of glycol molecules in the synthesized materials. That fact may cause some unexpected reactions between organic molecules and final products. In order to verify this hypothesis and found the evidence of by-products, the samples were examined by XPS. In this subchapter the XPS analysis for nickel hydroxides will consider the qualitative aspects of detected species. The quantitative details are given in appendix 1.

The measurements of XPS were carried out with a Kratos Axis Ultra spectrometer using a monochromator Al K $\alpha$  source (1486.6 eV). The spectra were recorded for hydroxide precursors dried at 120°C for 24h in air. The samples were in form of powdered pellets (for Ni(OH)<sub>1.67</sub>(NO<sub>3</sub>)<sub>0.33</sub> and Ni(OH)<sub>1.82</sub>(NO<sub>3</sub>)<sub>0.18</sub>) or deposited onto glass substrate by spin coating (for Ni(OH)<sub>1.7</sub>Cl<sub>0.3</sub>). The data were treated using Casa XPS software<sup>168</sup> after subtraction of Shirley background. For nickel hydroxides samples the spectra were recalibrated on binding energy coming from Ni 2p<sub>3/2</sub> states assigned to Ni(OH)<sub>2</sub>. The analysis was based on reference Ni(OH)<sub>2</sub> samples defined by *Biesinger*<sup>169</sup>.

Figure 73 shows the fitting of nickel states for hydroxide precursors and the reference described by *Biesinger*. The spectres were resolved for multiplets of 6 peaks attributed to Ni

$2p_{3/2}$  states assigned to  $\text{Ni(OH)}_2$ . The fitting of peaks gave a good correlation for the envelope of nickel states and is in agreement with the reference spectra.

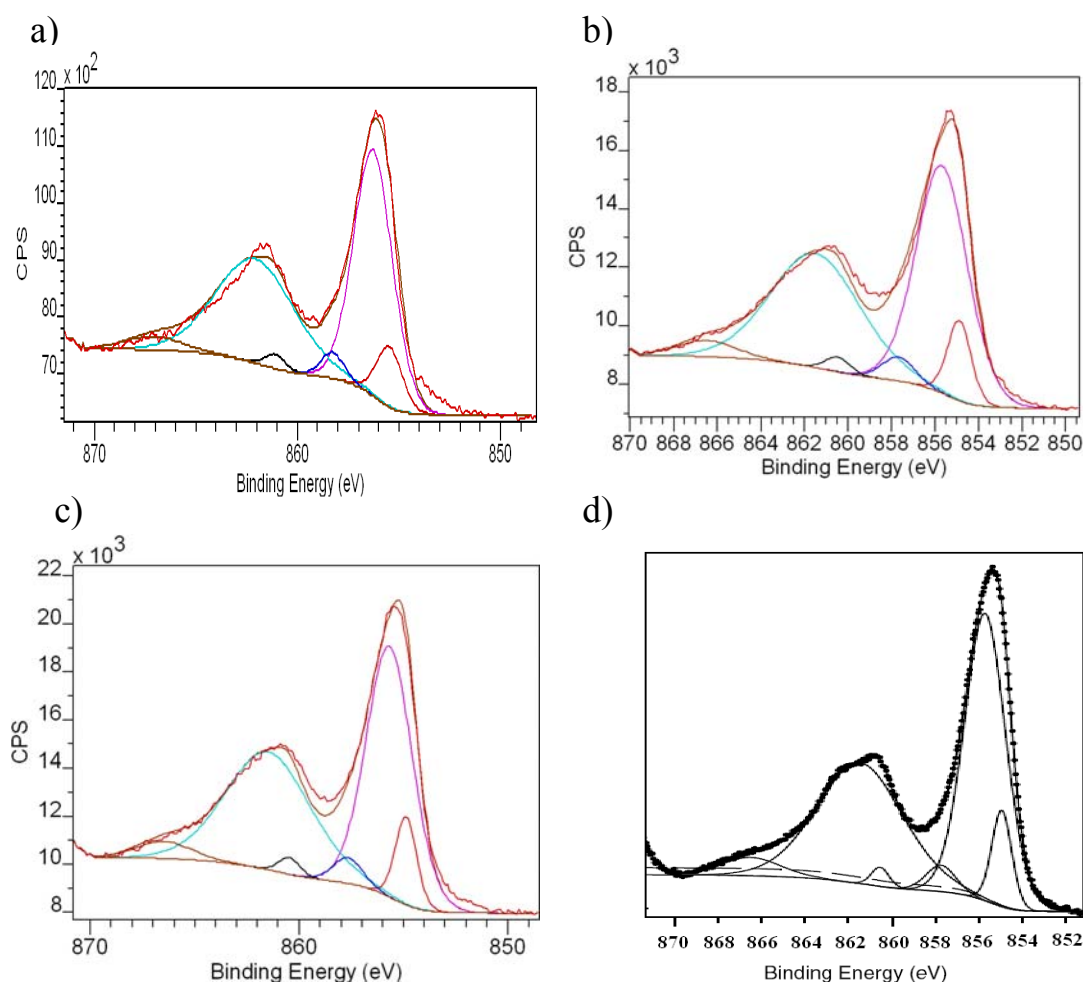


Figure 73. Nickel 2p spectra of hydroxide precursors: a)  $\text{Ni(OH)}_{1.7}\text{Cl}_{0.3}$ , b)  $\text{Ni(OH)}_{1.67}(\text{NO}_3)_{0.33}$ , c)  $\text{Ni(OH)}_{1.82}(\text{NO}_3)_{0.18}$ , d) reference *Biesinger*

According to the reference, the oxygen 1s signal for nickel hydroxide occurs at the binding energy of 530.9 eV ( $\pm 0.1$  eV). For presented here hydroxides, two contributions of oxygen signal were observed (Figure 74). The first major one at 531.0 eV due to hydroxide and a second one, unspecified at 532.3 eV. The presence of the second peak is not clear and might be related to surface absorbed/intercalated species (glycol). The eventual contribution of  $\text{NO}_3^-$  can be excluded, since that peak is also observed for hydroxides prepared from both nickel chloride and nickel nitrate salts.

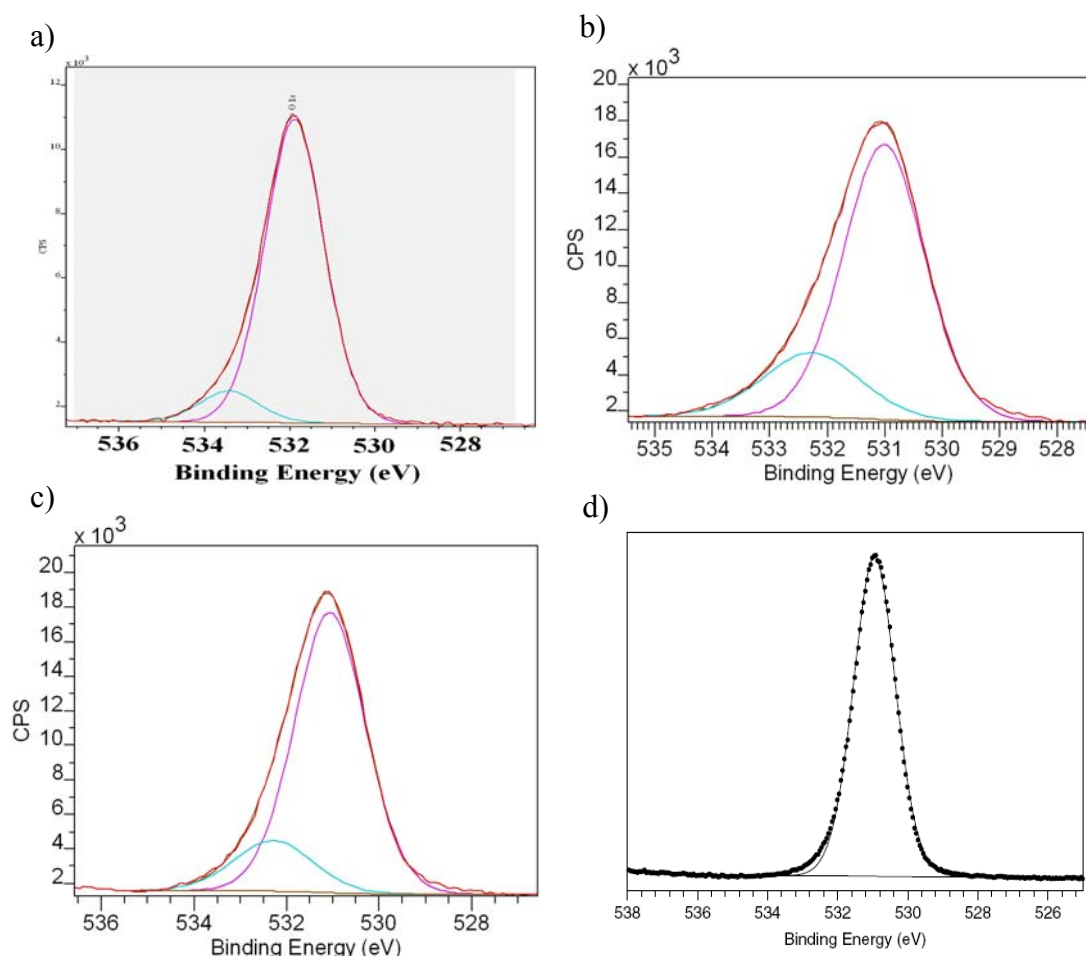


Figure 74. Oxygen 1s spectra of hydroxide precursors: a)  $\text{Ni(OH)}_{1.7}\text{Cl}_{0.3}$ , b)  $\text{Ni(OH)}_{1.67}(\text{NO}_3)_{0.33}$ , c)  $\text{Ni(OH)}_{1.82}(\text{NO}_3)_{0.18}$ , d) reference *Biesinger*

The use of organic solvents during the synthesis of the hydroxides appears through various contributions from carbon peaks. For all samples three carbon 1s peaks were detected (Figure 75). The peaks positions are slightly shifted in respect to the reference, since the calibration was performed for nickel states. The first peak at 284,4 eV is usually assigned to elemental carbon<sup>170</sup> and  $\text{H}_3\text{C-C}$ . The second at 285,6 eV related to  $\text{-C-O}$  bonds<sup>171</sup>, which is characteristic for the synthesis in a polyol media. The third at 288.0 eV was attributed to the carbon double bonded to oxygen atom ( $\text{C=O}$ )<sup>172</sup>. The presence of the first two peaks is not surprising since, the synthesis is carried out in glycol. For glycols, only single carbon bonds are expected ( $\text{C-C}$  and  $\text{C-O}$ ). The third peak, related to double bonded carbon is probably due to  $\text{CO}_3^{-2}$  contaminations, which are spontaneously absorbed on the sample surface.

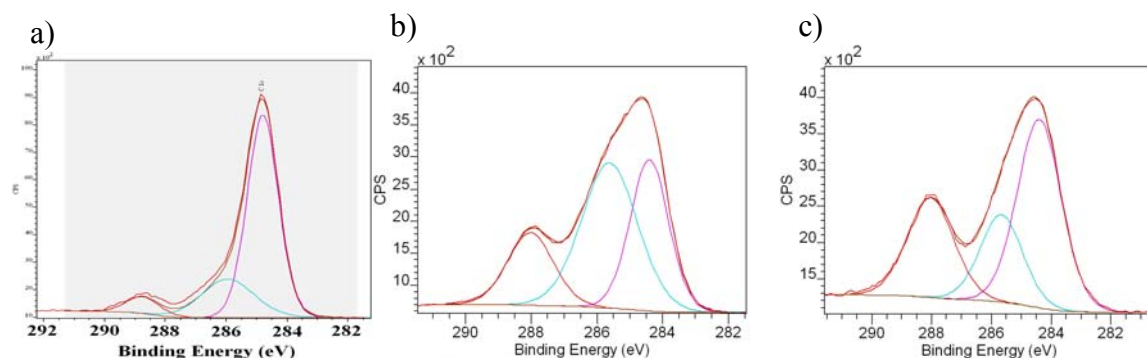


Figure 75. Carbon spectra of hydroxide precursors: a)  $\text{Ni}(\text{OH})_{1.7}\text{Cl}_{0.3}$ , b)  $\text{Ni}(\text{OH})_{1.67}(\text{NO}_3)_{0.33}$ , c)  $\text{Ni}(\text{OH})_{1.82}(\text{NO}_3)_{0.18}$ .

The next signals recorded for hydroxide samples were due to nitrogen (Figure 76). The source of nitrogen contamination might come from reactants ( $\text{TMA}^+$  and  $\text{NO}_3^-$ ), taken for the synthesis. For the hydroxide prepared from nickel nitrate salt the two different spectra were observed. For  $\text{Ni}(\text{OH})_{1.67}(\text{NO}_3)_{0.33}$  precursor only one peak was found at binding energy of 402.7 eV. That peak is due to  $\text{N}^+\text{-C}$  bonding and commonly observed for tetramethylammonium salts<sup>173</sup>. For the  $\text{Ni}(\text{OH})_{1.82}(\text{NO}_3)_{0.18}$  precursor four peaks contributed for the nitrogen signal. The peak at 405.6 eV is too low in binding energy to be associated to  $\text{NO}_3^-$ , which are normally observed at 407–408 eV<sup>174</sup>. That peak is rather due to the nitrogen chemical state from  $\text{NO}_2^-$  molecules, usually detected at 406 eV<sup>175</sup>. The next, most intense peak related to tetramethylammonium cation was found at 402.6 eV. The last two peaks were located at the binding energies of 399.7 eV and 398.0 eV. The origin of those peaks is not clear and may be the consequence of TMAOH decomposition. The peak at 399.7 eV might be assigned to  $\text{NH}_3$ <sup>176</sup> and that at 398.0 eV to nitrides compounds<sup>174</sup>.

The presence of those unexpected peaks for  $\text{Ni}(\text{OH})_{1.82}(\text{NO}_3)_{0.18}$  precursor is probably due to the temperature during titration step. The first step of the synthesis was carried out at room temperature for  $\text{Ni}(\text{OH})_{1.67}(\text{NO}_3)_{0.33}$  precursor and at 70°C for  $\text{Ni}(\text{OH})_{1.82}(\text{NO}_3)_{0.18}$ . The acid-base exchange between nickel nitrate and TMAOH at elevated temperature as well alkaline environment (pH~12 at the end of the titration) could initiate some unexpected reactions. Another reason can be related to reduction of nitrate species by X-rays during XPS measurements.



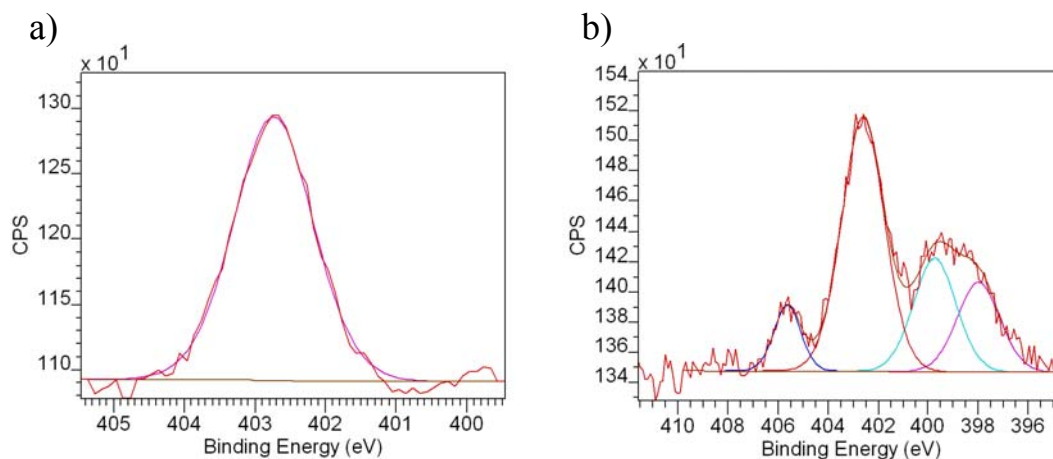


Figure 76. Nitrogen spectra of hydroxide precursors: a)  $\text{Ni}(\text{OH})_{1.67}(\text{NO}_3)_{0.33}$ , b)  $\text{Ni}(\text{OH})_{1.82}(\text{NO}_3)_{0.18}$ .

### III.2.7. XPS of nickel oxides

Samples of NiO were obtained from described earlier hydroxides:  $\text{Ni}(\text{OH})_{1.7}\text{Cl}_{0.3}$ ,  $\text{Ni}(\text{OH})_{1.67}(\text{NO}_3)_{0.33}$ ,  $\text{Ni}(\text{OH})_{1.82}(\text{NO}_3)_{0.18}$  by thermal annealing at 400°C for 2 hours in air and temperature ramp of 200°C/hour. The spectra were recalibrated on binding energy coming from carbon pollution at 284.8 eV. In this subchapter the XPS analysis for nickel oxides will consider the qualitative aspects of detected species. The quantitative details are given in appendix 2.

According to *Biesinger*, the nickel  $2p^{3/2}$  photoelectron line in NiO can be resolved for the multiplet of the 5 peaks (Figure 77d). Applying that procedure a good fitting was obtained only for the case of NiO prepared from  $\text{Ni}(\text{OH})_{1.7}\text{Cl}_{0.3}$  and  $\text{Ni}(\text{OH})_{1.67}(\text{NO}_3)_{0.33}$  precursors. For NiO prepared from  $\text{Ni}(\text{OH})_{1.82}(\text{NO}_3)_{0.18}$ , the spectrum was more complicated and resolved considering the impact of possible contaminants:  $\text{Ni}(\text{OH})_2/\text{Ni}_3\text{C}/\text{Ni}$ . The multiplicity of peaks indicates significant amount of by-products. Also the unexpected contaminants were found for corresponding hydroxide precursor (nitrogen based contaminants).

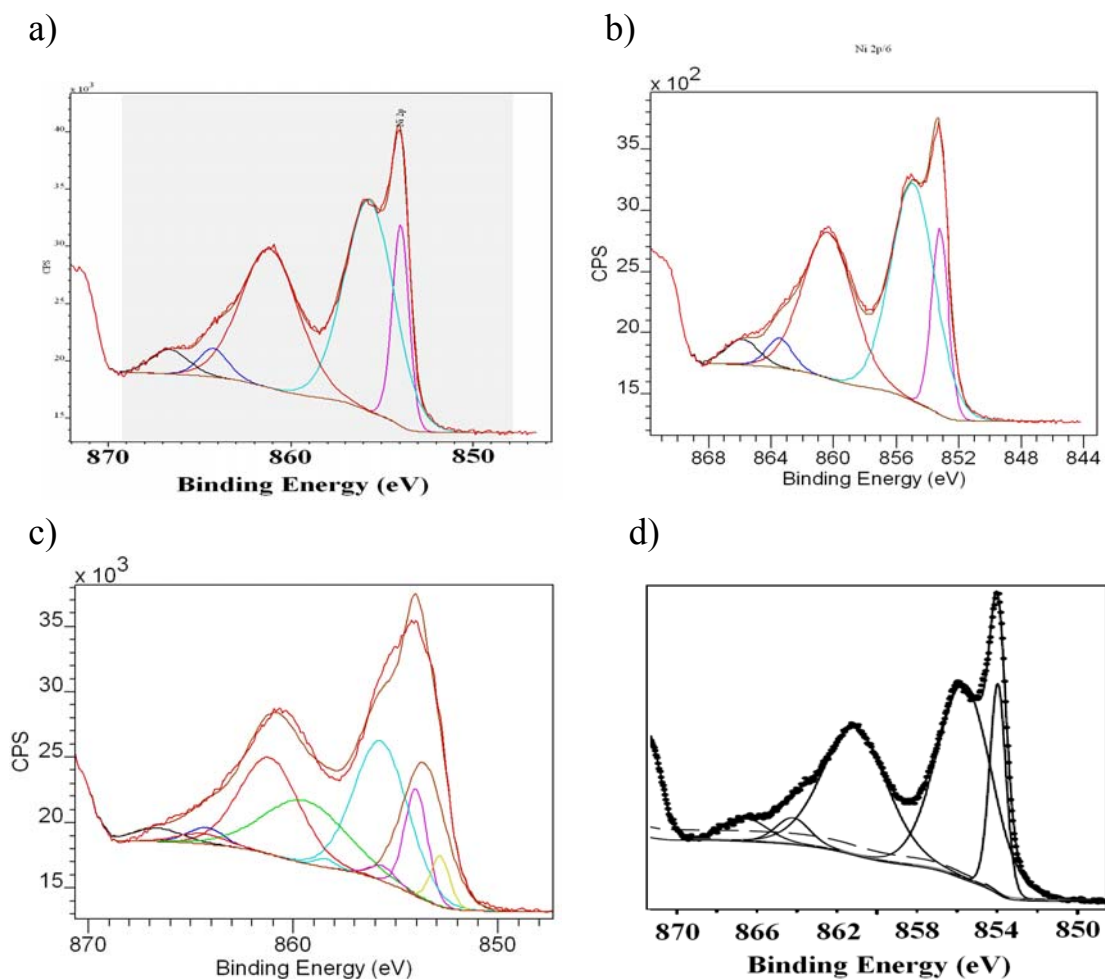


Figure 77. Nickel 2p<sub>3/2</sub> spectra of nickel oxide obtained from precursors: a) Ni(OH)<sub>1.7</sub>Cl<sub>0.3</sub>, b) Ni(OH)<sub>1.67</sub>(NO<sub>3</sub>)<sub>0.33</sub>, c) Ni(OH)<sub>1.82</sub>(NO<sub>3</sub>)<sub>0.18</sub>, d) reference *Biesinger*

The next signal of X-ray photoelectrons was resolved for oxygen 1s peaks. *Biesinger* defined the presence of three peaks allotted to oxygen in pure NiO. The first one at 529.3 eV attributed to NiO framework, second peak at 531.1 eV due to nickel hydroxide species and the third at 532.8 eV identified with absorbed water or possibly absorbed O<sub>2</sub>.

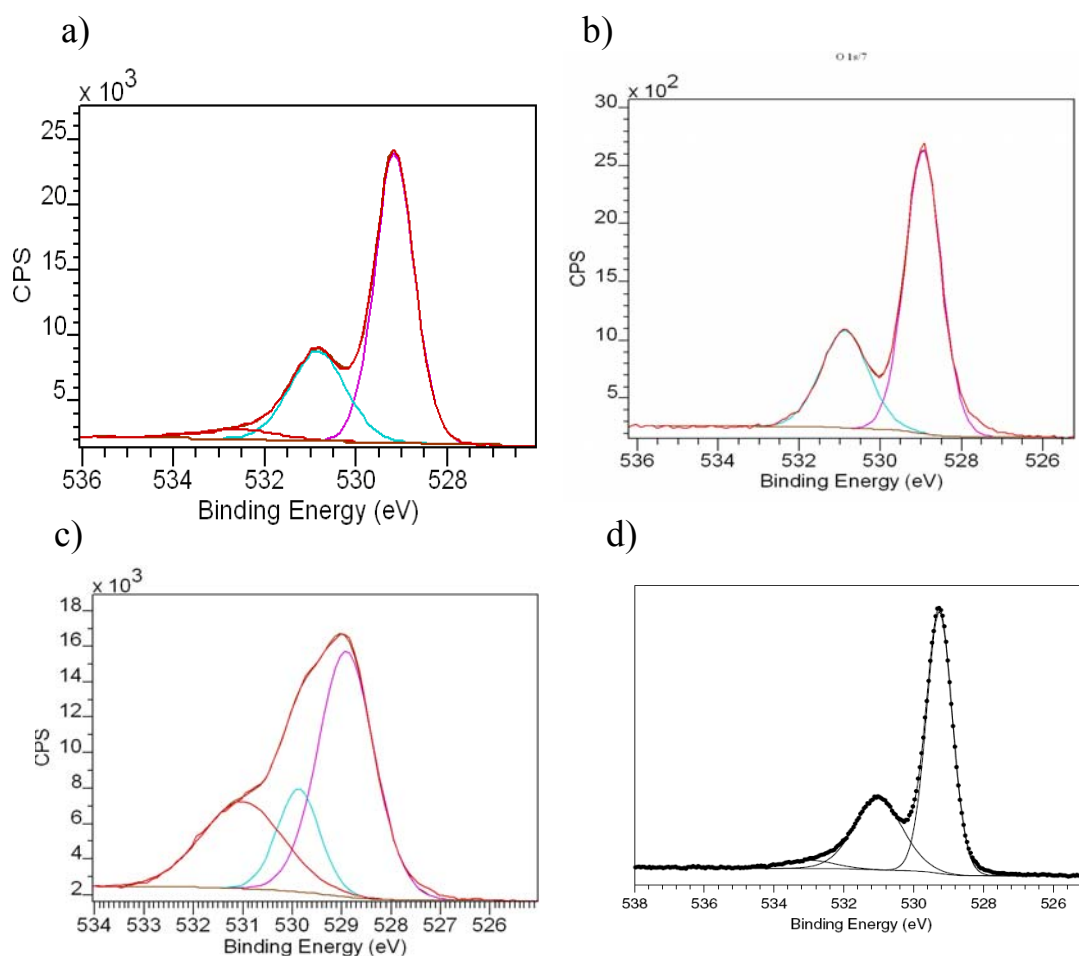


Figure 78. Oxygen 1s spectra of nickel oxide obtained from precursors: a)  $\text{Ni}(\text{OH})_{1.7}\text{Cl}_{0.3}$ , b)  $\text{Ni}(\text{OH})_{1.67}(\text{NO}_3)_{0.33}$ , c)  $\text{Ni}(\text{OH})_{1.82}(\text{NO}_3)_{0.18}$ , d) reference *Biesinger*

For NiO prepared from the  $\text{Ni}(\text{OH})_{1.7}\text{Cl}_{0.3}$  and  $\text{Ni}(\text{OH})_{1.67}(\text{NO}_3)_{0.33}$  precursors, the peaks fitting was in accordance with the reference (Figure 78a and b), but the  $\text{Ni}(\text{OH})_{1.67}(\text{NO}_3)_{0.33}$  does not show the contribution of absorbed water/oxygen at 532.8 eV. The peak positions, as well as width of peaks matched with the reference of *Biesinger*. However in the case of NiO from  $\text{Ni}(\text{OH})_{1.82}(\text{NO}_3)_{0.18}$ , the three oxygen peaks were found at 528.9 eV, 529.9 eV and 531.0 eV. The first peak, attributed to NiO framework is significantly shifted compared to the reference. It can be a consequence of sample contamination and incorporation of carbon atoms to NiO lattice, which might change the chemical environment of the oxygen. The peak position of the second peak can not be easily interpreted with the published literature. Only the last peak at 531.0 eV can be identified to surface nickel hydroxide.

The analysis of carbon signal for contaminated NiO sample (from  $\text{Ni}(\text{OH})_{1.82}(\text{NO}_3)_{0.18}$  precursor) confirmed the presence of carbide. The characteristic peak was found at the

binding energy of 282.7 eV. According to the reference, the signal is reported at 281.5 eV for  $\text{Ni}_3\text{C}$  and 283.3 eV for  $\text{Ni}_x\text{C}^{177}$ . Two other contributions were found at binding energy of 284.8 eV and 288.0 eV due to standard carbon contamination and C=O species.

The spectra of NiO prepared from the  $\text{Ni}(\text{OH})_{1.7}\text{Cl}_{0.3}$  and  $\text{Ni}(\text{OH})_{1.67}(\text{NO}_3)_{0.33}$  precursors does not show any carbide contaminants. The signals imply the presence of C=O, C-O and C-C/C-H surface species ( Figure 79a and b).

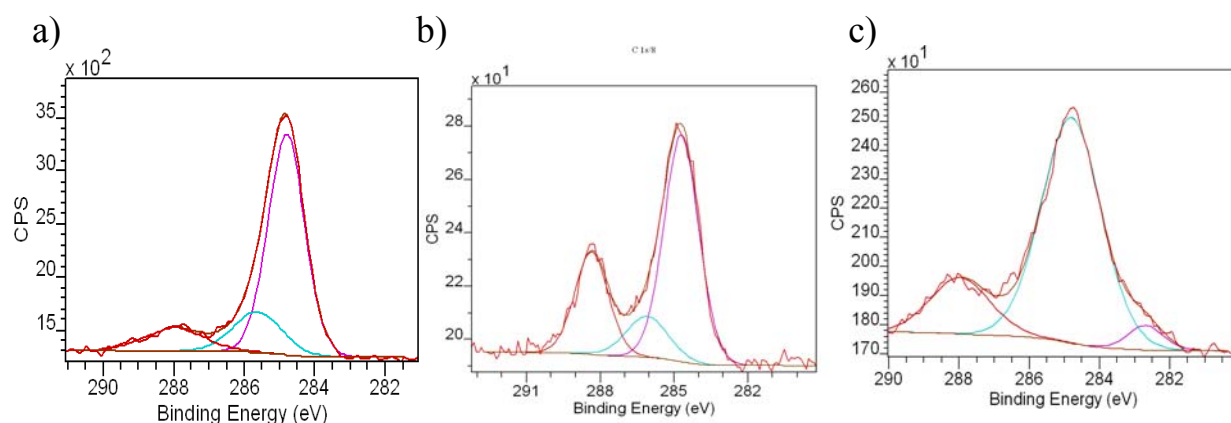


Figure 79. Carbon spectra of nickel oxide obtained from precursors: a)  $\text{Ni}(\text{OH})_{1.7}\text{Cl}_{0.3}$ , b)  $\text{Ni}(\text{OH})_{1.67}(\text{NO}_3)_{0.33}$ , c)  $\text{Ni}(\text{OH})_{1.82}(\text{NO}_3)_{0.18}$ .

Surprisingly for all examined samples (precursor hydroxides and nickel oxides), traces of chloride anions were found. It is especially curious for samples prepared from nickel nitrate salts. One of the reasons of chloride contamination can be due to purity of the reactants. The nickel nitrate is an analysis grade substrate, however TMAOH is 97% pure and no specification about the contamination is given by the suppliers. Another reason for the presence of chlorides can be related to pH controlled titration reaction and possible contamination of ions from pH electrode (Ag/AgCl in 3 mol.  $\text{L}^{-1}$  KCl).

The XPS results shown that synthesized hydroxide precursors as well final nickel oxides are significantly contaminated by carbonaceous species (organic carbon (OC) and element carbon). For all samples C-O and C=O signals were detected implying the presence of alcoholic molecules (probably glycols) and carbonates. In addition the synthesis of samples prepared from  $\text{Ni}(\text{OH})_{1.82}(\text{NO}_3)_{0.18}$  precursor resulted in contamination of carbide species in final NiO.

### III.3. The optimization of colloidal solutions

In this chapter the colloidal solutions were prepared in propylene glycol. Unfortunately, a dewetting process occurs at a solid–liquid interface during thin-film deposition on conductive glass substrates. After spin coating procedure, the colloidal solution spread over the substrate creating a continuous film of the liquid. However after deposition, the liquid spontaneously retracts and irregular patterns are formed. Dewetting is unwanted for the deposition of colloidal particles because it destroys the applied thin-film and causes the rupture of thin liquid film on the substrate and therefore it implies the formation of droplets. Additional problem arising from using propylene glycol as solvent is its high viscosity (44.4cp at 25°C), which does not match with the values recommended for ink-jet printing technique (8-15cP). In order to solve those two aspects, the colloidal solutions were mixed with a co-solvent. The selection of the co-solvent needs to respect two more requirements. The first one imposes to choose a solvent evaporating at the same rate as possible to propylene glycol. Similar values of vapour pressures permits maintaining the composition of the solvent/co-solvent mixture during the evaporation process. The last parameter was dedicated to stability of colloidal particles.

According to the previous considerations, the dipropylene glycol mono methyl ether (DPGME) appears as a suitable co-solvent. The vapour pressure of DPGME is equal to 0.28 mmHg at 20°C and close to that of propylene glycol 0.08mmHg at 20°C<sup>181</sup>. In addition, DPGME/PG create azeotropic mixture<sup>178</sup> at the molar ratio 0.57, meaning that solvents mixture will evaporate at the same rate, without changes in composition or physical parameters.

The wetting processes are complicated and strongly depend on : i) the physical properties of the liquid, ii) the nature of the substrate, and iii) the environmental conditions. However one approach can be done in order to control the wetting characteristic. Wetting equilibrium is characterized theoretically and practically, by the contact angle ( $\theta$ ). The contact angle depends on the interfacial tensions between the gas & liquid, liquid & solid, and gas & solid. The relation between those interfacial forces and contact angle was proposed by Young as:  $\cos \theta = \frac{\gamma_{SG} - \gamma_{SL}}{\gamma_{LG}}$ , where  $\gamma_{SG}$ ,  $\gamma_{SL}$  and  $\gamma_{LG}$  are solid-gas, solid-liquid and liquid-gas interfacial tensions. The contact angle is defined as the angle between the tangent to the liquid-air interface and the tangent to the solid-liquid interface (Figure 80)<sup>179</sup>.

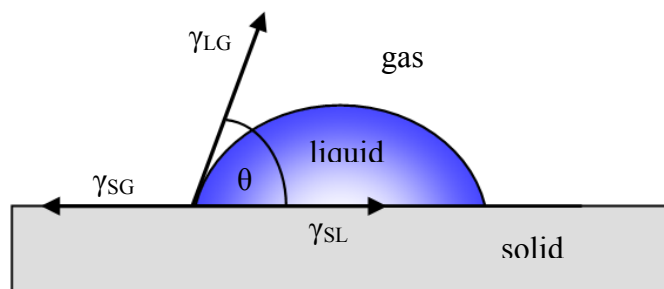
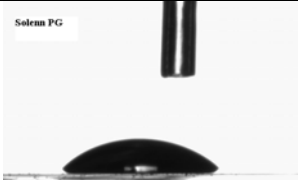
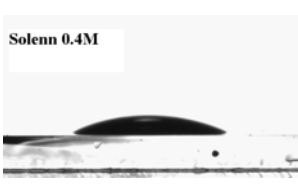


Figure 80. Contact angle of a liquid droplet on solid substrate

The contact angle can be controlled by matching the surface tension of the liquid to the surface tension of the substrate. The selection of dipropylene glycol mono methyl ether as a co-solvent was based on the impact on reduction of surface tension for DPGME/PG mixtures. The propylene glycol has a surface tension  $36\text{mN/m}^{180}$ , while DPGME  $28.8\text{mN/m}^{181}$  at  $25^\circ\text{C}$ . The behaviour of several mixtures of DPGME/PG was tested on the conductive glass substrates used for the deposition of colloidal particles. Table 1 shows the experimental contact angle measured by goniometer (GBX - Digidrop MCAT) for various mixtures of DPGME/PG. Before deposition, the substrate was cleaned with ethanol then dried under compressed air in order to remove the dusts. The measured values indicate different behaviour of the droplets on both substrates: FTO (ASAHI,  $80\text{ohm/sq}$ ) and ITO (ITO from PGO,  $10\text{ohm/sq}$ ). The contact angle was measured 30 seconds after the droplet deposition in order to reach wetting equilibrium. As shown in the table, droplets of pure propylene glycol create contact angles of  $30^\circ$  and  $40^\circ$  for ASAHI and ITO substrates, respectively. For the mole fraction of 0.166 DPGME/PG, the contact angle is reduced for ASAHI substrate to  $10^\circ$  and  $31^\circ$  for ITO substrate. The mixture of mole fraction 0.285 leads to contact angle of about  $0^\circ$  and a complete wetting for ASAHI substrate. But on ITO, the contact angle is only reduced to  $23^\circ$ , for the same DPGME/PG molar ratio. If contact angles vary according to the substrate, in all case, the DPGME addition avoids liquid retraction and improves homogeneity of deposited thin films.

Table 10. Behaviour of various DPGME/PG liquid-mixtures on conductive glass substrates

| Mole fraction of DPGME in PG | Image of the droplet at FTO (ASAHI 120)                                           | Contact angle (°) | Image of the droplet at ITO (PGO)                                                  | Contact angle (°) |
|------------------------------|-----------------------------------------------------------------------------------|-------------------|------------------------------------------------------------------------------------|-------------------|
| 0                            |  | 30                |  | 40                |
| 0.166                        |  | 10                |  | 31                |
| 0.285                        |  | 0                 |  | 23                |

As a third condition for choosing DPGME was related to its viscosity. The viscosity of pure propylene glycol is equal to 44.4cP, while for DPGME it is only 3.7cP at 25°. Using the mixture of both solvents allows matching the viscosity to the recommended value by jet-printing technique (8-15cP). Figure 81 shows the viscosity evolution for different mole fractions of DPGME in PG and experimental fitting for measured values.

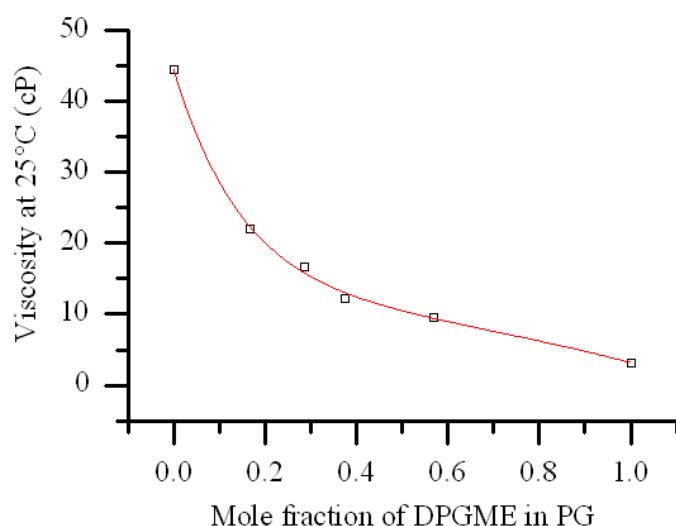


Figure 81. Viscosity of mixture DPGME and PG at 25°.

Based on the Figure 81, the optimal composition of the mixture DPGME/PG having the recommended viscosity value, was estimated to be in range 0.3-0.7 molar fraction of DPGME in DPGME/PG mixture. Those values correspond to an optimal dilution of colloidal solutions with the PG / DPGME in volume ratio of 1:1 to 1:5.

These results were confirmed when colloids were dispersed in described mixtures of solvents.

#### **III.4. Deposition of NiO on conductive transparent substrate**

The hydroxide precursors were deposited on the ASAHI 120 glass substrates by spin-coating technique. After two thermal treatments at 120°C and 400°C the conversion of deposited precursor allows obtaining thin films of nickel oxide. The Figure 82 shows the Scanning Electron Microscopy (SEM) images obtained for processing of 0.05 mol. L<sup>-1</sup> Ni(OH)<sub>1.7</sub>Cl<sub>0.3</sub> precursor redispersed in propylene glycol. Deposition of the hydroxide results in distribution of NiO particles on the entire glass substrate. The low magnification images show closely parallel defects created during sample preparation. In addition some local domains of the images exhibit various shade of gray colour suggesting that the thickness of NiO film is not homogenous. The image at magnification of 80 000 exposes the microstructure of deposited particles. The layer is composed of roughly spherical particles of about 20 nm which is consistent with TEM observations (Figure 69). The packing of the crystals indicates a rather porous layer with local discontinuities of the film.



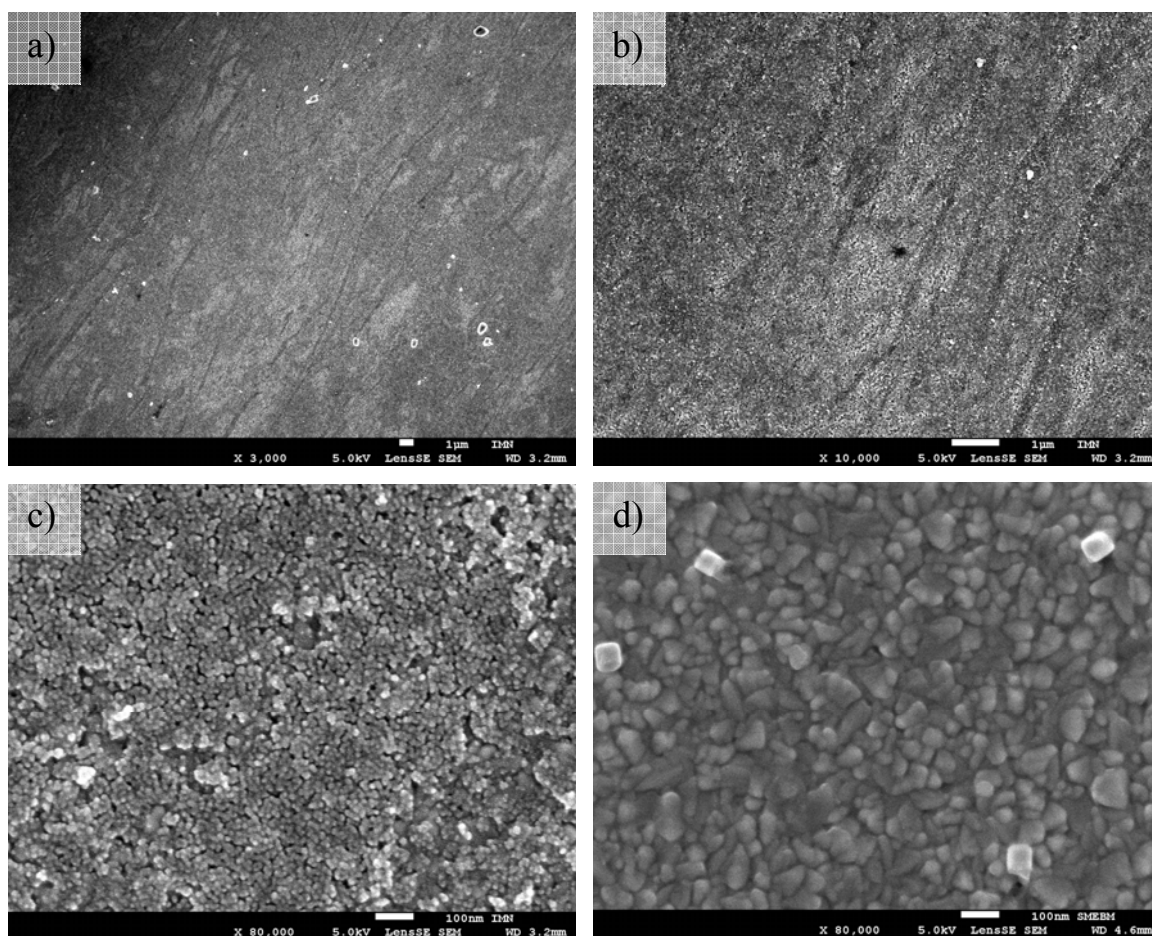


Figure 82. SEM images of NiO deposited using  $0.05 \text{ mol.L}^{-1} \text{ Ni(OH)}_{1.7}\text{Cl}_{0.3}$  precursor by spin-coating at 1000 r.p.m. for 60s at different magnifications: a) 3 000, b) 10 000, c) 80 000, d) bare substrate at 80 000.

The deposition of NiO particles was done using the second precursor:  $0.5 \text{ mol.L}^{-1} [\text{Ni(OH)}_{1.67}(\text{NO}_3)_{0.33}]$  in a solvent containing 1:1 volume ratio PG and DPGME. The Atomic Force Microscopy (AFM) image was performed using tapping mode for  $1 \mu\text{m}^2$  of the bare substrate ASAHI 100 and the surface covered by NiO thin-film (Figure 83). The surface of the substrate consists of nearly spherical grains with a size range of 100 nm. After deposition of colloids and heat treatment procedures, the characteristic morphology is affected by the coverage of smaller particles of about 20 nm. The deposit is observed along entire surface but peaks and valleys, which were characteristic for a bare substrate, are still pronounced. The measured Root Mean Square (RMS) roughness increases slightly from 5.34 nm for the substrate to 5.41 nm after the deposition of NiO, meaning that the magnitude between peak and valleys is not affected much by the deposition process. The skewness,  $R_{sk}$ , for substrate

and substrate coated by particles is positive meaning that asymmetry of the surface features is towards hills. For bare substrate  $R_{sk}$  is equal to 0.478 and decreases to  $R_{sk}= 0.182$  for coated substrate, meaning that surfaces become flatter. That is probable due to partial filling of the valleys by NiO particles.

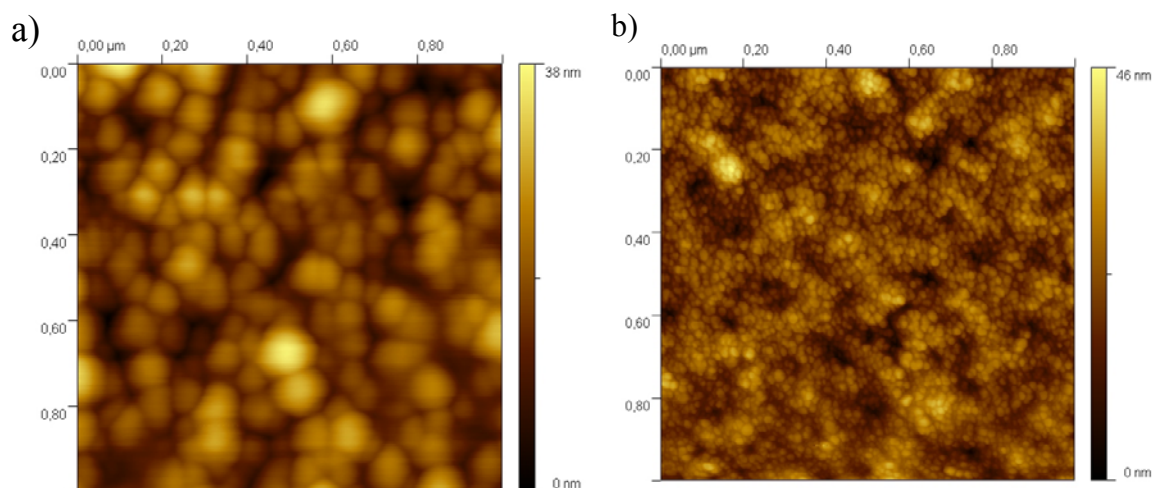


Figure 83. AFM image of glass substrate ASAHI 100: a) without the deposit, b) with 0.5 mol.L<sup>-1</sup> [Ni(OH)<sub>1.67</sub>(NO<sub>3</sub>)<sub>0.33</sub>] in DPGME/PG spin coated at 1000 r.p.m. for 60 s, dried at 120°C and 400°C.

### III.5. Tests of deposited NiO layers in hybrid device

The colloidal precursors of nickel hydroxides were deposited by spin coating on conductive glass substrate (ITO). After heat treatment at 120°C for 2h and 400°C for 2 hours obtained thin films of NiO were assembled in photovoltaic devices as a p-type conductive layers. The tests and cells assembly were done at the partnership unit (CEA-INES) by Solenn Berson. The results presented here were recorded for classic structure: glass / ITO/ NiO/ P3HT:PCBM / stable cathode. The 0.28 cm<sup>2</sup> cells were tested under standard AM1.5 illumination at 40°C.

Table 11 presents the representative results obtained for the solar cells having NiO layers. For all precursors, the recorded cell parameters ( $V_{oc}$ ,  $J_{sc}$ , FF) are not satisfactory. The low performance seems to be especially related to  $V_{oc}$  and FF. For prepared cells the  $V_{oc}$  is in range of 280-362mV and FF vary between 25 and 36%. Those values are almost twice lower than those recorded for the reference cells having a PEDOT:PSS layers. Since the power

conversion efficiency is proportional to  $V_{oc}$ ,  $J_{sc}$ , FF, thus the final efficiency is also drastically affected. The highest values of PCE equal to 0.9% and 1.03% were recorded for  $Ni(OH)_{1.7}Cl_{0.3}$  and  $Ni(OH)_{1.82}(NO_3)_{0.18}$  precursors respectively. The optimization of the film thicknesses caused only marginal effects in PV cells efficiency. For the precursors  $Ni(OH)_{1.67}(NO_3)_{0.33}$ , deposited at two different rotation speeds (1000 and 2000 r.p.m) the cells parameters were not affected and the final PCE was still in range of 0.5%. In the case of  $Ni(OH)_{1.82}(NO_3)_{0.18}$  precursor, the deposition at different rotation speeds resulted in increase of PCE from 0.67% to 1.03% for a thinner films. The gain in PCE was attributed to slight increase of  $V_{oc}$  and FF.

Table 11. Initial efficiency of PV solar cells using NiO

| Precursor:                   | Spin coating<br>speed (r.p.m.) | $V_{oc}$<br>(mV) | $J_{sc}$<br>(mA/cm <sup>2</sup> ) | FF<br>(%) | PCE<br>(%) |
|------------------------------|--------------------------------|------------------|-----------------------------------|-----------|------------|
| $Ni(OH)_{1.7}Cl_{0.3}$       | -                              | 357.1            | 8.62                              | 29.36     | 0.90       |
| $Ni(OH)_{1.67}(NO_3)_{0.33}$ | 1000                           | 301              | 7.20                              | 25.8      | 0.54       |
| $Ni(OH)_{1.67}(NO_3)_{0.33}$ | 2000                           | 280              | 7.33                              | 27.4      | 0.56       |
| $Ni(OH)_{1.82}(NO_3)_{0.18}$ | 1000                           | 309              | 7.72                              | 28.0      | 0.67       |
| $Ni(OH)_{1.82}(NO_3)_{0.18}$ | 2000                           | 362              | 7.79                              | 36.6      | 1.03       |
| Ref. pedot:pss               | -                              | 562              | 10.12                             | 56.6      | 3.22       |

Independently from the precursor and the optimization procedure, the solar cells having NiO layers show poor performance. In each case, the recorded open-circuit voltage was low; meaning that weak electrostatic field across the device is applied. As a consequence lower values of short-circuits current were observed, since charge carriers are less attracted to the electrodes. The poor PV cell efficiency is probably due to some mismatches between energy levels of P3HT:PCBM and NiO. Another possible reason can be related to p-type properties of as deposited films. In fact, beside the tests performed for complete solar cells, no further investigation has been done in order to verify the charge transport properties of NiO thin films. In addition, XPS measurement shown, those samples are significantly contaminated by carbonaceous species, which might change the electronic properties of NiO<sup>182</sup>.

## Conclusions chapter III

Colloidal solutions of nickel hydroxide were successfully prepared in organic solvents. For the synthesis, the ethylene glycol and propylene glycol were used in order control dispersive properties of particles and pass recommended physical parameters dedicated for jet-printing technique. The process was divided into three steps in order to: i) synthesize the hydroxide, ii) separate hydroxide particles from by-products and iii) stabilize the particles in a colloidal form. Two different nickel salts were tested as reactants for the synthesis: nickel chloride and nickel nitrate. Nickel salts were hydrolyzed by organic base (tetramethylammonium hydroxide) at two different temperatures (ambient and 70°C). The temperature of the hydrolysis was found to affect the stoichiometry of resulting hydroxides and size of colloidal particles. For resulting hydroxides the following formulas were proposed:  $\text{Ni(OH)}_{1.7}\text{Cl}_{0.3}$ , when nickel chloride was hydrolysed at room temperature;  $\text{Ni(OH)}_{1.67}(\text{NO}_3)_{0.33}$ , when nickel nitrate was hydrolysed at room temperature; and  $\text{Ni(OH)}_{1.82}(\text{NO}_3)_{0.18}$ , for hydrolysis of nickel nitrate at 70°C. The hydroxides prepared at room temperature were stabilized as colloids with the average particle size of 9 nm. The hydroxides prepared at 70°C were stabilized with a particle size of 80 nm. After evaporation of the solvent at 120°C, the colloids were crystallized in  $\alpha\text{-Ni(OH)}_2$  structure (disordered brucite), for each synthesis. The heat treatment of hydroxides at 400°C allowed obtaining nickel oxides, via dehydroxylation. The crystallographic and thermogravimetric studies shown that hydroxides contain glycols molecules as a structural or/and absorbed element. The presence of glycols caused unexpected reactions in the case of synthesis using nickel nitrate salt titrated at 70°C. The XPS analysis proved the presence of nitrides in the hydroxide samples and carbides in the final nickel oxide. The synthesis using nickel chloride precursors, titrated at room temperature was found to be free from by-products for a hydroxide and final oxide. In addition, all examined samples were surface contaminated by carbonaceous species. For nickel hydroxide precursors the surface was contaminated by C=O, C-O and C-C/C-H species. The same pollution was detected on the surface of resulting nickel oxides.

The nickel hydroxides were deposited on FTO (ASAHI 120) and ITO (PGO) conductive substrates by spin coating technique. The nickel oxides were obtained after thermal treatments at 120°C and 400°C. Resulting NiO particles had a non uniform morphology and not homogenous size distribution. The crystals were roughly spherical or rectangular with the size ranging between 5 to 20nm. The deposition by spin coating allows obtaining porous films of NiO distributed along entire substrates, but with local

discontinuities. Dewetting of the colloids on the conductive glass substrates, as well to high viscosity was adjusted by addition of co-solvent dipropylene glycol methyl ether.

The thin films of NiO were tested as p-type conductive layer in hybrid organic solar cells. The NiO layers were obtained from described here colloidal hydroxides. The best performance was recorded for NiO layers synthesized from  $\text{Ni(OH)}_{1.7}\text{Cl}_{0.3}$  and  $\text{Ni(OH)}_{1.82}(\text{NO}_3)_{0.18}$  precursors and was in range of 1%. The PCE for NiO obtained from  $\text{Ni(OH)}_{1.67}(\text{NO}_3^-)_{0.33}$  was close to 0.5%. Those values were not satisfactory in comparison to optimized cells having PEDOT:PSS as a hole transporting layer. The cells having NiO deposits had almost twice lower Voc and FF values, than reported for reference PEDOT:PSS. Those values indicate that presented here NiO have a poor p-type characteristic. One of the possible reasons for low efficiency in PV cells can be attributed to contamination of deposits by carbonate species. Another reason can be due to some mismatches of energy levels between NiO and P3HT:PCBM. Finally the concentration of positive charge carriers in NiO samples might be low and resulting layers could act as isolators.

The synthesis of nickel hydroxide in a glycol media gives an opportunity for good dispersion of particles in a colloidal form. The well dispersion of particles allows obtaining homogenous deposits of hydroxides and nickel oxides. However the resulting layers of NiO show poor performance as a p-type material in hybrid organic solar cells.

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# **Chapter IV: Deposition of NiO by direct current reactive sputtering**

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## **Introduction**

The chapter describes the fabrication of nickel oxide thin films by Physical Vapour Deposition technique. The process was carried out using two reactors of different dimensions. The first part of the chapter describes the process parameters for a laboratory scale reactor during deposition process. The electrical signal of the cathode was interpreted as a feedback signal for controlling a sputtering process for nickel oxide deposition. Fabricated thin films were characterized by various techniques in terms of crystallographic structure, chemical composition, microstructure growth, optical properties and electronic band configuration. The second part of the chapter describes elaboration of nickel oxide samples using an industrial PVD reactor. The process was scaled up by factor of 53.3 in respect to the surface of the nickel target. The evolution of process parameters was analyzed and compared with those for smaller reactor. The third part of the chapter describes the tests of nickel oxide samples as a p-type charge transporting layer in hybrid organic photovoltaic cells.

### **IV.1 Estimation of working conditions for deposition of thin films NiO by laboratory scale reactor**

The paragraph contains the evolution of process parameters occurring during a deposition of nickel oxide. The details related to PVD reactor and experimental arrangements were given. The evolution of discharge pressure, cathode voltage and crystal structure of products was analyzed as a function of oxygen partial pressure for three different discharge currents. The cathode voltage characteristic was discussed as a tool for controlling sputtering process.

#### **IV.1.1. Description of the PVD reactor, working conditions and arrangement**

Deposition of nickel oxide thin films has been done using laboratory made reactor (Figure 84). The volume of the chamber was approximately equal to 4.5 dm<sup>3</sup>. Circular nickel target of diameter 1.3 inches was purchased from Kurt J. Lesker company (purity 99.99%). The target temperature was cooled down by water heat exchanger. Direct current (DC)

variable power supply FUG MCN 700–1250, operating in a constant current mode was used to sustain a glow discharge. The cathode used was a Minimak unbalanced magnetron.

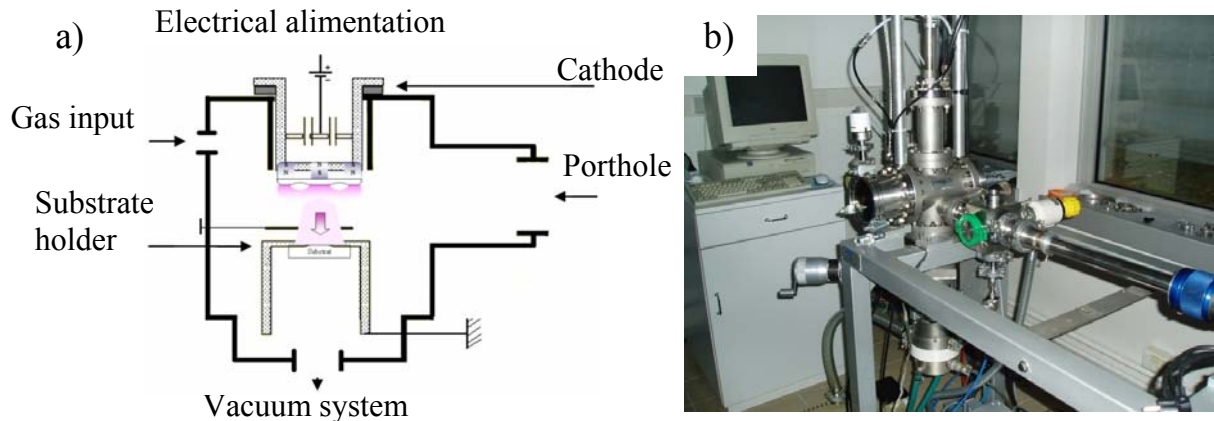


Figure 84. PVD reactor: a) schema of arrangement, b) photography

The distance between the target and a substrate was fixed to 3 cm. Working gases: argon and oxygen were introduced in to the reactor by mass flow controller and discharge pressure was measured by a capacitance manometer (or a Pirani-ionization gauge). Resulting oxygen content was defined as  $O_2\% = V(O_2)/(V(O_2) + V(Ar))$  and varied from 0 to 27%, where  $V(O_2)$  and  $V(Ar)$  are the flux of oxygen and argon, expressed in standard cubic centimeters per minute (sccm), respectively. The sputtering chamber was evacuated by means of a two step pumping unit (a 2 m<sup>3</sup>/h mechanical pump associated to a 260 l/s turbomolecular pump). The vacuum outlet was placed below the substrate. Before deposition, the vacuum system was pumped down to about 10<sup>-7</sup> Torr before each stage of sputtering and substrate deposition. Deposition was preceded by sputtering of the target in an argon atmosphere for 5 minutes to remove an oxide layer from the target and this should provide stable operation cathode potential.

#### IV.1.2. Cathode voltage as a feedback signal

The cathode voltage is one of the common feedback signals for controlling the sputtering reactive process<sup>183, 184, 185</sup>. In most of the direct current sputtering systems, cathode voltage changes as a function of the flow of reactive gas. To interpret correctly this evolution,

it is worth distinguishing two categories of current alimentation setup. Profiles of the discharge voltage are usually described for two particular systems, dependent from the electrical settings. The first one is the discharge in constant power mode. In that case, as reactive gas partial pressure increases, the cathode voltage and discharge current change simultaneously in an opposite way to maintain the plasma discharge. The second case is a discharge in a constant current mode. For this configuration, in respect to the reactive gas partial pressure, the cathode voltage changes to compensate minimum current needed to maintain the discharge. In the following paragraph the discharge characteristic in a constant current mode is discussed for sputtering of a metallic nickel target by oxygen and argon as a mixture of working gases.

In the literature, reported data illustrate that cathode voltage for reactive sputtering of metallic target can behave in a different manner depending on the sputtered material. For increasing partial pressure of reactive gas, the cathode voltage may increase in an absolute value upon sputtering of silver in Ar/O<sub>2</sub><sup>186</sup> (Figure 85a); or increase and reaching the plateau for zirconium in Ar/O<sub>2</sub><sup>187</sup> (Figure 85b). For sputtering of aluminium target in Ar/O<sub>2</sub><sup>188</sup> the cathode voltage decreases reaching a plateau (Figure 85c). In the case of Ge in Ar/O<sub>2</sub><sup>189</sup>, the cathode voltage shows dual behaviour; initially increasing, followed by abrupt decrease and stabilizing for higher partial pressure values (Figure 85d). Thus, the cathode voltage is not only function of reactive gas partial pressure and the interpretation of cathode signal has to be supported by additional techniques and experiments.

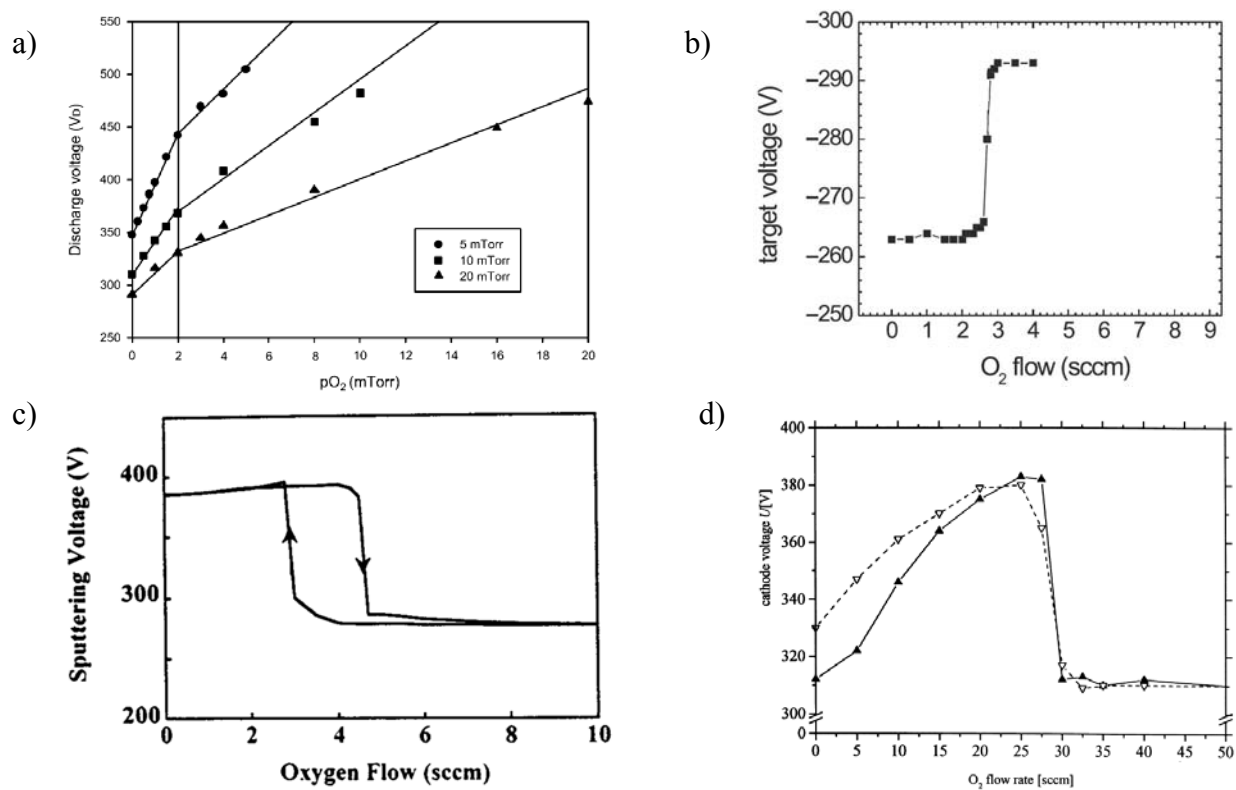


Figure 85. Cathode voltage vs. oxygen partial pressure of reactive gas Ar/O<sub>2</sub>, in constant current mode for different sputtered metals: a) Ag, b) Zr, c) Al, d) Ge.

Cathode voltage is mostly discussed on the basis of Secondary Electron Emission Yield (SEY). The emission of secondary electrons from cathode material is caused by ionic bombardment and emitted electrons sustain a glow discharge mechanism. During sputtering process the reactive gas arriving to the cathode surface causes oxidation of the metallic target and leads to the formation of metal-oxide layer. The changes in SEY are in a strong relation to the materials which are formed on the cathode surface. The electron emission coefficients from metal compounds are usually lower than their oxide compounds. It is because sputtering yield of oxides is lower than for pure metals and most of the energy of incident ions is used to break bonds resulting in creation of secondary electrons. However, from some reasons cathode voltage behaves in an unexpected way for each particular sputtered system.

By increasing a flow of reactive gas during sputtering process, the target voltage is affected by at least three ways. First, the target is bombarded by different ionic species with different energies ( $\text{Ar}^+$ ,  $\text{Ar}^{+2}$ ,  $\text{O}^+$ ,  $\text{O}_2^+$ ). Second, the surface of the target is no more metallic because of reactions with reactive gases. Thirdly, the partial pressure of reactive gas changes

due to consumption by substrate (chamber walls) and sputtering yield. All these processes make any interpretation complex and the electrical signal has to be regarded as a combined effect of several phenomena having an impact on electrical properties on plasma as well as target surface conditions.

Employing a discharge voltage as a feedback signal as a function of the relative gas flow ratio (partial pressure), the three following assumptions are considered. First, the variation of cathode voltage (magnitude of increment) for different gas flow is sufficiently large; second, there is a correlation between behaviour of cathode voltage and other measured parameters (ex. behaviour of cathode voltage is strictly related with changes of discharge pressure); the trend of discharge voltage has a consequence in properties of deposited thin films.

During sputtering of metallic nickel by Ar/O<sub>2</sub> system, the discharge voltage characteristic shows dual behaviours. Figure 86 represents the evolution of process parameters for fixed experimental conditions (DC=110mA, 10sccm of Ar). For increasing partial pressure of oxygen, the target voltage initially increases, until the maximum value and start to decrease reaching a plateau. Similar evolution of cathode voltage was found for each examined experimental condition. Additionally evolution of discharge pressure, deposition rate and specific crystallographic structures for corresponding thin films, suggested that the cathode voltage profile can be divided into 4 regimes.

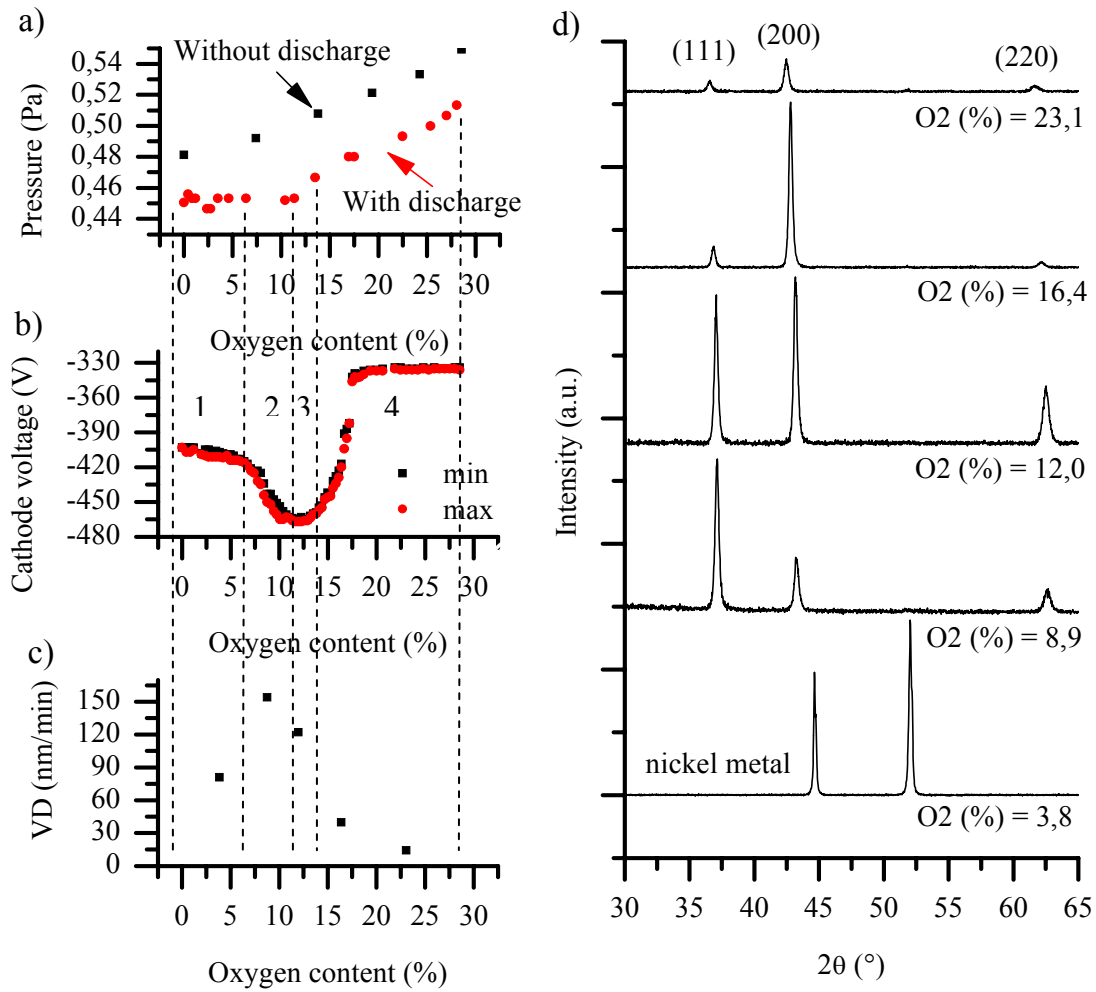


Figure 86. Evolution of process parameters vs. oxygen partial pressure in the mixture of working gases: a) gas total pressure, b) cathode voltage, c) deposition rate, d) X-ray diffraction of corresponding thin films.

The distinct regimes are marked in a Figure 86b and are interpreted in the following manner:

- First, the target is in a metallic state, the oxygen species reaching the target are removed by ion bombardment, allowing the target to remain metallic and therefore the discharge voltage does not change significantly. The total pressure during the discharge remains constant meaning that oxygen is effectively consumed by sputtering process (or chamber walls) and erosion rate of the target is higher than formation of oxide layer. In that region metallic nickel is deposited.



- Second, the target is in an intermediate state, the amount of oxygen arriving at the target becoming higher with respect to the target oxide layer removed by sputtering. An increase (absolute value) in the target potential is observed which indicates a decrease in electrical conductivity of the cathode. An increase in cathode voltage can be attributed to chemisorption of the oxygen and formation of Ni-O surface target coverage. In that region, occurs the instability of cathode voltage, suggesting that erosion rate and formation of oxide layer is a competitive process on the target surface. Thus target periodically changes its state from oxidized to metallic. It is also assumed that surface coverage by the oxide is not complete, target surface contains metallic sites and balance between those two states causes fluctuations of cathode voltage. In such conditions, nickel oxide is deposited. The reflections of X-ray diffraction diagrams show structure growing along (111) direction for nickel oxide cubic cell. In this region, deposition rate reaches the highest value among all 4 regions. The total pressure still remains at the constant value, meaning that oxygen is efficiently consumed by sputtering process. The erosion rate of the target and coverage of oxide layer is close to the balance.
- In the third region, the target potential stabilizes at the highest value, due to complete coverage of NiO layer on the target surface. The balance between erosion rate of the target and formation of oxide layer has been reached and slight decrease in deposition rate is observed. The total pressure increases slowly meaning that oxygen species arriving to the cathode or chamber walls are less consumed. The reflections of X-ray diagrams for deposited nickel oxide have peak intensities close to standard NiO powder-like structure. Some authors attribute this stabilization at higher potential to the formation of negative oxygen ions<sup>190, 191</sup>. In fact near the cathode we have two electron populations<sup>192</sup>, high energy electrons which can collide to O<sub>2</sub> molecules leading to dissociation-ionization (Maximum of the cross section at about 100eV<sup>193</sup>) of the O<sub>2</sub> molecules with the creation of low energy electrons increasing the second population of electrons which are thermalized (4eV) and which can get attached to O atoms or O<sub>2</sub> molecules but also collide to O<sub>2</sub> molecules to form 2O<sup>-</sup> (Maximum of the cross section at about 6eV<sup>193</sup>). These negative ions consume electrons and are not trapped by the magnetic field, hence we observe a diminution of the ionic density ( $n_i = n_e$ ) in the plasma and thus, in order to maintain the discharge current, the cathode voltage increases.

- Fourth, the target is fully oxidized, the discharge voltage stabilizes again at a lower (absolute value) discharge voltage and reaches a plateau. The deposition rate starts to decrease and oxygen which is not consumed by sputtering process or chamber walls causes increase in total pressure. This is the so-called poisoned mode of the cathode. The drop of voltage can be due to an increase in the secondary electron emission coefficient and slight increase in discharge pressure. However, plateau of cathode voltage for highest oxygen content seems to be not affected for increasing total pressure and probably is related to constant erosion rate of the target. Region 4, oxygen-rich content was characterized by predominance of (200) growth for deposited nickel oxide thin films.

Summarizing the evolution of process parameters and response of cathode voltage, the main conclusion can be drawn as follow:

- deposition rate and profile of discharge voltage are in close correlation;
- discharge pressure starts to increase for an absolute maximum of cathode voltage;
- corresponding nickel oxide thin films change their preferential growth along the structure from (111) to (200) around the maximum cathode voltage.

Among the data available in the literature it is worth mentioning about *Hotovy's* works<sup>194,195, 196</sup> who published several publications related to deposition of nickel oxide by DC reactive sputtering. However, his experiments were limited to certain flux of reactive oxygen and they do not describe the evolution of cathode voltage in a continuous manner. *Hotovy et al.*<sup>197</sup> suggested the existence of three regimes related to the behaviour of the cathode voltage and defined then in the following manner:

1. metal-sputtering mode when the discharge voltage increases to (370-375V)
2. transition-sputtering mode characterized by an abrupt increase in the value of the target voltage
3. oxide-sputtering mode with a low value of the target voltage (275-295V)

Additionally they also claimed that those sputtering modes depend on the oxygen content in the sputtering mixture, the sputtering power and the pumping speed. This description is in close relation with the results observed using our reactor arrangement and supplying flow controller.

#### IV.1.2.a Influence of discharge current and composition of gas mixture

The behaviour of the cathode voltage was studied for three different discharge currents in the range of 50 and 110 mA. The discharge voltage was recorded for increasing oxygen flux while maintaining the argon flux at the constant value of 10 sccm. For each value of current, the cathode voltage exhibits the same shape (Figure 87). Detected signal shows periodic fluctuations and the maxima and minima were recorded. Instability of the cathode is especially pronounced in the second regime, before the voltage reaches the maximum. After absolute maximum the cathode signal stabilizes. For each discharge currents the same trend was observed.

Increasing the discharge current induces an increase in ionization efficiency and therefore in the sputtering yield of the target. For nickel sputtering, increasing current leads to a shift of the cathode voltage towards higher oxygen contents. In addition, increase in discharge current is accompanied by increase in the absolute maximum of the cathode voltage (at the 3 defined region). This behaviour might be explained by an increase in the reaction rate at the target surface.

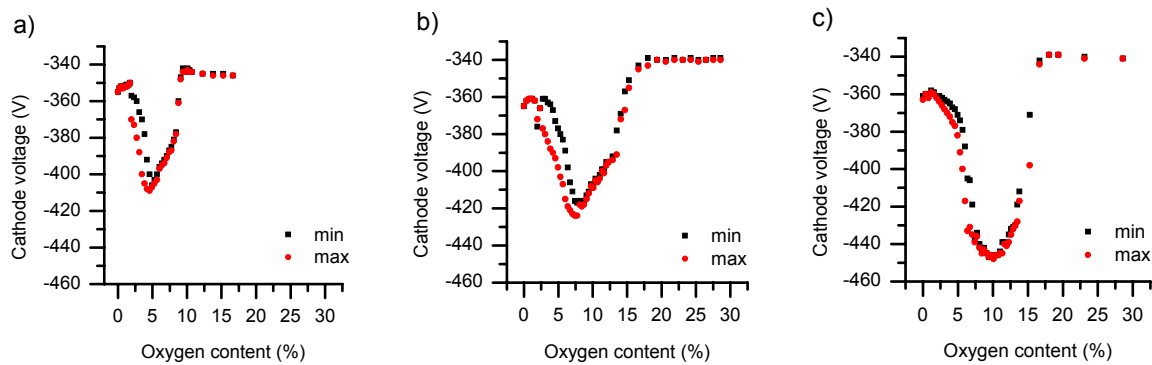


Figure 87. Cathode voltage as a function of oxygen content for discharge current: a) 50 mA, b) 80 mA, c) 110 mA. Minimum of cathode voltage marked by black squares and maximum by red circles.

The shift towards higher oxygen value is caused by the increase of the sputtering yield of the target, thus more oxygen is needed to balance the sputtering process. For increasing discharge current, an increase in an absolute value of the cathode voltage, in the regime 3, is especially pronounced. For DC=50 mA the cathode voltage reaches maximum at  $V_{\max}=-410$  V, for DC=80 mA  $V_{\max}=-420$  V, and for DC=110 mA  $V_{\max}=-450$  V. That might be a consequence of our choice to operate with a constant discharge current. In fact, the current represent the sum

of electron current (electrons emitted by the target) and ion current (ions bombarding the target). Thus, when the cathode is not fully oxidized, the increase of the SEEY is low and not sufficient to reach the fixed current. Then it is necessary to increase the discharge voltage in order to increase the ion current. Surprisingly for each discharge current, the discharge voltage stabilizes at the same value (at around 340V) when regime 4 is reached. This is probably due to the fact, that SEEY is high in the target poisoned regime and increasing current does not change significantly the ion current.

#### IV.1.2.b Crystallographic growth of NiO thin films

Structure of nickel oxide is often described as face centered cubic NaCl-type. However in most of the cases ideal cubic symmetry is rather difficult to achieve. Non-stoichiometric nature of NiO, impurities, crystallite size, stress or strain and the temperature of measurement causes that recorded diagrams often indicate on lower symmetry than the cubic one. The distortion of the lattice causes that in reality NiO exist as a rhombohedral structure. For rhombohedral NiO, diffraction planes lie at similar distances than for the cubic one. From that reason, distortion of the NiO structure is often ignored and lattice is described as pseudo-cubic system. Table 12 shows the parameters for cubic and rhombohedral symmetry.

Table 12. Comparison of NiO structure parameters for cubic and rhombohedral symmetry

| f.c.c. Fm3m (225)<br>JCPDS-No.: 89-7130 |           |     | Rhombohedral R-3m (166)<br>JCPDS-No.: 44-1159 |           |     |
|-----------------------------------------|-----------|-----|-----------------------------------------------|-----------|-----|
| d(hkl) (Å)                              | Intensity | hkl | d(hkl) (Å)                                    | Intensity | hkl |
| 2.42164                                 | 674       | 111 | 2.41197                                       | 600       | 101 |
| 2.09720                                 | 999       | 200 | 2.08849                                       | 1000      | 012 |
| 1.48294                                 | 438       | 220 | 1.47733                                       | 300       | 110 |

For thin films deposited by reactive sputtering, the pseudo cubic cell will be used as a model to explain the growth of thin films.

The structure of as-deposited NiO was found to be polycrystalline but with preferential orientations, strictly related to the oxygen content in the mixture of working gases. Figure 88 shows the X-ray diagrams for thin films NiO deposited for three different discharge currents. The preferential growth of NiO was always depending on the shape of the discharge curve

(Figure 86b), and therefore on the oxygen partial pressure for each examined discharge current. The region defined as 1 was out of consideration because the deposited films were composed of metallic nickel. The region 2 with relatively low oxygen content was accompanied by an increase in the nickel oxide (111) diffraction peak, however in that region (depending on oxygen content) metallic grains can be included in an oxide matrix (Figure 88d). In Region 3, where the discharge voltage reaches its absolute maximum, the NiO X-ray diffraction pattern is very close to standard JCPDS card (Bunsenite, NaCl-type structure, 2003 No: 89-7130) i.e; NiO powder-like structure; region 4, rich in oxygen content was characterized by the predominance of the (200) peak intensity, in the X-ray diffraction pattern.

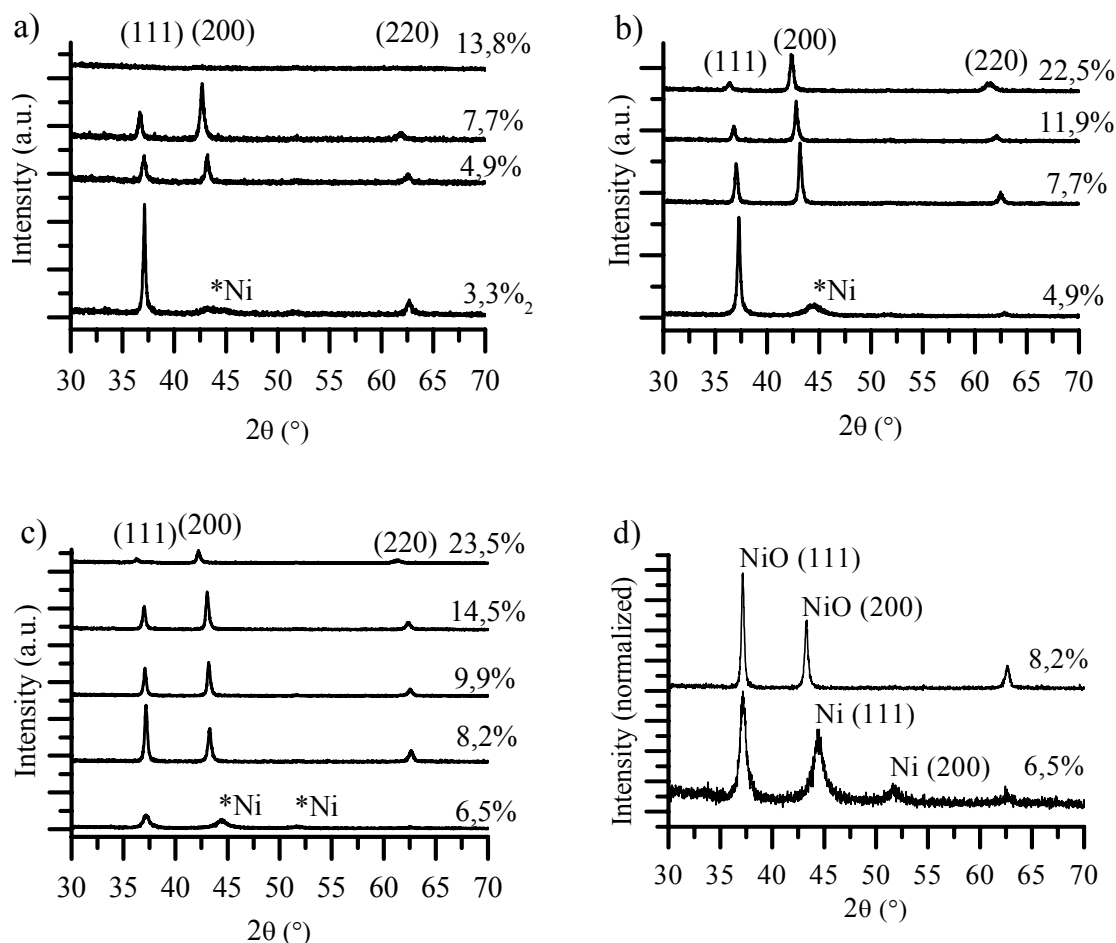


Figure 88. XRD diagrams for NiO thin films of about 1  $\mu\text{m}$  thickness, deposited at: a) 50 mA, b) 80 mA, c) 110 mA and d) at 110 mA with normalized peaks intensity. Peaks of nickel metal marked by asterisk (\*).

Thin films deposited in the oxygen range allowing transition of preferential growth from [111] to [200] directions are crystallized, however XRD diagrams of the deposits carried out in relatively high oxygen content show less intensity signal for films having similar thickness. This may indicate the presence of an amorphous phase or decrease in the crystallite domains. As well under stoichiometric  $\text{Ni}_{1-x}\text{O}$ , may also cause the same effect, causing less X-rays diffraction from the heaviest Ni atoms.

Among the data available for deposition of nickel oxide from metallic target, for DC reactive sputtering, *Hotovy et al.*<sup>194</sup> found the same evolution of texture, changing from (111) to (200) for increasing  $\text{O}_2/\text{Ar}$  content in the gas mixture, however the structures has been described in the rhombohedral system with diffraction peaks indexed as (101) and (012), respectively. *Lei A*<sup>198</sup>, for RF reactive sputtering, found changing preferential orientation from (200) to (111) for increasing substrate temperature. *Awais*<sup>199</sup> reported changing the preferential orientation from (200) to (111) for increasing pressure for DC reactive sputtering. On another hand, deposition of NiO from nickel oxide target resulted also in preferential orientations. *Chen*<sup>200</sup> found for RF sputtering the evolution from (111) to (200) for increasing substrate temperature and applying pure oxygen atmosphere. Later on *Chen*<sup>201</sup> observed for RF sputtering the evolution of (111) to (200) for increasing gas ratio  $\text{O}_2/\text{Ar}$  at elevated temperatures. However studies related to deposition of nickel oxide are rather limited to the process description and final products, without models or explanations of the origin for crystallographic growth.

The evolution of NaCl-type cubic structure has been explained for transition metal nitrides. Nitrides, from their technical importance were more extensively studied and the numbers of available papers lead to some general conclusions. In fact plasma nitridation and plasma oxidation is a different process. However because of their crystallographic similarities, it is worth looking at the deposition conditions and comparing them with deposition of nickel oxide. Growth along [111] or [002] directions, as well competitive as texture evolution were reported for cubic structures of TiN and TaN by controlling different parameters. Table 13, taken from reference summarizes these parameters.

Table 13. Main relationships between preferential orientation of and process parameters<sup>202</sup>

| Material | Parameters   | Preferential orientation with increasing parameter |
|----------|--------------|----------------------------------------------------|
| TiN      | $J_i/J_{Ti}$ | (111)→(002)                                        |
|          | $N_2/Ar$     | (111)→(002)                                        |
|          | $T_h$        | random→[(002)→](111)                               |
|          | $V_b$        | (002)→(111)→(220)                                  |
|          | $W$          | (002)→(111)→(002)                                  |
|          | $T$          | (002)→(111)                                        |
| TaN      | $N_2/Ar$     | (111)→(002)→(111)                                  |
|          | $V_b$        | (111)→(220)                                        |
|          | $J_i/J_{Ti}$ | (111)→(220)                                        |
|          |              | (111)→(002)                                        |

The preferred orientation has been achieved by changing: ion flux to metal ratio ( $J_i/J_{Me}$ ), gas mixture ( $N_2/Ar$ ), film thickness ( $T_h$ ), negative bias voltage ( $V_b$ ), power ( $W$ ) and temperature ( $T$ ). Taking into account the complexity of plasma chemistry, changing one parameter is often accompanied by the change of another one. Thus isolation of one single parameter, which is responsible for preferential orientation, has to be considered with attention and in respect to all deposition conditions. Mechanisms for development of preferential texture has been discussed at the atomic level in terms of: binding energies of incident adatoms to the growing surface, affinity of specific crystallographic planes in respect to incoming atoms, diffusion of adatoms along oriented grains and kinetic energies of adatoms.

The discussion about preferential orientation for transition metal nitrides or pure metals crystallizing in fcc cubic system leads to agreement for formation of preferential (111) planes. The surface aligned [111] out of substrate has a privilege to grow over [002] due to sticking anisotropy of adatoms. The model was proposed by *Hartman and Perdok*<sup>203</sup> and they predict the difference in sticking coefficient on each plane which is proportional to the number of nearest neighbours between add-particle and growing plane. It means, that the arriving particle has a higher probability to be incorporated (and higher sticking coefficient) on (111) plane because that plane offers 3 dangling bonds while the (200) plane provides only one. On another hand the adatom reaching the (002) surface will have a higher probability to be transported to the surface with a higher atom affinity. However, Hartman-Perdok's model explains only the case when the growing structure is composed from the same atoms.

During reactive sputtering, plasma can be composed from atomic and poly atomic molecules. *Yumoto*<sup>204</sup> proposed an extended periodic bond chain (PCB) model. According to

this model, if the growing film is composed of AB (e.g., Ti-N or Ni-O), and in the plasma state, precursors are Ti+N or Ni+O, the sticking coefficient will be larger on (111) plane, because that plane has a largest number of dangling bonds per atom on the top of the surface (as predicted by Hartman-Perdok model). However, when the precursor is a polyatomic molecule Ti-N or Ni-O, the precursor has a higher probability to be incorporated to (200) surface because that surface contains both atoms in the equal number as the precursor.

In addition a third model was proposed by *Mathieu*<sup>205, 206</sup> for rock-salt structures. This model takes into account the presence of reactive gas in two states: molecular and atomic as well as adparticles as single atom or dimmers. This model relies on the same two assumptions than previously, but the discussion is extended to more complex systems. Table 14 summarizes the plasma state and preferential orientations for that model.

Table 14. The number of nearest neighbours offered to the incoming particle for three main index planes in a rocksalt structure

| Structure | Adparticles | State of reactive gas | Number of nearest neighbours on: |       |       | Fastest geometric growth direction |
|-----------|-------------|-----------------------|----------------------------------|-------|-------|------------------------------------|
|           |             |                       | (100)                            | (110) | (111) |                                    |
| Rocksalt  | Atomic      | Molecular             | 1                                | 2     | 3     | [111]                              |
|           | Atomic      | Atomic                | 5                                | 4     | 3     | [001]                              |
|           | Compound    | Molecular             | 2                                | 4     | 3     | [111]                              |
|           | Compound    | Atomic                | 5                                | 4     | 3     | [001]                              |

The defined above models only indicate the tendency of crystal growing to be preferentially oriented. Models do not include any energetic aspects of adatoms or molecules arriving on the substrate. They do not describe in a quantitative manner the mobilities of arriving species, which are difficult to measure experimentally. Thus despite of many models, which are supported by plasma diagnostic and experiments, the discussion in the literature is still open.

Back to the nickel oxide depositions described here, it can be suggested that the experiments has been done in conditions allowing manipulation of crystal orientations. For the three examined discharge currents, the same trend was observed: increasing oxygen content in the mixture of working gases and orientation of the grown films were in close relation to discharge voltage characteristic. However, from the reason of lack in plasma



diagnostic, no clear conclusion can be drawn by referring to the mechanisms of preferential orientation.

#### IV.1.2.c Deposition rates

The experimental deposition rates of NiO as a function of oxygen content in the gas mixture for 3 current discharges are presented in Figure 89. The deposition rate increases with increasing discharge current as commonly observed. For each examined currents, the deposition rate reaches a maximum in region (zone 2) and then decreases strongly for zones 3 and 4. The same evolution of the deposition rate as a function of oxygen content has been observed for nickel oxide deposited by RF magnetron sputtering by *Liu*<sup>207</sup>.

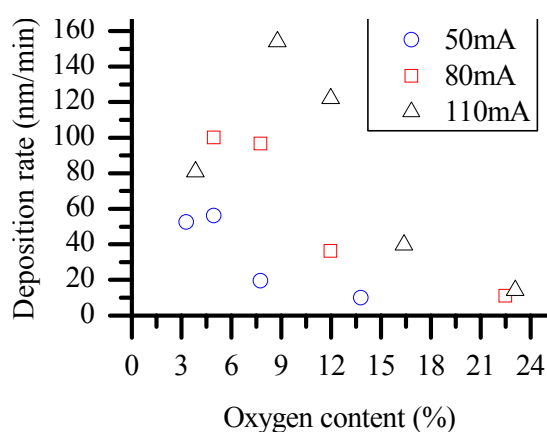


Figure 89. Experimental deposition rate of nickel oxide for three discharge currents

Commonly, deposition rate decreases as a function of oxygen content in the mixture of gases. This is related to the poisoned state of the target. In case of nickel oxide, maximum of deposition rate is observed. It can be explained in the following manner. Initially, for low oxygen contents, the target is not yet poisoned, the sputtering yield is high and the deposition rate is limited by the amount of available oxygen. At the same time, the cathode voltage increases causing more efficient ion bombardment. Then, poisoning of the target occurs, the sputtering yield decreases significantly and drop of deposition rate is observed for further increasing amount of oxygen.

## IV.2. Influence of oxygen partial pressure for properties of nickel oxide thin films deposited at 110 mA

In this paragraph, the influence of oxygen content on the properties of thin films will be discussed. The deposits at discharge current equal to 110 mA were taken as representative features to summarize the evolution of thin film properties. Morphology, crystal growth, chemical composition and optical properties will be analyzed.

### IV.2.1. X-ray diffraction

In the paragraph IV.1.2.b, the evolution of preferred orientation of the NiO structure was presented for three different discharge currents and thin films close to 1 micron thickness (Figure 88). The growth along (111) or (200) planes in a cubic symmetry was related to one of four discrete regimes. In parallel with the evolution of preferential orientation, the diffraction planes were found at smaller or bigger diffraction angles than expected for powders. This indicates larger or smaller distances between lattice planes and distortion of the cubic symmetry. Table 3 summarizes the evolution of lattice planes and relative intensities of peaks for different oxygen contents, compared to powder-like NiO in a cubic symmetry (JCPDS No.: 89-7130).

Table 15. XRD peak positions for thin films of about 1 micron deposited at 110 mA (for cubic symmetry).

| Oxygen content (%) | Distance between atomic planes $d_{hkl}$ (Å) |         |         | Relative peak intensities |       |       |
|--------------------|----------------------------------------------|---------|---------|---------------------------|-------|-------|
|                    | (111)                                        | (200)   | (220)   | (111)                     | (200) | (220) |
| 6.5                | -                                            | -       | -       | -                         | -     | -     |
| 8.2                | 2.417                                        | 2.088   | 1,482   | 0,511                     | 0,336 | 0,152 |
| 9.9                | 2.423                                        | 2.091   | 1,483   | 0,372                     | 0,485 | 0,141 |
| 14.5               | 2.428                                        | 2.098   | 1,487   | 0,324                     | 0,532 | 0,143 |
| 23.5               | 2.473                                        | 2.137   | 1,510   | 0,180                     | 0,528 | 0,290 |
| JCPDS No.: 89-7130 | 2.42164                                      | 2.09720 | 1.48294 | 0.319                     | 0.473 | 0.207 |

At room temperature, NiO crystallizes in the trigonal system with  $a_H=2.9549$  Å and  $c_H=7.232$  Å in the hexagonal cell or  $a_R=2.953$  Å and  $\alpha=60.036^\circ$  in the rhombohedral one (ICSD file No.: 92-133). These trigonal parameters are not easy to compare with the most

usually used cubic ones. Their transformation in a pseudo-cubic system leads to the following parameters:  $a_c=4.179$  and  $\alpha=90.05^\circ$  (ICSD file No.: 76-699). In the hexagonal cell, the first peak (1 1 1) in a cubic cell is split into two indexation: (0 0 3) and (1 0 1); the second one (0 0 2) in cubic is indexed as (1 -1 2), whereas the last one (2 0 2) in cubic is also split and allotted to (1 0 4) and (2 -1 0).

Despite the quality of the X-ray diffraction patterns, an attempt to refine the cell parameters was conducted using Jana 2006. The cell refinement was done for NiO thin films of  $1\mu\text{m}$  thickness, deposited at 110mA for various oxygen contents (Figure 88). At first identification of peaks indicates that the sample deposited at lowest 6.5% of  $\text{O}_2$  mainly consist in Ni metal, additionally the (1 1 0) peak of  $\text{SnO}_2$  is detected at  $2\theta=26.5^\circ$ . If the intermediate samples cannot be treated in the cubic symmetry, is the case for the first and last one. In any case, some preferential orientations are to be accounted to improve the fit quality. The main affected peak is the first one: (1 1 1) in cubic cell. Since it is split in the trigonal system, affecting one or the other (h k l) with the preferential orientation leads to some differences on the cell parameters. But no clear improvement of the reliability factors could really be noticed to ascertain the most valuable hypothesis. However in both cases, the trend is the same. Because the intensity of (1 0 1) reflection is higher than the (0 0 3), we chose to report the refined cell parameters with the preferential orientation along the former direction in Figure 90.

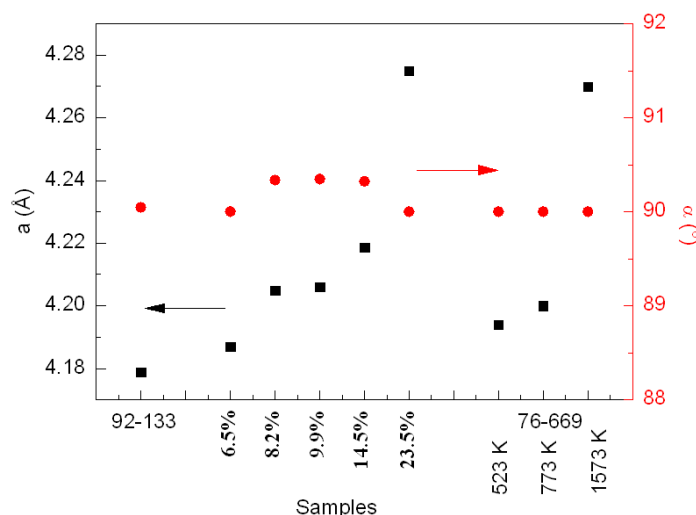


Figure 90. Evolution of the unit cell parameters for NiO deposited at 110 mA for various oxygen pressure and reference NiO (ICSD file No.: 92-133) and (ICSD file No.: 76-699) at various temperatures.

It is worth noting that, for PVD thin film, the cell parameters are always larger than the expected value at room temperature for powder (ICSD file No.: 92-133). Moreover we also noticed that for sample deposited at 6.5% of O<sub>2</sub>, if the *a* parameter is close to the value measured at 523K (ICSD file No.: 76-699), and equal to 4.187Å instead of 4.194 Å. For the other samples, the *a* parameter is larger than the value at 773K together with  $\alpha$  angle, which is still larger than in the room temperature value: 90.3° versus 90.05°. That indicates on stronger distortion. The sample obtained in the most oxidized conditions can be refined in a cubic cell with *a* parameter equal to 4.279 Å. This value is very similar to the cell parameter at 1573K: 4.27 Å. It seems that PVD conditions stabilize high temperature varieties of NiO. Increasing the oxidizing conditions in the plasma enhances this trend.

However, the pattern matching does not take into account the effects of constrain and relative peak intensities. Thus, it is complex to refine the real symmetry and distortion of the cell having only XRD diagrams.

Studies of the deposits at lower thicknesses indicated that the preferential growth of the NiO structure is not only affected by oxygen content but also depends on the thickness of the films. Figure 91a shows the reflection peaks of samples having round 80 nm thicknesses, for increasing oxygen contents. The intensity of the (111) peak decreases with increasing oxygen content from 8.2 to 9.9% O<sub>2</sub>. For the deposits at 14.5% or 23.5% O<sub>2</sub> the intensities of the (111) and (200) reflections are comparable. This gives an idea that at high oxygen content the grain growth process is competitive for all the directions, for thin layers (lower than 100 nm) and at high oxygen values.

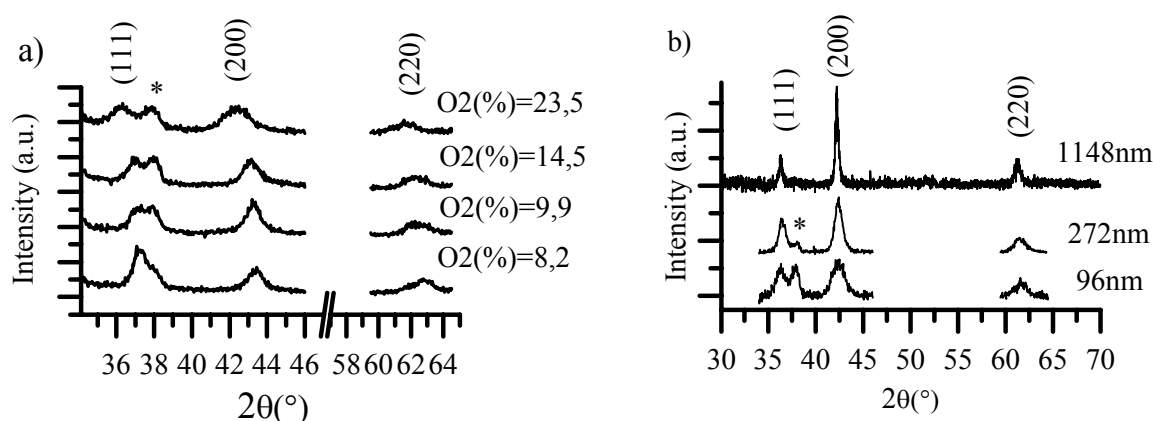


Figure 91. XRD of thin films deposited at 110 mA: a) for various oxygen contents having round 80 nm thickness, b) at 23.5% O<sub>2</sub> for three different thicknesses. Peaks of SnO<sub>2</sub>:F conductive substrate marked by asterisks (\*).

The structural evolution is clearly observed for samples deposited at 23.5% O<sub>2</sub> when the thickness of thin film increases (Figure 91b). At the thickness of 96 nm, both (111) and (002) grains are present. Further growth leads to progressive predominance of the growth in the [200] direction when the thickness reaches 272 nm and 1148 nm. The thin film, at the very beginning of the growth, is randomly oriented while overall microstructure evolves towards a final well crystallized state driven by the appropriate deposition conditions<sup>208</sup>.

#### **IV.2.2. Morphology and cross-section**

Evolution of NiO microstructure seems to follow the fundamental model of pure elemental polycrystalline films. According to the model, growth is initiated by nucleation, islands growth, and islands coalescence, leading to formation of continuous structure. In all examined cases, evolution of the microstructure was related to defined earlier deposition regimes. As a consequence of competitive growth and preferential orientations in each regime, the thickening of films was accompanied by change in morphology as a function of film thickness and arrangement of columnar structures. At the beginning of the growth, nearby the substrate (up to 100 nm), deposited thin films have similar surface topography for each deposition zone. Figure 92 shows a typical surface of 80 nm thin films deposited for various oxygen contents. The surface appears composed of round grains with size ranging from 50 to 100 nm. At that stage, the grain growth is rather random and does not affect the surface topography.

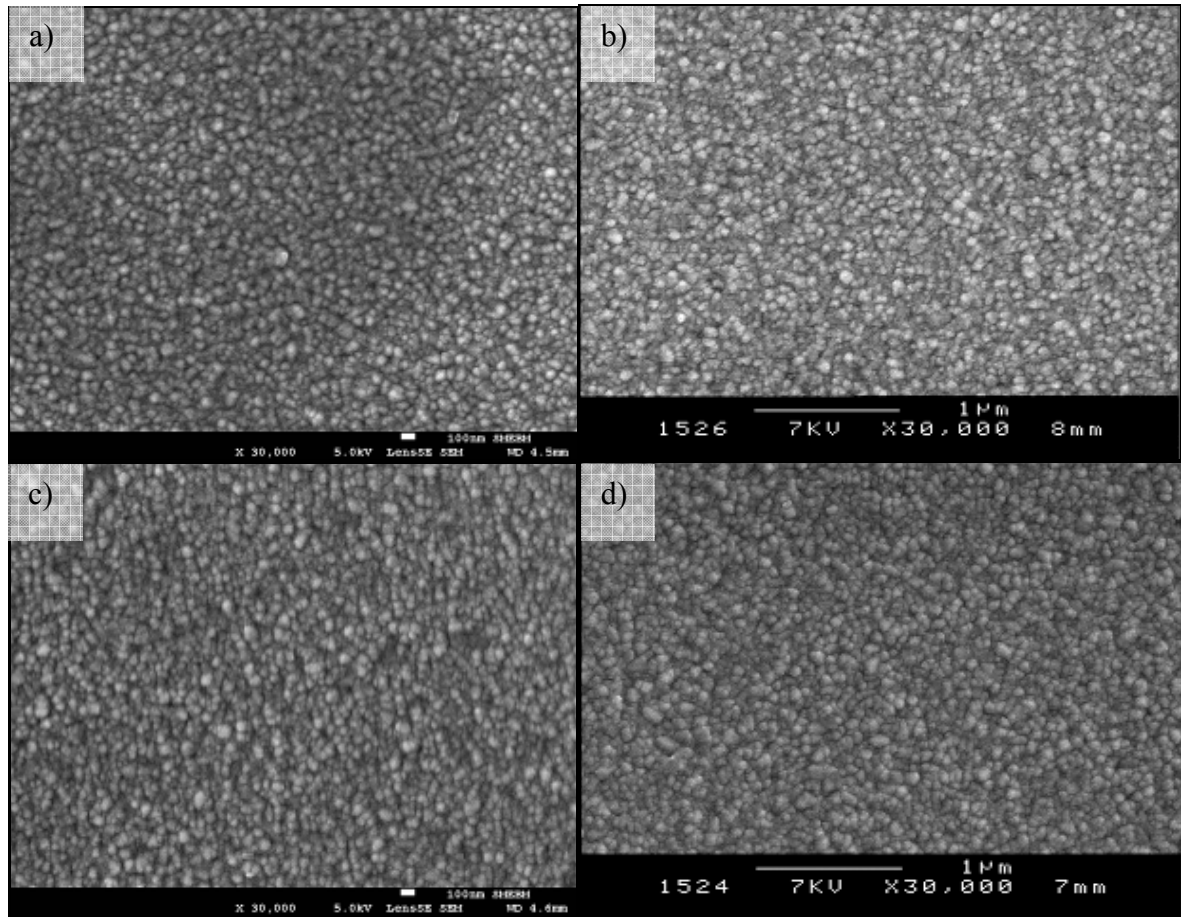


Figure 92. Surface of 80 nm thin films deposited at 110 mA: a) 8.2% O<sub>2</sub>, b) 9.9% O<sub>2</sub>, c) 14.5% O<sub>2</sub>, d) 23.5% O<sub>2</sub> at (magnification  $\times 30\,000$ )

When the NiO thickness increases up to about 1  $\mu\text{m}$ , the grain coarsening is significant (Figure 93). Initial round grains evolve to flakes-like crystals close to 300 nm for low oxygen contents (Figure 93a). The surface seems to be composed from faceted grains growing out-of-plane. For higher oxygen contents (Figure 93b and c) the surface is still composed of large crystals however it seems to be smoother, and statistical voids are observed. For the highest oxygen value (Figure 93d), the surface aspect is different with rectangular and triangular grains in the size range close to 100 nm. The surface is composed of more uniform, repetitive units with higher symmetry compared to deposits at lower oxygen contents.

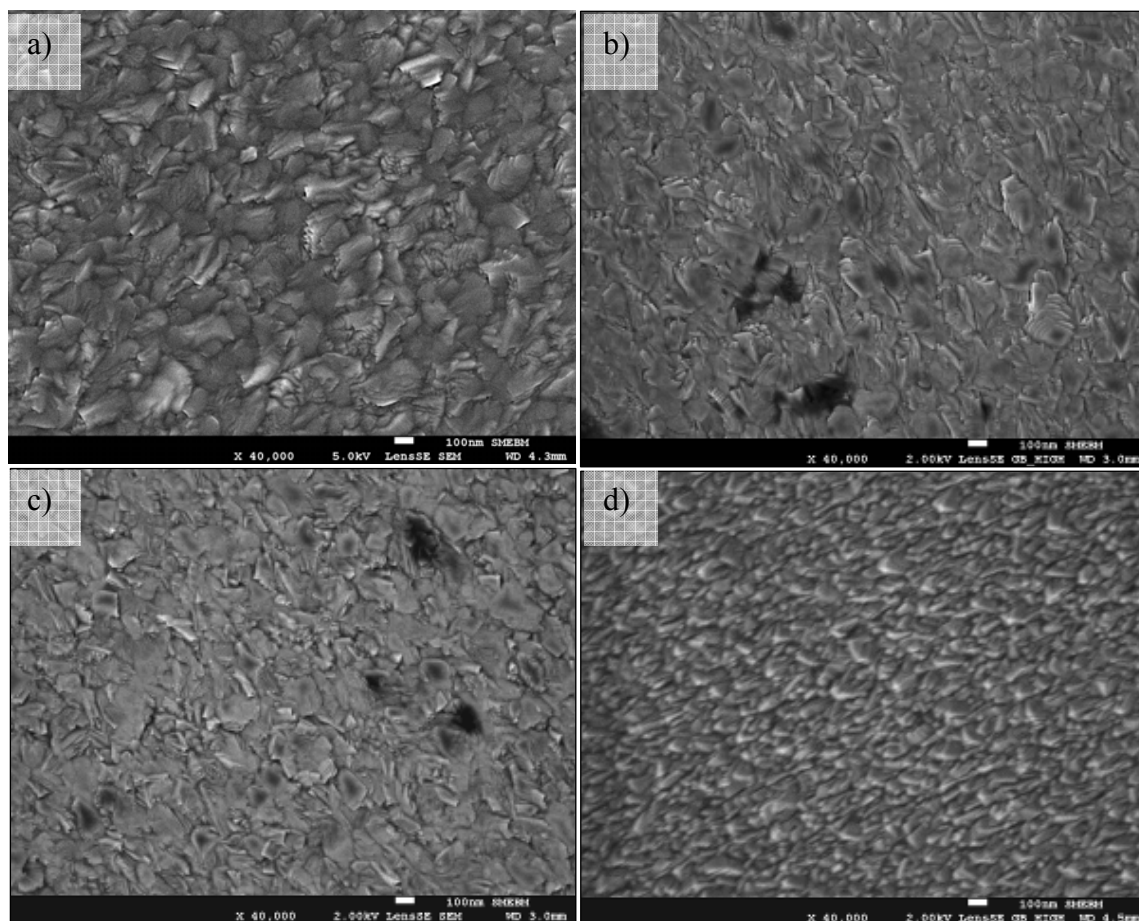


Figure 93. Surface of 1  $\mu\text{m}$  thin films deposited at 110 mA: a) 8.2%  $\text{O}_2$ , b) 9.9%  $\text{O}_2$ , c) 14.5%  $\text{O}_2$ , d) at 23.5%  $\text{O}_2$  (magnification  $\times 40\,000$ )

The in-plane texture is a consequence of the micro structural evolution of columnar growth and grain coarsening. Cross-section images (Figure 94) reveal the columnar nature of the films in every case. The sample deposited at lowest oxygen value grows as fibers column with limited extension (10-20 nm) and different growth directions, leading to low ordering of the micro-structure. The length of the columns is limited (less than 100 nm) and not continuous along all film thickness. This indicates that secondary nucleation take place and new columns start to grow on already existing ones. NiO deposited at 9.9 and 14.5%  $\text{O}_2$  are also composed of columns, expanding during nucleation process, which is affected by competition between differently oriented neighbouring crystals. The width of columns near to the surface is about 50 nm and in the widest place reaches around 200nm. However the columns are not continuous along all the film thickness, which indicates a secondary nucleation process. For that oxygen values the formation of inter-columnar voids is observed (Figure 94b and c). The sample deposited at the highest oxygen flow (Figure 94d) consists in

ordered cylindrical grains. The columns grow parallel to each other and perpendicular to the substrate along all sample thickness. The width of the columns reaches about 50 to 100nm.

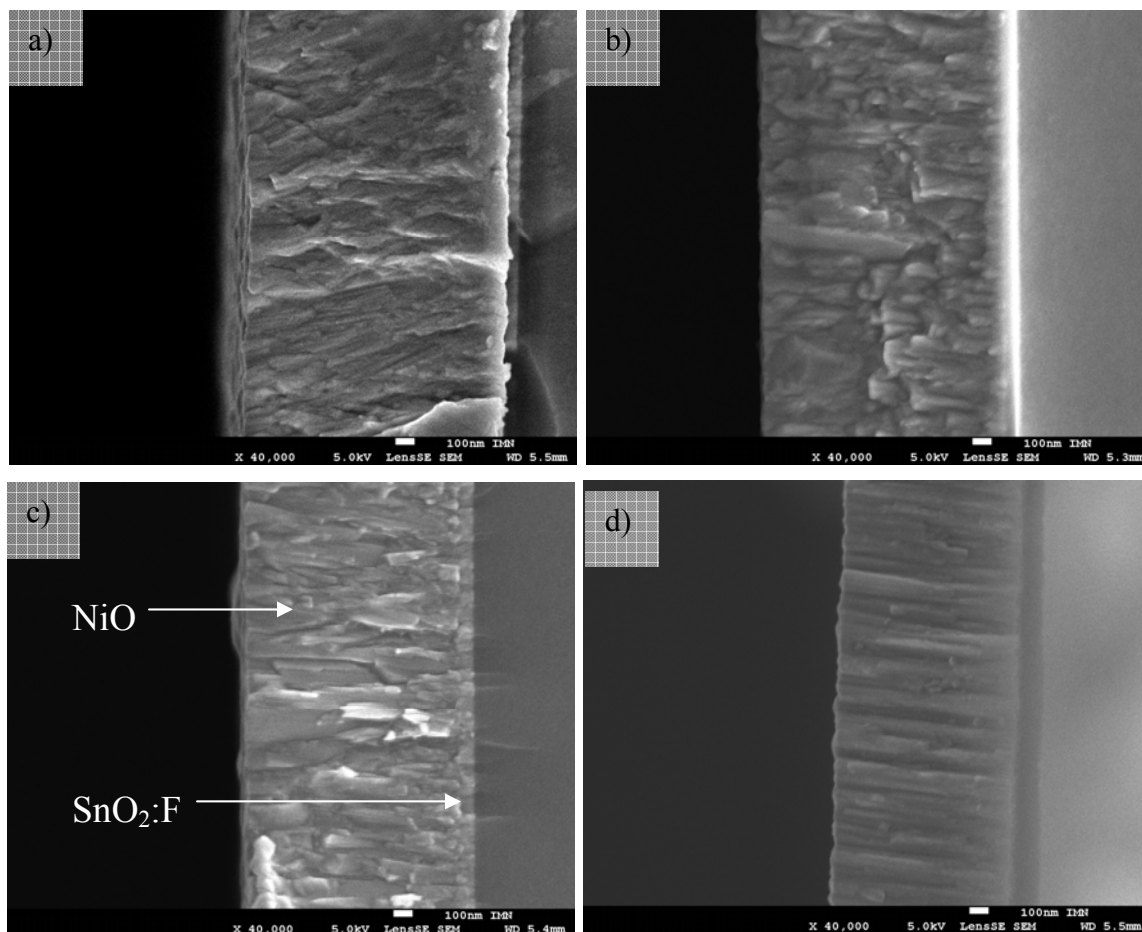


Figure 94. Cross-section of 1  $\mu\text{m}$  thin films deposited at 110 mA: a) 8.2%  $\text{O}_2$ , b) 9.9%  $\text{O}_2$ , c) 14.5%  $\text{O}_2$ , d) at 23.5%  $\text{O}_2$  (magnification  $\times 40\,000$ )

Considering the morphology evolution, the growth of NiO can be categorized using the structure zone model (SZM) for deposition of polycrystalline metallic compounds<sup>209</sup>. The model allows one to predict growth type as a function of two parameters: temperature and pressure. Figure 95 shows the schematic representation of the SZM. Roughly speaking, it explains the formation of wide, parallel columns at high deposition temperatures as a consequence of high diffusion of grain boundaries and surface adatoms (zone II). For low temperatures of the substrate, the diffusion phenomenon is limited, temperature is not high enough to reach thermodynamic equilibrium of crystal formation and the model describes growth of smaller polycrystalline structures or amorphous forms, with narrow columns (zone I). This model indicates also an intermediate zone where columns expand while growing perpendicularly to the substrate (zone T).



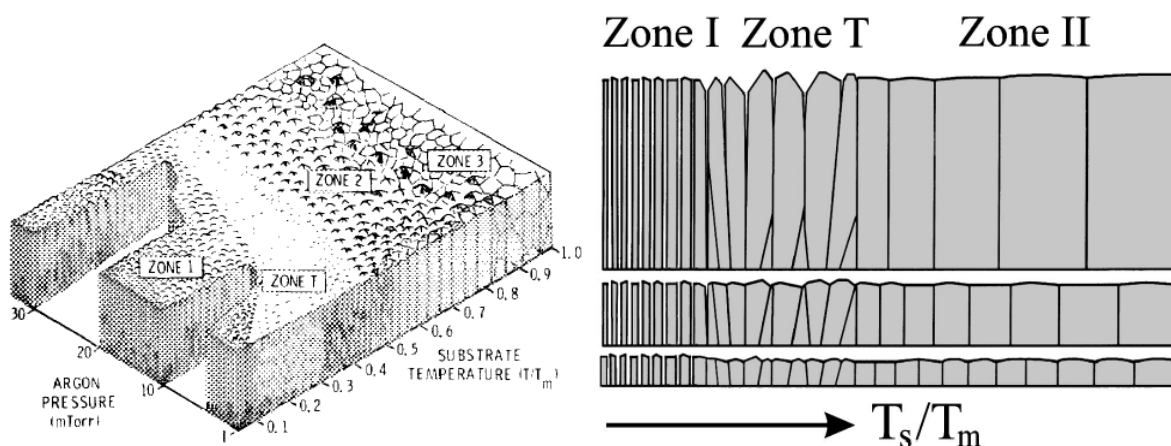


Figure 95. Microstructure evolution of pure metals plotted versus thickness: a) including temperature and pressure<sup>210</sup>, b) cross-section between the three identified main zones.  $T_m$  is the melting temperature of metals and  $T_s$  the substrate temperature in Kelvin.

However, SZM predicts the growth of pure metal compounds and does not take into account the presence of contaminations or effect of co-deposited species which contribute to the crystal formation. The deposition of NiO is affected by the presence of oxygen and its ionic species. Thus nucleation, coalescence and grain growth can be affected by the presence of reactive gas. The model takes as a parameter the ratio of substrate temperature, and melting temperature of the deposited metal. Considering the melting temperature of metallic nickel (or nickel oxide) for described here sputtering process, we are in range of  $T_s/T_m$  equal to 0,17 (or 0,13). In that region, the model suggests, that texture should develop as narrow columns according to zone I or V-shaped columns, expanded during thickening for zone T. The cross-section of NiO 1  $\mu\text{m}$  thin films indicates that the width of columns does not exceed 200 nm for any deposited sample, thus the presence of rather narrow columns is in agreement with a standard growth model for low temperature deposition.

#### IV.2.3 Chemical composition of NiO thin films (XPS and EDX analysis)

The measurements of XPS were carried out with a Kratos Axis Ultra spectrometer using a monochromator Al K $\alpha$  source (1486.6 eV). The spectra were recorded for NiO thin films deposited at various oxygen contents for samples having 1  $\mu\text{m}$  thickness. The data were treated using Casa XPS software<sup>211</sup> after subtraction of Shirley background. The obtained spectra were recalibrated on binding energy coming from carbon pollution at 284.8 eV. The

quantitative specification was based on reference Ni and NiO samples defined by *Biesinger*<sup>212</sup>. The spectra of NiO were resolved for multiplets of 5 peaks attributed to Ni 2p<sub>3/2</sub> states and set of 3 peaks related to the oxygen. The analysed samples were air exposed before acquisition thus contribution of absorbed oxygen or water and formation of surface hydroxyl groups was considered. The envelop of the oxygen peaks was resolved for three peaks related to: O 1s component at a binding energy of 529.3 eV attributed to NiO framework; second peak at 531.1eV attributed to nickel hydroxide species; and the third of the smallest intensity due to absorbed water or oxygen. Figure 96 presents the fitting of XPS spectrum and Table 16 defines peak parameters in respect to the reference, for thin film of NiO deposited at 23.5% of oxygen content.

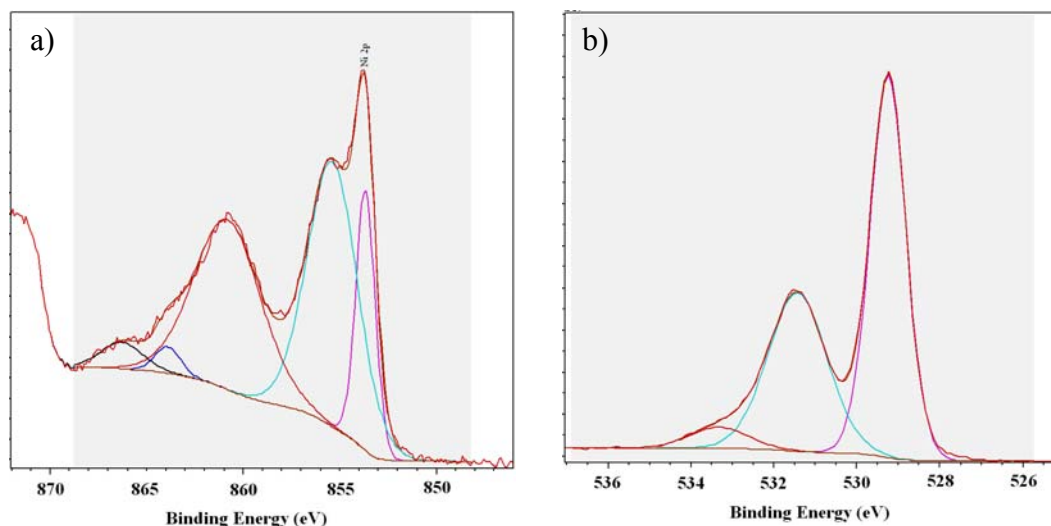


Figure 96.XPS spectra of NiO deposited at 23.5% of oxygen: a) fitting of Ni 2p<sub>3/2</sub> peaks, b) fitting of oxygen peaks.

The analyzed spectra do not show significant shift for Ni 2p<sub>3/2</sub> peaks in respect to the reference except for the sample which contained metallic nickel. The fitting of oxygen peaks leads to a maximal chemical shift up to 0.5eV. The details for other samples are given in appendix 3.

Table 16. Peak parameters for sample deposited at 23.5% of oxygen content and reference sample reported by *Biesinger*.

| Peak No. | Peak origin                             | Binding energy (eV) |           | FWHM (eV) |           | Intensity (%) |           |
|----------|-----------------------------------------|---------------------|-----------|-----------|-----------|---------------|-----------|
|          |                                         | Ref. NiO            | NiO 23.5% | Ref. NiO  | NiO 23.5% | Ref. NiO      | NiO 23.5% |
| 1        | Ni 2p <sub>3/2</sub>                    | 853.7               | 853.7     | 1.02      | 1.16      | 14.3          | 15.84     |
| 2        |                                         | 855.4               | 855.4     | 3.25      | 3.05      | 44.2          | 42.42     |
| 3        |                                         | 860.9               | 860.8     | 3.76      | 4.09      | 34.0          | 36.36     |
| 4        |                                         | 864.0               | 863.9     | 2.04      | 1.55      | 3.6           | 1.98      |
| 5        |                                         | 866.3               | 866.3     | 2.44      | 2.40      | 3.9           | 3.03      |
| 6        | O 1s                                    | 529.3               | 529.3     | 0.92      | 1.02      | -             | -         |
| 7        | Surf.OH                                 | 531.1               | 531.4     | 1.5       | 1.66      | 30            | -         |
| 8        | Abs. H <sub>2</sub> O or O <sub>2</sub> | 532.8               | 533.3     | 1.5       | 1.66      | -             | -         |

Due to the relative intensities of three oxygen peaks the elemental atomic composition was calculated for each of oxygen species and chemical formulas were proposed in Table 17. In all the examined samples the presence of hydroxide species is pronounced. The absorbed water /oxygen ratio contributes in a less significant manner.

Table 17. Surface chemical composition of NiO thin films deduced from XPS.

| Deposition conditions | Chemical composition                                                                                                                                 | Ni/O <sub>total</sub>             |
|-----------------------|------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------|
| 6.5 % O <sub>2</sub>  | Ni <sub>1</sub> O <sub>0.82</sub> OH <sub>0.98</sub> [(O <sub>2</sub> ) <sub>0.095</sub> or (H <sub>2</sub> O) <sub>0.19</sub> ](20at.% of Ni metal) | Ni <sub>1</sub> O <sub>1.99</sub> |
| 8.2 % O <sub>2</sub>  | Ni <sub>1</sub> O <sub>0.73</sub> OH <sub>0.28</sub> [(O <sub>2</sub> ) <sub>0.015</sub> or (H <sub>2</sub> O) <sub>0.03</sub> ]                     | Ni <sub>1</sub> O <sub>1.04</sub> |
| 9.9 % O <sub>2</sub>  | Ni <sub>1</sub> O <sub>0.9</sub> OH <sub>0.45</sub> [(O <sub>2</sub> ) <sub>0.03</sub> or (H <sub>2</sub> O) <sub>0.06</sub> ]                       | Ni <sub>1</sub> O <sub>1.41</sub> |
| 14.5 % O <sub>2</sub> | Ni <sub>1</sub> O <sub>0.84</sub> OH <sub>0.52</sub> [(O <sub>2</sub> ) <sub>0.05</sub> or (H <sub>2</sub> O) <sub>0.1</sub> ]                       | Ni <sub>1</sub> O <sub>1.46</sub> |
| 23.5 % O <sub>2</sub> | Ni <sub>1</sub> O <sub>0.83</sub> OH <sub>0.56</sub> [(O <sub>2</sub> ) <sub>0.04</sub> or (H <sub>2</sub> O) <sub>0.08</sub> ]                      | Ni <sub>1</sub> O <sub>1.47</sub> |

The sample deposited for the lowest oxygen content contains around 20 at% of metallic nickel. Both phases of nickel metal and nickel oxide were also confirmed by XRD (Figure 88d). It is believed that metallic sites are exposed to the surface leading to chemical reactions with the atmospheric gases. In that case surface terminated hydroxyl groups and absorbed water/oxygen are detected in the highest number compared to the other samples. The presence of OH groups can be explained by dissociative chemisorption of water on metallic surface<sup>213</sup>. For the case of samples deposited for higher oxygen contents, the

hydroxyl terminated groups are still present. The lowest value of OH was recorded for the sample deposited at 8,2 % of oxygen.

Additionally three different carbon signals were found on each examined sample. The first peak, at 284.8 eV is usually assigned to elemental carbon<sup>214</sup> and H<sub>3</sub>C-C. The second at 285.9 eV related to -C-O bonds<sup>215</sup>. The third at 288.3 eV attributed to carbon double bonded to oxygen atom<sup>215</sup> (C=O).

Since the XPS composition analysis concerns only the 10 first nanometers, the chemical composition was completed by EDX measurements (Figure 97) which provides an information coming from round 1  $\mu$ m below the surface (depending on the applied accelerating voltage). The EDX analysis indicates that the Ni/O ratio depends on the oxygen pressure. The less hydrolysed sample appears to be close to stoichiometric NiO. The increasing oxygen content during deposition process is associated to the formation of under stoichiometric Ni<sub>1-x</sub>O. For the sample prepared at the highest oxygen value the EDX analysis indicates the following formula: Ni<sub>0.87</sub>O. The same trend in stoichiometry was found by *Hotovy*<sup>194</sup> and reported nickel deficiency reaches up to Ni<sub>0.71</sub>O for amorphous nickel oxide thin films, which is in good agreement with our XRD measurements and the decrease of the crystallinity of the films elaborated with high oxygen content.

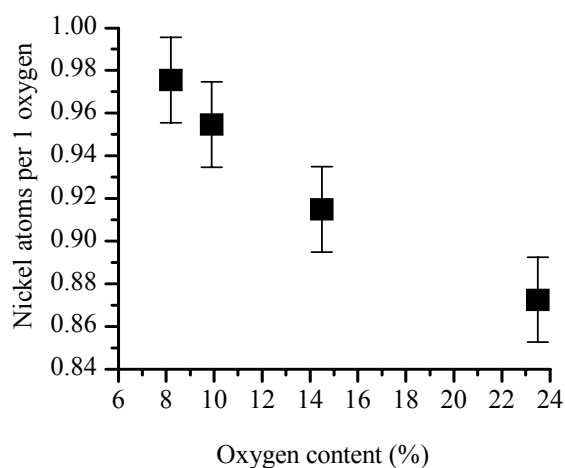


Figure 97. Stoichiometry of thin films NiO deduced from EDX

The experiments in a high vacuum have shown that perfect NiO structure displays no interaction with exposure to water or oxygen. However defective structure gives rise to surface interaction with oxygen and water dissociative chemisorption<sup>216</sup>. In fact in the literature, the interpretation of oxygen peak at 531,1 eV leads to some discussions and is

either attributed to defective structure of NiO<sup>217</sup> or to hydroxide terminated species<sup>218</sup>. Both of them are indeed lying at the same binding energy.

Ageing thin films for 6 months (not presented here), shows an evolution of absorbed oxygen species detected by XPS. The amount of hydroxyl groups significantly increases for all recorded samples. Also the presence of carbeneous species is unexpected. This leads to the conclusion that controlling the storage conditions is mandatory and better understanding of the process of surface interactions is required.

#### IV.2.4. Optical properties

For the NiO thin films on glass/FTO substrates deposited at different oxygen partial pressure, the optical transmittance spectra are shown (Figure 98), as a function of the wavelength. The analyzed samples have different thicknesses varying from around 80 nm following by 100nm, 250 nm up to 1  $\mu$ m. The transmittance of conductive glass substrate was subtracted from the spectra. As commonly observed the transmittance depends on the film thicknesses.

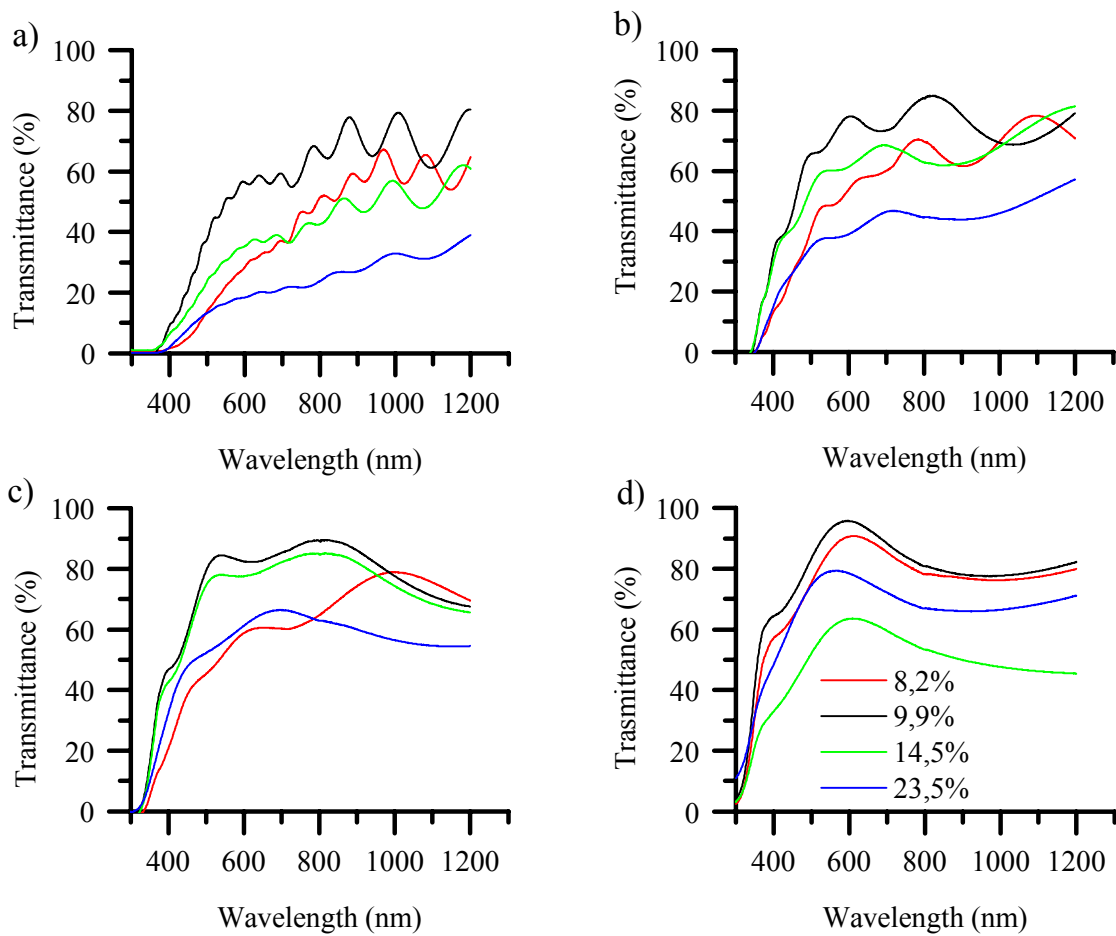


Figure 98. Transmittance spectra of the nickel oxide films deposited at different oxygen partial pressure a) 1  $\mu$ m b) 250 nm c) 100 nm and d) 80 nm.

Moreover optical properties of the NiO films were dependent primarily on  $O_2$  content in the sputtering gas. In the visible domain, the films become more transparent with increasing oxygen flow ratio, up to a maximum of transparency at 9.9% and then the transparency decreases. The same trend was found for samples deposited at 3 different discharge currents

and the maximum of transparency occurred at deposition conditions where the cathode voltage reaches an absolute maximum (Figure 87). As the thickness of the samples decreases, the absorption edge shifts towards shorter wavelengths. The shift of adsorption edge for lower thickness indicates an increase in the band gap energy, which can be attributed to smaller crystal domains and quantum size effect. Indeed, the crystal size is a result of the continuous evolution of the microstructure during film thickening (Figure 92 and Figure 93). For thinner films the onset of absorption edge becomes sharper, which can be attributed to the fact that smaller crystallites are deposited, and the scattered light is enhanced due to surface roughness<sup>219,220</sup>. In the most transparent zone, the samples are opaque and light brownish in colour. The maximum transmittance at 9.9% of oxygen may be related to both: the chemical composition of nickel oxide thin films, which are close to the stoichiometry (Figure 97) and to the good crystalline microstructure which leads to less defect and therefore this limits diffuse scattering. For high oxygen values, the colour of the NiO films was dark brown. In the literature, it is admitted that the coloration of NiO thin films is related to the presence of Ni<sup>3+</sup> ions. The trivalent ions are created in NiO when nickel vacancies exist in the structure. Each Ni<sup>+2</sup> vacancy is replaced by two Ni<sup>+3</sup> ions<sup>221</sup> to balance the net charge and these trivalent ions act as colour centres.

The fundamental absorption that corresponds to the electron excitation from the valence band to the conduction band can be used to determine the nature and value of the optical band gap. Assuming that the optical absorption coefficient  $\alpha$  is related to the extinction index  $k$  (complex part of the refraction index) it is possible to calculate  $\alpha$  from transmittance measurements with the following expression<sup>222</sup> :

$$\alpha = \frac{1}{d} \ln \frac{1}{T}$$

Where,  $d$  is the thickness of the nickel oxide film,  $T$  its transmittance. The relation between the absorption coefficient ( $\alpha$ ) and the incident photon energy ( $h\nu$ ) can be written as<sup>223</sup>:

$$(\alpha h\nu)^{\frac{1}{n}} = A_n (h\nu - E_g)$$

where  $A_n$  is a constant,  $E_g$  corresponds to the band gap of the material and  $n$  exponent depends on the type of transition.  $n=1/2, 2, 3/2, 3$  values correspond to the allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions, respectively. Figure 99 presents the variation of  $(\alpha h\nu)^2$  versus the photon energy ( $h\nu$ ) for nickel oxide films deposited at different oxygen partial pressure. The nature of plots suggests direct interband transition. The

optical band gap energy is evaluated by extrapolating the linear portion to zero absorption coefficient ( $\alpha=0$ ).

Among the films with the same thickness, the band gap reaches the highest value for the most transparent film, obtained at 9.9% of oxygen content. The increase in band gap energy was always related to the decrease in sample thickness. This increase is due to reduction of grain size with decreasing thickness, which is commonly observed in reactive sputtering process<sup>224</sup>. In the transparent region for samples at around 1  $\mu\text{m}$  thickness, the deduced band gap reaches the value of

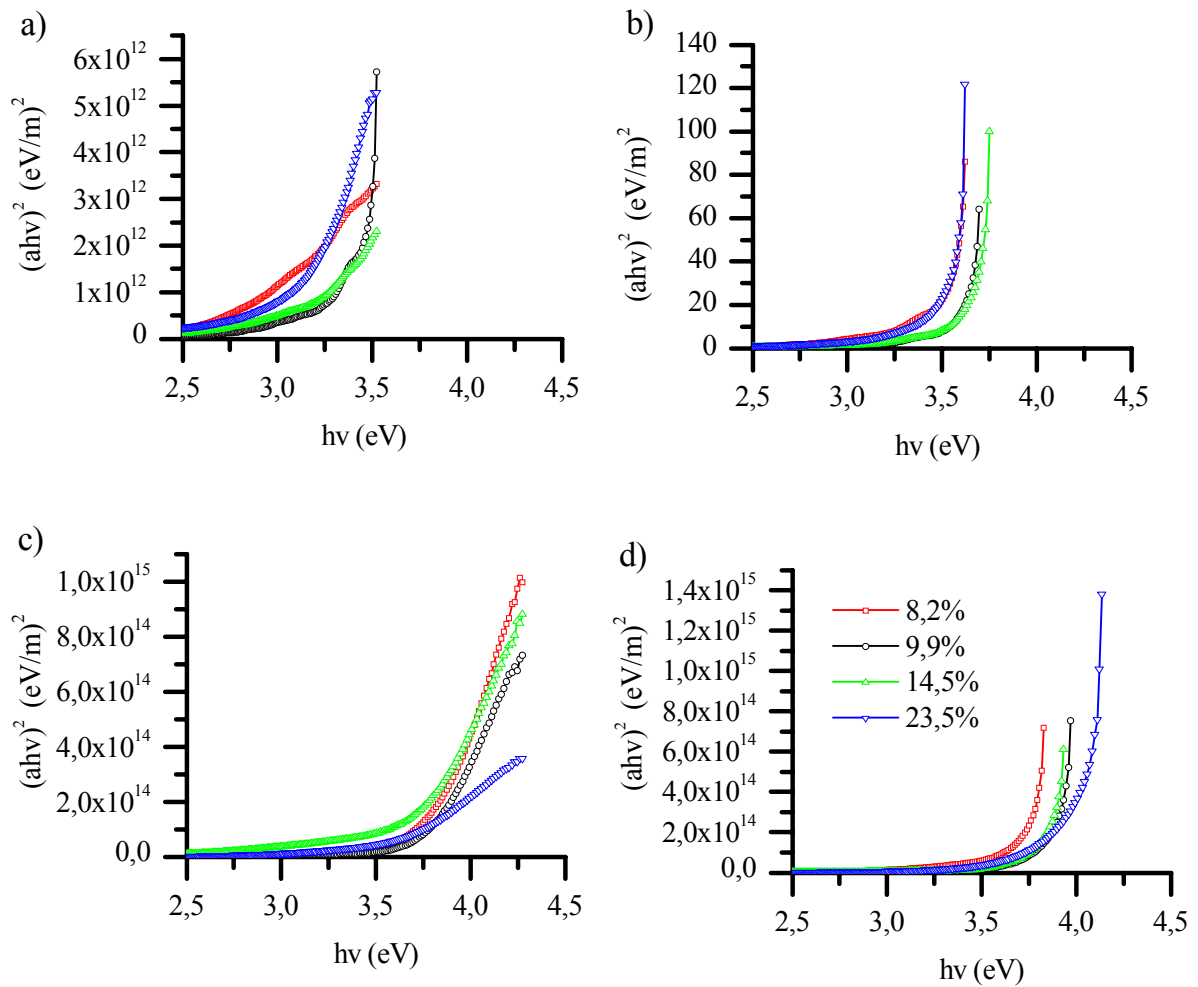


Figure 99. The dependence of  $(\alpha h\nu)^2$  on  $h\nu$  for nickel oxide films deposited at different oxygen partial pressure: a) 1  $\mu\text{m}$ , b) 250 nm, c) 100 nm, d) 80 nm.

$E_g=3.35$  eV, and for thickness of 100 nm increases up to  $E_g=3.76$  eV. For the thinnest samples some discrepancies were observed in a trend of band gap evolution. For the 80 nm



film deposited at 23.5% O<sub>2</sub>, the band gap is high and equal to 4.2 eV. Note that for samples at the very beginning of the growth, the crystal structure of samples was not well established. This surprisingly high band gap may be attributed to the presence of amorphous structure domains. In all other cases, the direct band gap energy varies from 3.2 to 3.8 eV, which is in good agreement with the results commonly reported (3.6–4.0 eV)<sup>225</sup>.

### IV.3 Comparison of results obtained by industrial reactor in SOLEMS

This paragraph gathers the description of PVD process for the industrial reactor in SOLEMS company. The electrical characteristic of discharge voltage will be discussed. The deposited samples will be characterized. The conclusions related to scaling up the deposition process will be given.

#### IV.3.1 Description of the PVD reactor and arrangement

Deposition of nickel oxide thin films has been done using an industrial reactor type MRC 903 (Material Research Corporation) (Figure 100). The volume of the chamber was approximately equal to 1 m<sup>3</sup>. Rectangular nickel target of purity 99.95% (HERAEUS) and dimensions of 12 cm by 38 cm. The target temperature was not controlled during sputtering. Direct current (DC) power supply of a maximum, operating in a constant current mode was used to sustain the plasma discharge. The system was supported by unbalanced magnetron. The distance between the target and a substrate was approximately 6 cm.

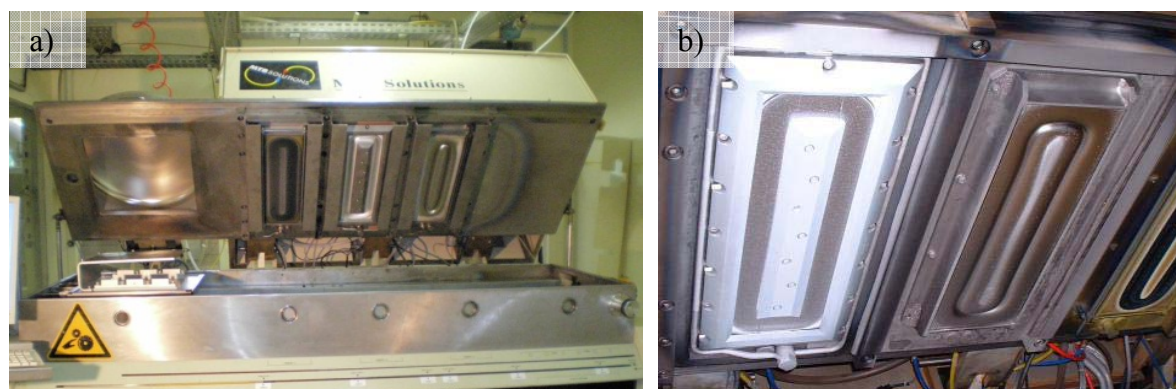


Figure 100. Image of PVD reactor in SOLEMS: a) view on the reactor, b) view of the target

Working gases: argon and oxygen were introduced into the reactor by mass flow controller. Resulting oxygen content was defined as  $O_2\% = V(O_2)/(V(O_2) + V(Ar))$ , where  $V(O_2)$  and  $V(Ar)$  are respectively: the flux of oxygen and argon, expressed in standard cubic centimetres per minute (sccm). The sample was fixed in a band sample support moving with a controlled speed. Therefore the homogeneity and thickness can be increased by moving the sample several times, in front of the target.

### IV.3.2 Cathode voltage as a feedback signal

Scaling-up of nickel oxide deposition by the industrial reactor was preceded by finding preliminary working conditions. Experimental data for laboratory-scale reactor at IMN showed that the evolution of process parameters and products are strictly related to the electrical signal from the cathode during the plasma discharge. The behaviour of cathode voltage was verified for three different discharge currents for increasing oxygen content in the mixture of working gases (Figure 101).

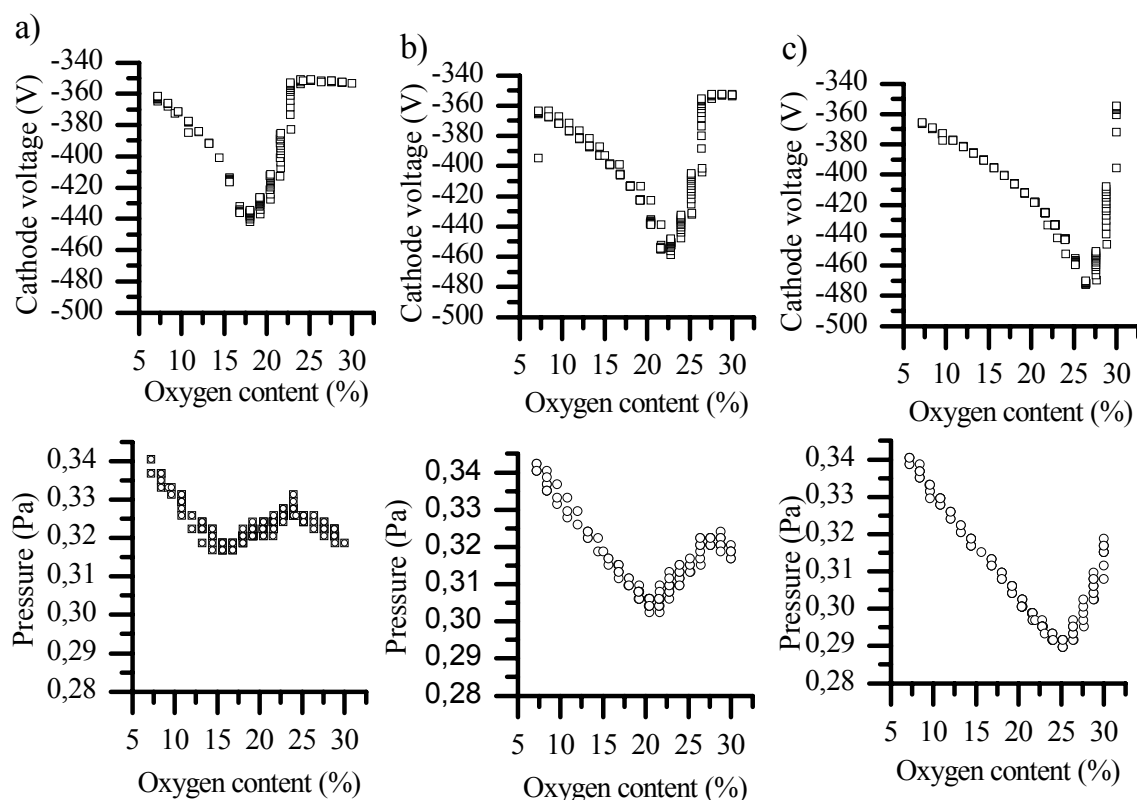


Figure 101. Cathode voltage and pressure characteristic during plasma discharge in SOLEMS reactor at discharge currents: a) 3.9 A, b) 4.9 A, c) 5.9 A

To achieve similar current densities on the target surface in the reactor at IMN and SOLEMS, the discharge current was recalculated in respect to the cathode surface area. The scaling-up factor is calculated to be 53.3.

The characteristic of discharge voltage for increasing oxygen content shows similar profile as it was observed for smaller, laboratory made reactor. For increasing oxygen content, the cathode voltage increases up to the maximum absolute value and then decreases to reach a plateau. The same behaviour was found when the discharge current was increased. The maximum of cathode voltage is shift towards the region of higher oxygen content and is higher in magnitude when the discharge current increases. For a similar current density, the shape of the discharge curve at SOLEMS is the same but the oxygen pressure required to reproduce the different 4 regimes is different than using the reactor at IMN. For the highest discharge current of 110 mA in the laboratory made reactor, the maximum of discharge voltage indeed occurs at 10% of oxygen in a gas mixture (Figure 87c). For the corresponding 5.9 A current in the reactor at SOLEMS, the maximum cathode voltage occurs at about 26% of oxygen. This shift may be attributed to the difference in residence time of gases in the reactor chamber, consequence of the high volume as compared to the flow rate. The experiments at SOLEMS were conducted at lower discharge pressure than at IMN. Table 18 shows the comparison of the parameters during plasma discharge. Besides, the way of introducing the working gases has been done in a different manner. At the IMN, the flux of inert argon was kept constant, while introducing reactive oxygen. At SOLEMS the total flux of gases was kept at a constant value and the introduction of oxygen induced a diminution of the argon flux.

Table 18. Comparison of the main parameters for both reactors with scaling up factor equal to 53.3

|                    | IMN                            | Scale-up factor x 53.3 | SOLEMS                             |
|--------------------|--------------------------------|------------------------|------------------------------------|
| Target surface     | Ø1.3 inch=8.56 cm <sup>2</sup> | 456 cm <sup>2</sup>    | 12cm x 38 cm = 456 cm <sup>2</sup> |
| Discharge current  | 110 mA                         | 5.86 A                 | 5.9 A                              |
| Tension            | 340 – 450 V                    | -                      | 354-470 V                          |
| Power              | 37.4 - 49.5 W                  | 1992- 2637 W           | 2089-2770 W                        |
| Discharge pressure | 0.45-0.51 Pa                   | -                      | 0.29-0.34 Pa                       |
| Oxygen content     | ≤ 30%                          | ≤ 30%                  | ≤ 30%                              |

The manner of introducing the working gases affects the evolution of the discharge pressure. Figure 101 shows the behaviour of the pressure for three different discharge currents for the industrial reactor. Initially the pressure starts to decrease linearly for increasing oxygen content, until it reaches the minimum. It is suspected that the total amount of introduced oxygen is efficiently consumed by the reaction on the cathode and/or chamber walls. Decrease in the discharge pressure in this region is a consequence of the lowering in argon flux. At the minimum of pressure, the consumption of oxygen reaches the highest value. Further increase in oxygen content leads to increase in discharge pressure until the cathode voltage reaches a plateau. This effect is due to poisoning of the target and lower consumption of reactive oxygen. However, from the moment the cathode reaches a plateau; the discharge pressure starts to decrease again. This last decrease in discharge pressure may be due to a significant degree to oxygen consumption by the chamber walls. Initially the discharge pressure is affected by the degree of reaction on the target surface. After target poisoning, the chamber walls contribute to the oxygen consumption in a remarkable manner.

The discharge voltage characteristic as well as the evolution of pressure leads to similar conclusions about the process when using laboratory reactor and an industrial one. The cathode voltage can be used as feed back signal for deposition of NiO. It allows one to monitor the target reaction degree and this signal also helps to find working conditions.

### IV.3.3 Morphology, crystal structure and optical properties of thin films NiO

Nickel oxide samples prepared using industrial reactor were deposited on clear glass (CORNING 1737) and conductive glass substrates (ASAHI 120 - FTO). The optical properties, crystal structure and morphology were analysed for samples deposited for various O<sub>2</sub>/Ar gas mixture. Table 19 presents the deposition conditions for three representative samples.

Table 19. Deposition parameters for NiO samples at 3 A and total pressure 0.333 Pa

| Substrate | Oxygen content (%) | Tension (V) | Scan speed (cm/min) | Thickness (nm) | Flux No.1 of argon (sccm) | Flux No.2 argon + oxygen (sccm) |
|-----------|--------------------|-------------|---------------------|----------------|---------------------------|---------------------------------|
| CORNING   | 15.6               | 300         | 3x5cm/min           | 1236           | 48                        | 52(Ar+30%O <sub>2</sub> )       |
| ASAHI 120 | 15.6               | 300         | 3x5cm/min           | 1200           | 48                        | 52(Ar+30%O <sub>2</sub> )       |
| CORNING   | 20.4               | 320         | 3x5cm/min           | 468            | 32                        | 68(Ar+30%O <sub>2</sub> )       |
| ASAHI     | 20.4               | 320         | 3x5cm/min           | 480            | 32                        | 68(Ar+30%O <sub>2</sub> )       |
| CORNING   | 27                 | 305         | 3x5cm/min           | 300            | 8                         | 92(Ar+30%O <sub>2</sub> )       |
| ASAHI     | 27                 | 305         | 3x5cm/min           | 380            | 8                         | 92(Ar+30%O <sub>2</sub> )       |

The products deposited in the industrial reactor do not show exactly the same trend than the one we observed using the laboratory reactor. The main difference may be attributed to difference in the crystallographic structure of the deposited thin films. Figure 102 shows the X-ray diagrams of as deposited thin films and their lattice distances are listed in table 20. For thin films deposited at the lowest oxygen content (15.6%), the X-ray diffraction pattern indicates the presence of two phases: metallic nickel and nickel oxide oriented along the [111] direction. Position of peak (111) is close to the reference of nickel powder (JCPDS-No.: 89-7130). For sample deposited at intermediate oxygen content (20.4%) the X-ray diffraction pattern shows nickel oxide phase with strong intensity of peak (111). In that case some differences were also observed in the X-ray diagrams for samples deposited on glass and conductive glass substrate. In a Bragg Brentano mode, only one (111) diffraction peak of NiO is detected on glass whereas for the same oxygen conditions, the sample deposited on ASAHI substrate shows both: strong (111) peak and weak intensity of (200) and (220).

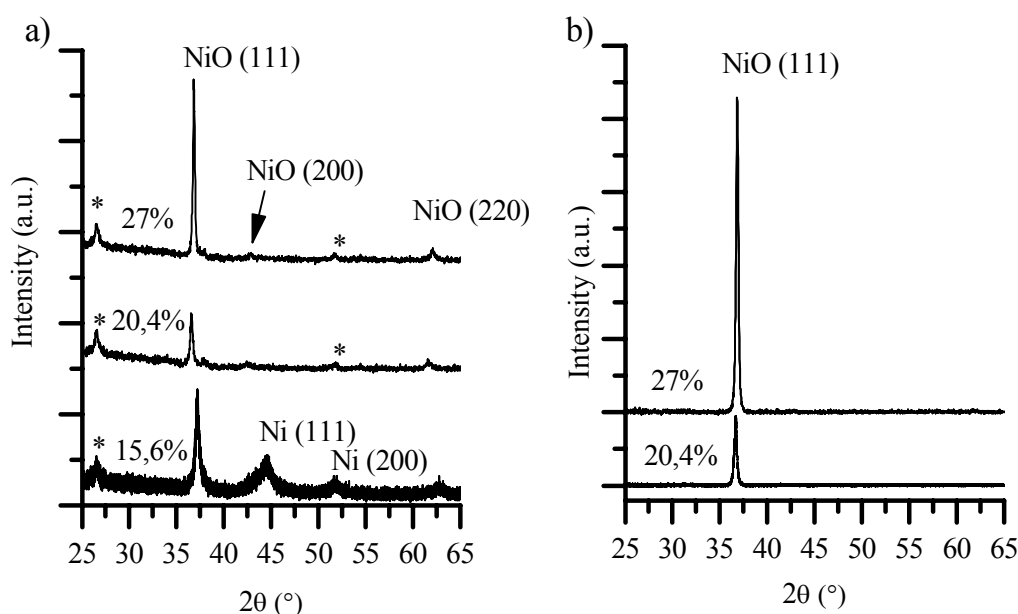


Figure 102. X-ray diagrams of NiO thin films deposited for various oxygen content: a) on conductive glass substrate (ASAHI 120), b) on glass (CORNING 1737). The peaks related to conductive glass substrate are marked by (\*).

Table 20. X-ray diffraction peak positions for samples deposited in SOLEMS and the expected distances for NiO and Ni metal.

| Substrate                   | Oxygen content (%) | Distance between atomic planes $d_{hkl}$ (Å) |         |         |
|-----------------------------|--------------------|----------------------------------------------|---------|---------|
|                             |                    | (111)                                        | (200)   | (220)   |
| ASAHI                       | 15.6               | 2.414                                        | -       | 1,478   |
| ASAHI                       | 20.4               | 2.453                                        | 2.125   | 1,502   |
| CORNING                     | 20.4               | 2.448                                        | -       | -       |
| ASAHI                       | 27                 | 2.437                                        | 2.107   | 1,493   |
| CORNING                     | 27                 | 2.437                                        | -       | -       |
| NiO ref. JCPDS No.: 89-7130 | -                  | 2.42164                                      | 2.09720 | 1.48294 |
| Ni ref. PDF No.: 00-0850    | -                  | 2.03400                                      | 1.76200 | 1.24600 |

These observations indicate that the crystallographic growth is affected by the nature of the substrate. For the first case, the deposition takes place on an amorphous substrate and in the second case the substrate is crystallized. For this deposition condition, the [111] growth direction is favoured. In the case of ASAHI substrate, the reconstruction of NiO lattice also occurs along the other crystallographic directions. For those samples, the peaks positions are shifted towards larger distances as it was observed for samples deposited using the laboratory reactor, when gas mixture was rich in oxygen. The NiO deposited at the highest value of oxygen (27%) in the target poisoned region, has a similar crystal structure growth as it was observed for the sample deposited at 20.4%. High orientation along [111] direction is pronounced together with weak (200) and (220) peaks for deposit on ASAHI substrate. However, the peak (111) is much more intense in respect to deposit at lower oxygen content and similar thickness. The possible reason for that can be related to the degree of crystallization for sample deposited at high oxygen content and arrangement of the columnar microstructure.

During the industrial process, the sample holder moves in a continuous manner with a minimum speed limitation of 5 cm/min, therefore deposition was repeated three times in order to obtain sample which are thick enough for characterization purpose. This way of deposition interrupts the crystal growth and its effect is noticeable in the cross-section views. The crystal growth is not continuous and secondary nucleation is forced.

The sample deposited at the lowest oxygen content is composed of 50 nm columns, growing in a low ordered manner (Figure 103). The surface morphology is composed of small crystals and spacing between the grains indicates a porous structure. The surface is not smooth due to many voids and spherical grains.

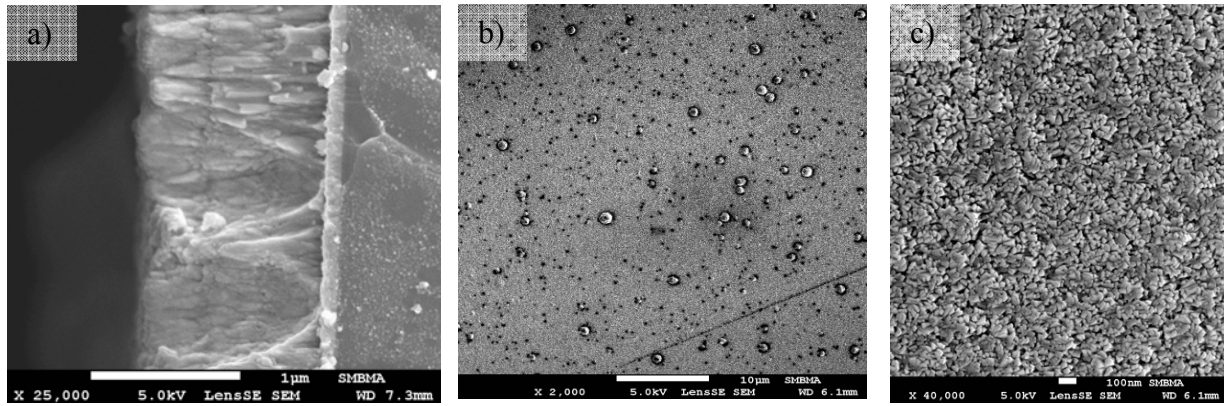


Figure 103. SEM image of sample deposited on ASAHI 120 at 15.6 % of oxygen content: a) cross-section (x 25 000), b) surface (x 2 000), c) surface (40 000)

The sample deposited in intermediate oxygen content grows in a columnar manner (Figure 104). However the surface grains size and columns width are different for CORNING and ASAHI substrate. Nickel oxide growing on ASAHI is composed of grains in-plane of about 50-100nm. The columns seem to have the dimensions equivalent to the surface grains. For sample deposited on CORNING substrate, the grains in-plane size, as well as columns width is notably smaller and in the order of 50 nm. The columnar structure is more ordered compared to the sample deposited at lower oxygen content. The secondary nucleation caused by the three-fold deposition process is pronounced. The grain boundaries between each of three layers of NiO are remarkable and columns do not grow in a continuous way along all the sample thickness.

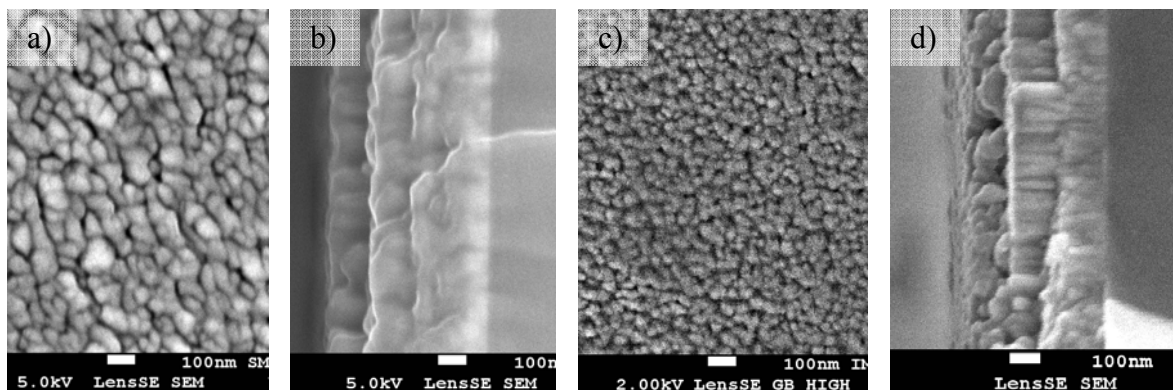


Figure 104. SEM images (x 40 000) of sample NiO deposited at 20.4% of oxygen: a) surface on ASAHI, b) cross-section on ASAHI, c) surface on CORNING, d) cross-section on CORNING.

Nickel oxide deposited at 27% of oxygen content shows similar dependence with substrate (Figure 105). The columns width and grain sizes are smaller on an amorphous

substrate. On conductive glass, the surface grains and columns size distribution lies between 30-100 nm. Thin films on CORNING substrate exhibit an uniform morphology with average surface grains size around 30 nm. In oxygen-rich region, the columnar structure is much more ordered compared to lower oxygen values. The three fold deposition process results in merged columns and secondary growth seems to take place on already existing grains.

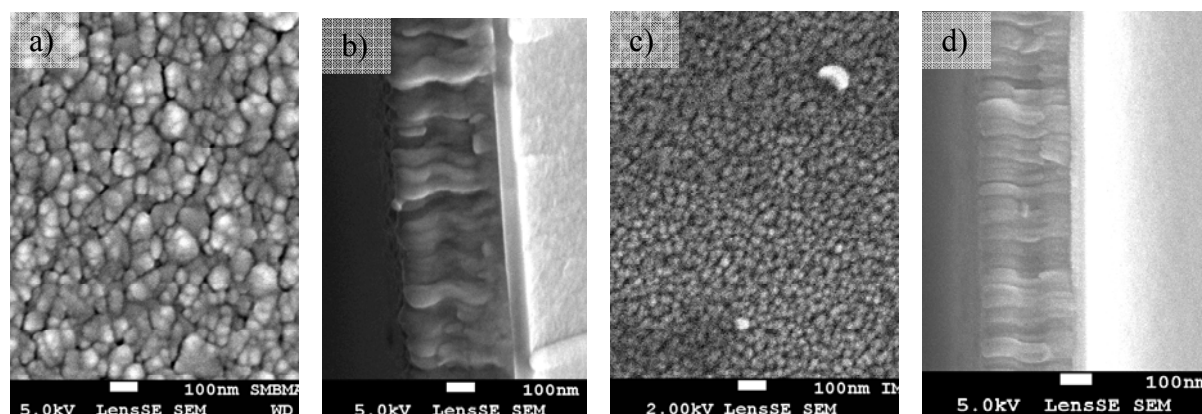


Figure 105. SEM images (x 40 000) of sample NiO deposited at 27 % of oxygen: a) surface on ASAHI, b) cross-section on ASAHI, c) surface on CORNING, d) cross-section on CORNING.

The comparison of surface morphology for samples deposited at 20.4 and 27% of oxygen leads to similar trend than those observed for deposition NiO using laboratory made reactor. The increase in oxygen flux is related to the formation of smaller grain. It might be due to the absorption of oxygen species at the grain boundaries and prohibition of grain expansion or coalescence during thickening.

Among three representative samples, the deposits carried out at 20.4 and 27% oxygen were found to be transparent. The sample deposited at 15% of oxygen contains a significant amount of metallic nickel and was opaque. Figure 106 presents the transmittance of NiO deposited on conductive glass substrate for 20.4 and 27% of oxygen.



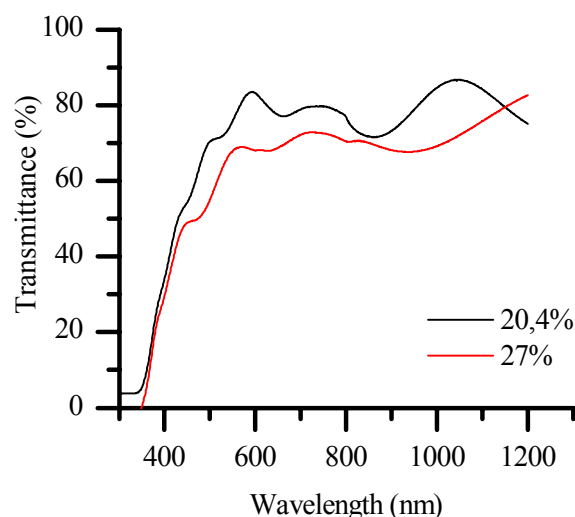


Figure 106. Transmittance of NiO thin films deposited on ASAHI substrate for 20.4 and 27% of oxygen in the mixture of working gases.

The sample deposited in oxygen-rich region (27%) is thinner of about 100 nm than the sample deposited at moderate oxygen value (20,4%). Despite a lower thickness the sample shows lower transmittance. The same trend concerning transparency was observed for samples using laboratory made reactor.

#### IV.3.4 Conclusions for scaling up the process

Deposition of nickel oxide using the industrial reactor results in the formation of polycrystalline thin films growing as columnar structures. Scaling-up the process by adjusting discharge current and total pressure of working gases, close to those optimised in the laboratory reactor does not lead to deposition of films, having the same preferential growth of the crystals. Applying comparable current densities and pressure of gases, results in the same characteristic of the cathode voltage. This indicates that physical and chemical processes taking place on the target surface are in close relation for both reactors. Using the laboratory scale reactor, the change of preferential orientation was achieved by manipulating the value of oxygen content in the mixture of working gases. The deposits elaborated in the industrial reactor were characterized by predominance of (111) preferential orientation independently from the content of reactive oxygen in the gas mixture. Since, the oxygen partial pressure was comparable and the cathode voltage response was similar for both reactors, this may lead to the following conclusion: the processes determining the preferential growth of thin films are

weakly dependent on reactions occurring on the target surface and oxygen content in the gas mixture. The origin of preferential growth is probably more influenced by other parameters which could not be precisely defined in presented here manuscript. There are few aspects which were not the same for both reactors. First, the distance between target and the substrate was 3 cm and 6 cm for laboratory-scale and industrial reactor respectively. Secondly, the magnetic field produced by magnetron for both reactors was not defined and compared. The thickness of both targets was different and could affect the gradient of magnetic field across the target-substrate distance (since the nickel metal is a ferromagnetic compound). From those reasons it is difficult to compare the energetic aspect of ionic species, which might contribute to structure growth. Despite few experiments were carried out in the industrial reactor, one can conclude that deposition rates and trend of transmittance for increasing oxygen content are similar to that observed for laboratory scale reactor.

#### **IV.4. Tests of NiO thin films obtained by PVD in a hybrid device**

##### **IV.4.1. Results of thin films prepared at IMN**

Thin films of NiO were deposited on conductive glass substrate (ITO) and tested as a p-type conducting layer in photovoltaic devices. The tests were carried out at the partnership unit (CEA-INES) by Solenn Berson. The performance of each cell were recorded for classic structure: glass/ ITO/ **NiO**/ P3HT:PCBM / Ca/Al and compared to the optimized system with PEDOT:PSS (poly 3,4-ethylenedioxythiophene: polystyrenesulfonate) as a hole transporting layer. The cells of total surface area of 0.25 cm<sup>2</sup> were tested under standard AM1.5 illumination at 40°C. The cell performance was examined for NiO thin films deposited at discharge current of 50 mA for various oxygen/argon gas mixtures and different film thicknesses. Table 21 presents the cell parameters after processing with 20 nm NiO thin layers. The samples deposited at low oxygen content (<6.5%) shows low performance in a photovoltaic device. The short-circuit current density ( $J_{sc}$ ), fill factor (FF) and open-circuit voltage ( $V_{oc}$ ) are probably affected because of the poor resistance of NiO layers. In fact, those samples were deposited in the cathode voltage zone 2 (Figure 86b) where NiO is expected to be stoichiometric (Figure 97). Due to the reported properties of nickel oxide, the stoichiometry is related to the absence of Ni<sup>+3</sup> ions which are responsible for p-type conduction mechanism, thus the low performance of solar cells can be explained by the low concentration of charge carriers. For samples deposited at higher oxygen values (>7.4%), an

abrupt increase in cell performance is observed. Those samples were deposited in the cathode poisoned regime, where under-stoichiometric  $\text{Ni}_{1-x}\text{O}$  is expected. For thin films deposited in between 7.4-9.9% of oxygen pressure, the cell performance is comparable. However it is still lower than the PEDOT:PSS reference system. The possible reasons may be related to the presence of hydroxyl species created on the oxide surface. Reported experiments have shown that NiO exposed to the atmosphere is covered rapidly by atmospheric pollutants. It was also observed that just after short exposure to the air the work function of NiO decreases rapidly<sup>226</sup>.

Table 21. Performance of organic solar cells with NiO buffer layer.

| NiO            | Thickness (nm) | Work function (eV) | $V_{oc}$ (mV) | $J_{sc}$ (mA/cm <sup>2</sup> ) | FF (%) | PCE (%) |
|----------------|----------------|--------------------|---------------|--------------------------------|--------|---------|
| 5.7            | 20             | 5.05               | 330.6         | 0.851                          | 32.26  | 0.09    |
| 6.5            | 20             | 5.04               | 303.6         | 6.08                           | 23.86  | 0.48    |
| 7.4            | 20             | 5.27               | 545.2         | 8.39                           | 47.78  | 2.18    |
| 8.3            | 20             | 5.27               | 545.5         | 8.19                           | 49.35  | 2.21    |
| 9.1            | 20             | 5.29               | 541.3         | 8.4                            | 48.24  | 2.19    |
| 9.9            | 20             | 5.24               | 532.7         | 8.35                           | 49.58  | 2.20    |
| Ref. PEDOT:PSS | -              | 5.1                | 556           | 9.76                           | 53.11  | 2.88    |

The measurements of work function (Table 21) indicate that for thin films used in the experiments the value is close the one of PEDOT:PSS. The hole transporting properties of NiO arise from the relative position of Fermi level versus valence band. For undoped nickel oxide the reported position of the Fermi level ( $E_f$ ) varies between 3.8 eV<sup>102</sup> and 5.4 eV<sup>227</sup>. The valence band (VB) sits at about 0.4 eV below the Fermi level<sup>229</sup>. In order to verify the conduction properties of NiO thin films, the difference between valence band and Fermi level was deduced from XPS spectra for films deposited at 110 mA and various oxygen contents (Table 22). The relative difference between VB and  $E_f$  was estimated for two cases. The first value was taken from the inflection point near the absorption edge. The second value was taken from the offset of the absorption edge.

Table 22. The difference in valence band and Fermi level for samples NiO deposited at 110 mA and various oxygen contents. Sample thicknesses around 1  $\mu\text{m}$ .

| Sample                  | $\Delta E (\text{VB}-E_f)$ (eV)<br>(inflection of absorption adge) | $\Delta E (\text{VB}-E_f)$ (eV)<br>(offset of absorption adge) |
|-------------------------|--------------------------------------------------------------------|----------------------------------------------------------------|
| NiO 8.2 % $\text{O}_2$  | 1.4                                                                | 0.85                                                           |
| NiO 9.9 % $\text{O}_2$  | 1.34                                                               | 0.80                                                           |
| NiO 14.5 % $\text{O}_2$ | 1.15                                                               | 0.60                                                           |
| NiO 23.5 % $\text{O}_2$ | 1.10                                                               | 0.55                                                           |

From these estimated relative differences in  $\text{VB}-E_f$  it is clearly observed that the Fermi level is closer to the VB than the conduction band, indicating that the conductivity is p-type. For samples deposited at higher oxygen values, the position of Fermi level is closer to the valence band. This observation is consisted with the improvement of cell performance. The estimated values indicate that p-type conductivity is enhanced for samples deposited in an oxygen-rich region. It is believed that the low-level performance of the cells is affected by some mismatch in electronic configuration.

The performance was also tested for 4 different thicknesses of NiO layers obtained in the oxygen-rich region. Table 23 summarizes the measured parameters. The experiments suggest that thickness of about 20 nm buffer layer seems to be an optimum among the tested ones. For 15 nm layers an unexpected decrease in PCE is observed. It is believed that at low thicknesses (<15nm), the coverage of NiO layer on ITO substrate is not really homogenous. At the very beginning of the crystal growth, the nucleated islands may form regions with thick and thin layers of nickel oxide, affecting the contact resistance<sup>228</sup>.

Table 23. Preformance of organic solar cells with NiO buffer layer for various thicknesses.

| NiO               | Thickness (nm) | Voc (mV) | Jsc<br>( $\text{mA}/\text{cm}^2$ ) | FF<br>(%) | PCE<br>(%) |
|-------------------|----------------|----------|------------------------------------|-----------|------------|
| 7.2%              | 5              | 484.3    | 9.60                               | 49.2      | 2.29       |
| 7.2%              | 10             | 518.0    | 8.58                               | 51.24     | 2.28       |
| 7.2%              | 15             | 427.6    | 7.13                               | 38.25     | 1.17       |
| 7.2%              | 20             | 519.3    | 8.26                               | 61.33     | 2.63       |
| Ref.<br>PEDOT:PSS | -              | 611      | 9.23                               | 66.19     | 3.73       |

For similar hybrid systems using NiO buffer layer in organic solar cells, *Irwin*<sup>229</sup> found the optimum of the thickness to be 10 nm, when NiO is obtained by pulsed laser deposition. In that case the PCE reaches 5.16% and excellent stability over 60 days of continuous illumination was observed. On another hand *Park*<sup>230</sup> found the best performance regarding

PCE of 2.8% at 3-5nm thin film and observed 50% of lost after 120 hours for magnetron radio frequency sputtering technique. The last reference is consistent with the results presented here. The initial PCE is in close value (2.6%) and the stability is comparable.

The long term stability of solar cells using NiO buffer layer was found to be rather poor. The experiments showed that the devices lose 20% of PCE after 24 hours of continuous illumination (Figure 107). Perhaps the reason of low efficiency and short time stability lies in the surface absorbed species or crystallite nature of the sample. However exposure of the sample to air cannot be simply avoided.

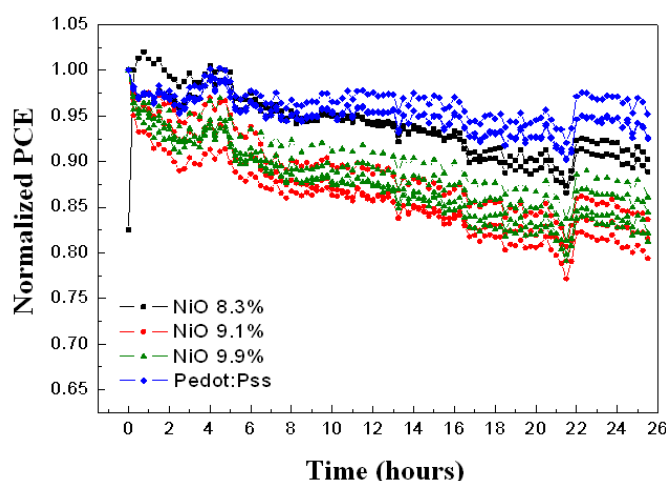


Figure 107. Normalized PCE of hybrid solar cells with 20 nm NiO buffer layer deposited for various oxygen contents.

Another reason for the low performance of the cells can be allotted to the crystalline nature of NiO thin films. In the reference article of *Irwin*<sup>229</sup>, XRD diagrams show well defined, sharp peaks of NiO films having about 77 nm thickness or cristllite size (using grazing angle mode). In the case of the thin films described here, the XRD signal in a grazing mode shows broad, not well pronounced peaks for samples of about 80 nm thickness (Figure 91a). This may lead to conclusions that samples described here have a poor crystallization degree. In addition in a hybrid photovoltaic device the film thickness is much lower than 80 nm and amorphous phase of NiO may be expected near the substrate interface. This can modify the electronic band positions, inter-face contacts and final performance of the photovoltaic devices.

#### IV.4.2. Results of thin films prepared by SOLEMS

The thin films of NiO prepared at SOLEMS were tested as photovoltaic component. The testing conditions were kept the same as described in the previous paragraph. The NiO buffer layers were deposited in the target poisoned region for two different thicknesses and two discharge currents (Table 24).

Table 24. Performance of organic solar cells with NiO buffer layer for various thicknesses

| Sample name    | NiO   | Discharge Current (A) | Thickness (nm) | Voc (mA/cm <sup>2</sup> ) | Jsc (%) | FF (%) | PCE (%) |
|----------------|-------|-----------------------|----------------|---------------------------|---------|--------|---------|
| SN0087         | 26.8% | 3                     | 10             | 431.1                     | 8.6     | 50.56  | 1.87    |
| SN0089         | 36.7% | 3                     | 10             | 415.6                     | 8.62    | 48.38  | 1.73    |
| SN0088         | 47.4% | 6                     | 10             | 416.8                     | 8.74    | 51.25  | 1.87    |
| SN0084         | 26.8% | 3                     | 20             | 414.4                     | 8.45    | 51.71  | 1.81    |
| SN0086         | 36.7% | 3                     | 20             | 360.0                     | 8.32    | 45.29  | 1.36    |
| SN0085         | 47.4  | 6                     | 20             | 404.2                     | 8.39    | 50.97  | 1.73    |
| Ref. pedot:pss | -     | -                     | -              | 611                       | 9.23    | 66.19  | 3.73    |

As it was observed in the previous section, the thin films do not significantly improve features. The PCE is lower than for cells deposited in the laboratory made reactor. The lost in PCE are caused by significantly lower Voc indicating an increase in series resistance.

### Conclusions of chapter IV

In the chapter the deposition of nickel oxide thin films was described for plasma reactive sputtering process using metallic nickel as a target, and oxygen/argon as a mixture of working gases. The deposition was carried out for two reactors having different dimensions. The process was controlled by monitoring the cathode voltage. For both reactors, the cathode voltage response had the same profile for changing the gas composition (oxygen/argon). The unique profile of cathode voltage was used to find working conditions for sputtering process when the discharge current was changed. The cathode voltage response was considered as an indication of the reaction degree between oxygen and the sputtered target. For the laboratory made reactor, using this diagnostic, the deposited thin films were found to grow with preferential orientations. Depending on the profile of cathode voltage the NiO thin films were

oriented along [111] or [002] crystallographic direction (description in a pseudo cubic lattice). As a consequence of preferential orientation, thin films thickening resulted in specific microstructure evolution. Additionally, profile of cathode voltage allowed us to tune the stoichiometry of the deposited thin films. The samples deposited at the absolute maximum of cathode voltage were close to theoretical stoichiometric NiO. For each particular discharge current, in the oxygen-rich region, the cathode voltage dropped down and under stoichiometric  $\text{Ni}_{1-x}\text{O}$  was deposited. The stoichiometry of NiO directly influences the optical properties of thin films. The samples, elaborated at conditions where NiO was close to stoichiometry, were characterized by the highest transparency. The samples deposited in oxygen-rich region, where NiO structure showed nickel atoms deficiencies, lead to the drop in light transmittance. The experiments elaborated using industrial reactor showed, that crystallographic growth of NiO thin films is not only related to the cathode voltage profile. The deposited thin films were characterized by growth along the [111] crystallographic direction independently from the cathode voltage profile. In fact deposition conditions were not exactly the same as for the laboratory made reactor. The crystallographic growth of NiO thin films is probably related to energetic aspect of adatom particles. The main difference between the two reactors was: target to substrate distance and magnetic field of the magnetrons. Those two parameters significantly affect the energetic aspect of adatoms. Besides the crystallographic growth of NiO structure, the samples deposited in an industrial reactor followed the trend in transparency. In oxygen-rich region, the samples showed lower transmittance. The tests of deposited thin films as a buffer layer in organic photovoltaic device proved that defective NiO can acts as p-type charge transporting layer. The best performance were recorded for nickel oxide thin films deposited in the oxygen-rich conditions. For the optimal NiO thin films, the power conversion efficiency was in the range of 2,6%. However, the lifetime of the devices still remained limited. The fabricated cells showed 20% loss in power conversion efficiency after 24 hours of continuous illumination. It is believed, that surface of as-deposited thin films exhibits strong interactions with the atmospheric pollutants. Those surface absorbed species can change the electronic band configuration of as-deposited NiO and affect charge transport properties of thin films.

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## General conclusions

The concept of organic solar cells having inorganic semiconductive oxides is a very promising solution to extend the lifetimes of those devices. The manuscript presented an opportunity of using titanium dioxide and nickel oxide, which act as a selective charge transporting layers for organic photovoltaic devices. The theoretical electronic band configuration of those oxides matches well with the HOMO and LUMO levels of organic active layer P3HT:PCBM. The good alignment of energy level is a crucial factor for efficient charge collection on the metallic electrodes. Also band gap energy of those semiconductors is sufficiently large and gives an opportunity for incorporation of NiO and TiO<sub>2</sub> on the front transparent electrode without significant absorption loss of the visible part of solar spectrum.

The manuscript presented synthesis and deposition techniques of both semiconductive oxides. The titanium dioxide was elaborated by chemical solution processing in organic solvents. The nickel oxide thin-films were deposited by two methods: chemical solution process and physical vapor deposition. First, chemical solution deposition involved synthesis of nickel hydroxide which requires additional thermal annealing to form nickel oxide. The second processing of nickel oxide thin films was elaborated by reactive sputtering. The physical properties of thin-films depend strongly on the choice of the elaborating process. Consequently, the efficiency of organic solar cells integrating TiO<sub>2</sub> and NiO as interfacial layers was affected.

Titanium dioxide thin films were obtained via sol-gel method using hydrolysable titanium precursor "Ti<sub>8</sub>O<sub>12</sub>". Three types of formulation were proposed to stabilize the TiO<sub>2</sub> nanocrystallites in colloidal solutions while respecting the specifications of the printing with ink jet..

The first formulation involved the use of solvent mixture of water and propylene carbonate. Those solvents at the temperature of 120°C and in the presence of Ti<sub>8</sub>O<sub>12</sub> precursor react with each other to form 1,2-propanediol. The solvents reaction is important from three aspects. First: it allows preparing colloidal solutions with desired viscosity in one step process. Second: the solvent reaction affects the stability of colloidal particles. Third: it permits to eliminate the water from the colloidal solution. The presence of water is unwanted because of ink-jet printing recommendations as well high surface tension, which could affect wetting properties of colloids. The best conditions were found for a solvent mixture of  $R=[\text{H}_2\text{O}]/[\text{PC}]=0.712$ . For that ratio of solvents, the colloidal solution has the recommended

value of viscosity and is composed of monodispersed nanoparticles. For different ratio of solvent mixture  $R=[\text{H}_2\text{O}]/[\text{PC}]$  the colloidal particles were aggregated and the physical parameters of the solution do not match to requirements of the ink-jet printing. Independently from the ratio of  $R=[\text{H}_2\text{O}]/[\text{PC}]$ , the primary crystals of colloidal particles were found to be in range of 5nm and crystallize as anatase form of  $\text{TiO}_2$ . Due to small size of particles, the colloids were sensitive to the exposure of ultraviolet light. Extended illumination by UV, without the oxygen contact, resulted in improvement in dispersion degree of aggregated particles.

The second chemical formulation for synthesis of colloidal solution  $\text{TiO}_2$  employed the propylene carbonate, 1,2-propanediol and water as solvents. In this formulation the propylene carbonate reacts with water and the presence of 1,2-propanediol allows to obtain the well dispersed colloids in a wider range of  $R=[\text{H}_2\text{O}]/[\text{PC}]$  comparing to the first formulation of the synthesis. However, this setup of the synthesis limits the reaction between water and propylene carbonate. The residual water might affect the wetting abilities of prepared colloidal solutions.

The third formulation for the synthesis of colloidal  $\text{TiO}_2$  involves the use of water and 1,2-propanediol. This chemical composition governs the high dispersion of colloidal particles and size control of primary crystals. For low  $[\text{H}_2\text{O}]/[\text{PC}]$ , the synthesized particles are in range of 2nm. For higher ratio of  $[\text{H}_2\text{O}]/[\text{PC}]$ , the colloidal particles are not homogenous in size with a diameter range from 4 to 10 nm.

Summarizing the role of each solvent for the synthesis of colloids, the following conclusions can be given. Water is a high dielectric solvent and is necessary to dissolve the “ $\text{Ti}_8\text{O}_{12}$ ” crystals for the further hydrolysis of titanium precursor. The amount of water affects the crystal growth phenomena. The hydrolysis rate of titania precursor is of order of seconds or minutes when the pH is equal to four, closed to the PCN value. As consequence, an excess of water favors the formation of amorphous precipitate. The role of propylene carbonate is to eliminate the water from the colloidal solution via ester hydrolysis reaction that conduct to the 1,2-propanediol formation. Propylene carbonate impacts to viscosity of colloidal solutions. 1,2-propanediol is a dispersive agent for freshly nucleated particles and governs long term stability of colloids at elevated temperatures (up to  $120^\circ\text{C}$ ).

The colloids of  $\text{TiO}_2$  prepared in described processes were used for elaboration of thin films for organic solar cells. The solutions were deposited on the front transparent electrode and were tested in inverted configuration of the solar device. The best results were obtained for the solution  $R=[\text{H}_2\text{O}]/[\text{PC}]=0.712$ . The organic solar cell has shown the initial power

conversion efficiency of 3.7% with a loss of 17% after 6500 hours of continuous illumination. The deposition of  $\text{TiO}_2$  interfacial layer validates the concept of stable organic solar cells.

The colloidal solution  $R=[\text{H}_2\text{O}]/[\text{PC}]=0.712$  was used to elaborate the thin films by ink-jet printing technique. The process resulted in homogenous deposits along entire substrate. The physical parameters of the solvents were properly adjusted for the reliability of the printing process. The preliminary experiments have shown the compatibility of colloids with the industrial equipment; however the slight acidic properties might cause problems arising from corrosion phenomena.

Nickel oxide thin films were prepared by chemical solution processing via acid-base hydrolysis of nickel nitrate or nickel chloride with tetramethylammonium hydroxide. As a solvent for the reactions the 1,2-propanediol and ethylene glycol were used. The acid-base exchange allows obtaining the nickel hydroxide colloidal particles. Dependently from the temperature of reaction the hydroxides have a different stoichiometry. The synthesis carried out at room temperature results in formation of  $\text{Ni}(\text{OH})_{1.7}\text{Cl}_{0.3}$  and  $\text{Ni}(\text{OH})_{1.67}(\text{NO}_3)_{0.33}$ , for hydrolysis of nickel chloride and nickel nitrate, respectively. The synthesis at  $70^\circ\text{C}$  results in formation of  $\text{Ni}(\text{OH})_{1.82}(\text{NO}_3)_{0.18}$ , for hydrolysis of nickel nitrate. As prepared, colloids were purified from by-products by sedimentation using acetone and redispersion in 1,2-propanediol. The procedure allows obtaining a stable colloidal solutions of nickel hydroxides, which after deposition crystallize in a form of  $\alpha\text{-Ni}(\text{OH})_2$ . The synthesis carried out in different temperatures affects the size of hydroxide colloidal particles. The colloids prepared at room temperature, after redispersion were composed of particles having 9 nm. The synthesis at  $70^\circ\text{C}$  consequence in larger particles with the average diameter of 80 nm.

In order to transform the nickel hydroxide onto nickel oxide the two thermal treatments were applied. First one at  $120^\circ\text{C}$  in order to remove the excess of solvent and at second one at  $400^\circ\text{C}$  to dehydrate the hydroxides. The XPS analysis has shown that the nickel oxide prepared from  $\text{Ni}(\text{OH})_{1.82}(\text{NO}_3)_{0.18}$  precursor contain nickel carbide pollutions. The XRD suggested the presence of metallic nickel impurities in the case of nickel oxide, prepared from  $\text{Ni}(\text{OH})_{1.67}(\text{NO}_3)_{0.33}$ . The synthesis of nickel hydroxide in glycol medium causes unexpected chemical reactions. The reaction arises from reductive nature of glycol molecules in respect to nickel compounds.

As in the case of synthesis of  $\text{TiO}_2$  colloids, the 1,2-propanediol was found to be effective solvent for stabilization of colloidal nickel hydroxide particles.

The nickel hydroxide colloidal solutions were used for elaboration of organic solar cells in a classic architecture. However, the solar cells have shown unsatisfactory results. The best achieved power conversion efficiency was in range of 1%. The low performance can be a result of the pollutants, which were found on the particle surface. Despite possible nickel carbide and metallic nickel, the surface of as prepared nickel oxide particles was affected by the presence of carbonous species. Another, possible explanation can be related to semiconductive properties of as prepared nickel oxides. The bibliographic reports suggest that nickel oxide loses its p-type semiconductive character and become insulator, when heated at elevated temperatures. Perhaps, the thermal annealing process has to be optimized in order to control semiconductive properties of NiO.

The nickel oxide thin films were deposited by reactive sputtering of nickel target with oxygen and argon as a mixture of working gases. The deposition was carried out for three different discharge currents. The control of the sputtering process was achieved by analysis of the discharge voltage. For different values of discharge current, the cathode signal gave the characteristic response when increasing the oxygen partial pressure. Using this diagnostic, the deposited thin films were found to grow with preferential orientations. Depending on the profile of cathode voltage the NiO thin films were oriented along [111] or [002] crystallographic direction. As a consequence of preferential orientation, thin films thickening resulted in specific microstructure evolution. The cathode voltage diagnostic was also used to control the stoichiometry of  $\text{Ni}_{1-x}\text{O}$  thin films and optical properties.

The discharge voltage diagnostic was applied to control the sputtering process for an industrial reactor in SOLEMS. The increase of oxygen partial pressure in the mixture of working gases resulted in the similar cathode voltage signal. However, crystallographic growth of the NiO structure was independent from the electrical diagnostic. Deposited thin films were always oriented along [111] crystallographic direction.

The thin films prepared by reactive sputtering process were used to elaborate the organic solar cells in classic architectures. The cells shown very low performance for thin films deposited at relatively low and moderated values of oxygen partial pressure. The performance of solar cells was improved significantly when films were deposited at high oxygen partial pressures. For those conditions nickel oxide is expected to be non-stoichiometric and have a p-type semiconductive character. The highest power conversion efficiency values were achieved for deposits having a thickness of 20nm. The power conversion efficiencies reached 2.6% and 1.8% for laboratory scale and industrial reactor, respectively. However,

these cells undergo rapid degradation and lose more than 20% of initial efficiency within 20 hours of continuous illumination. The origin of rapid damage may be due surface absorbed species. The XPS analysis showed the presence of nickel hydroxide, water and carbonous species. Recent literature reports have shown that electronic properties of NiO are strongly affected by exposure to atmospheric pollutants. The presented here solar cells were assembled at least few days after the sample preparation and not special care was given to the protection of samples from atmospheric pollutants. The control of surface treatment and sample protection might be the key for a stable and efficient organic solar cells having NiO charge transporting layer.





## Appendix 1

Table 1. XPS analysis for Sample  $\text{Ni(OH)}_{1.7}\text{Cl}_{0.3}$

| Element              | Origin             | Peak position (eV) | FWHM (eV) | Stoichiometry per Ni atom |
|----------------------|--------------------|--------------------|-----------|---------------------------|
| Ni 2p <sub>3/2</sub> | hydroxide          | 856.3              | 2.243     | -                         |
|                      |                    | 862.1              | 4.588     | -                         |
|                      |                    | 855.5              | 1.500     | -                         |
|                      |                    | 858.3              | 1.400     | -                         |
|                      |                    | 861.1              | 1.196     | -                         |
|                      |                    | 867.1              | 3.300     | -                         |
| O 1s                 | hydroxide          | 531.9              | 1.62414   | 3.02                      |
|                      | unspecified        | 533.4              | 1.64243   | 0.32                      |
| C 1s                 | CH <sub>3</sub> -C | 284.8              | 1.19815   | 5.95                      |
|                      | C-O                | 286.0              | 2.02439   | 1.90                      |
|                      | C=O                | 288.8              | 1.29345   | 0.53                      |
| Cl 1s                | -                  | 198.8              | 1.39392   | 0.68                      |
|                      | -                  | 200.4              | 1.37537   | 3.02                      |

Table 2. XPS analysis for Sample  $\text{Ni(OH)}_{1.67}(\text{NO}_3)_{0.33}$

| Element              | Origin             | Peak position (eV) | FWHM (eV) | Stoichiometry per Ni atom |
|----------------------|--------------------|--------------------|-----------|---------------------------|
| Ni 2p <sub>3/2</sub> | hydroxide          | 855.68             | 2.795     | -                         |
|                      |                    | 861.48             | 4.828     | -                         |
|                      |                    | 854.88             | 1.287     | -                         |
|                      |                    | 857.68             | 1.750     | -                         |
|                      |                    | 860.48             | 1.300     | -                         |
|                      |                    | 866.48             | 3.200     | -                         |
| O 1s                 | hydroxide          | 531.02             | 1.667     | 2.00                      |
|                      | unspecified        | 532.28             | 2.000     | 0.56                      |
| C 1s                 | CH <sub>3</sub> -C | 284.41             | 1.369     | 0.93                      |
|                      | C-O                | 285.62             | 2.000     | 1.31                      |
|                      | C=O                | 288.03             | 1.640     | 0.54                      |
| N 1s                 | TMA <sup>+</sup>   | 402.74             | 1.324     | 0.04                      |

Table 3. XPS analysis for sample  $\text{Ni}(\text{OH})_{1.82}(\text{NO}_3)_{0.18}$ 

| Element              | Origin                       | Peak position (eV) | FWHM (eV) | Stoichiometry per Ni atom |
|----------------------|------------------------------|--------------------|-----------|---------------------------|
| Ni 2p <sub>3/2</sub> | hydroxide                    | 855.68             | 2.600     | -                         |
|                      |                              | 861.48             | 4.800     | -                         |
|                      |                              | 854.88             | 1.200     | -                         |
|                      |                              | 857.68             | 1.650     | -                         |
|                      |                              | 860.48             | 1.200     | -                         |
|                      |                              | 866.48             | 3.100     | -                         |
| O 1s                 | hydroxide                    | 531.07             | 1.804     | 1.84                      |
|                      | unspecified                  | 532.29             | 2.000     | 0.37                      |
| N 1s                 | nitrides                     | 398.01             | 2.000     | 0.01                      |
|                      | NH <sub>3</sub>              | 399.75             | 2.000     | 0.02                      |
|                      | TMA <sup>+</sup>             | 402.61             | 2.000     | 0.04                      |
|                      | NO <sub>2</sub> <sup>-</sup> | 405.63             | 1.253     | 0.006                     |
| C 1s                 | CH <sub>3</sub> -C           | 284.40             | 1.722     | 0.82                      |
|                      | C-O                          | 285.66             | 1.665     | 0.37                      |
|                      | C=O                          | 288.04             | 1.820     | 0.46                      |
| Cl 1s                | -                            | 198.07             | 1.614     | 0.03                      |
|                      | -                            | 199.75             | 1.550     |                           |

## Appendix 2

Table 4. XPS analysis for NiO from  $\text{Ni}(\text{OH})_{1.7}\text{Cl}_{0.3}$ 

| Element              | Origin                                 | Peak position (eV) | FWHM (eV) | Stoichiometry per Ni atom |
|----------------------|----------------------------------------|--------------------|-----------|---------------------------|
| Ni 2p <sub>3/2</sub> | NiO                                    | 853.5              | 1.087     | -                         |
|                      |                                        | 855.2              | 3.206     | -                         |
|                      |                                        | 860.7              | 3.759     | -                         |
|                      |                                        | 863.8              | 1.900     | -                         |
|                      |                                        | 866.2              | 2.423     | -                         |
| O 1s                 | NiO                                    | 529.2              | 1.025     | 0.72                      |
|                      | hydroxide                              | 530.8              | 1.440     | 0.32                      |
|                      | abs.H <sub>2</sub> O or O <sub>2</sub> | 532.6              | 2.007     | 0.05                      |
| C 1s                 | CH <sub>3</sub> -C                     | 284.8              | 1.217     | 0.28                      |
|                      | C-O                                    | 285.6              | 1.637     | 0.07                      |
|                      | C=O                                    | 288.0              | 2.005     | 0.05                      |
| Cl 1s                | -                                      | 198.0              | 1.250     | 0.02                      |
|                      | -                                      | 199.7              | 1.222     | 0.003                     |

Table 5. XPS analysis for NiO from  $\text{Ni}(\text{OH})_{1.67}(\text{NO}_3)_{0.33}$ 

| Element              | Origin             | Peak position (eV) | FWHM (eV) | Stoichiometry per Ni atom |
|----------------------|--------------------|--------------------|-----------|---------------------------|
| Ni 2p <sub>3/2</sub> | NiO                | 853.23             | 1.248     | -                         |
|                      |                    | 854.94             | 3.300     | -                         |
|                      |                    | 860.38             | 3.793     | -                         |
|                      |                    | 863.48             | 1.971     | -                         |
|                      |                    | 865.86             | 2.502     | -                         |
| O 1s                 | NiO                | 528.95             | 1.048     | 0.63                      |
|                      | hydroxide          | 530.89             | 1.373     | 0.28                      |
| C 1s                 | CH <sub>3</sub> -C | 284.7              | 1.660     | 0.09                      |
|                      | C-O                | 286.09             | 2.000     | 0.02                      |
|                      | C=O                | 288.34             | 1.592     | 0.04                      |

Table 6. XPS analysis for NiO from  $\text{Ni}(\text{OH})_{1.82}(\text{NO}_3)_{0.18}$ 

| Element              | Origin             | Peak position (eV) | FWHM (eV) | Stoichiometry per Ni atom |
|----------------------|--------------------|--------------------|-----------|---------------------------|
| Ni 2p <sub>3/2</sub> | NiO                | 854.02             | 1.300     | 0.56                      |
|                      |                    | 855.73             | 3.101     |                           |
|                      |                    | 861.17             | 3.434     |                           |
|                      |                    | 864.27             | 2.098     |                           |
|                      |                    | 866.65             | 2.915     |                           |
| Ni 2p <sub>3/2</sub> | hydroxide          | 853.64             | 2.499     | 0.44                      |
|                      |                    | 859.44             | 4.721     |                           |
|                      |                    | 852.84             | 1.101     |                           |
|                      |                    | 855.64             | 1.501     |                           |
|                      |                    | 858.44             | 1.191     |                           |
|                      |                    | 864.44             | 2.800     |                           |
|                      | unspecified        | 528.91             | 1.339     | 0.52                      |
|                      | unspecified        | 529.87             | 1.003     | 0.16                      |
|                      | hydroxide          | 531.00             | 1.943     | 0.27                      |
|                      | C-N                | 282.69             | 1.187     | 0.01                      |
|                      | CH <sub>3</sub> -C | 284.80             | 1.999     | 0.13                      |
|                      | C=O                | 287.97             | 2.000     | 0.03                      |
| Cl 1s                | -                  | 198.26             | 1.767     | 0.02                      |
|                      | -                  | 199.87             | 1.789     |                           |

### Appendix 3

Table 7. XPS analysis for NiO deposited at 9.9% of oxygen.

| Element              | Origin                                 | Peak position (eV) | FWHM (eV) | Intensity (%) |
|----------------------|----------------------------------------|--------------------|-----------|---------------|
| Ni 2p <sub>3/2</sub> | NiO                                    | 853.8              | 1.10      | 17            |
|                      |                                        | 855.6              | 3.17      | 44            |
|                      |                                        | 861.0              | 3.82      | 33            |
|                      |                                        | 864.1              | 1.82      | 3             |
|                      |                                        | 866.5              | 2.24      | 3             |
| O 1s                 | NiO                                    | 529.6              | 1.05      | -             |
|                      | hydroxide                              | 531.5              | 1.77      | -             |
|                      | abs.H <sub>2</sub> O or O <sub>2</sub> | 533.1              | 1.77      | -             |
| C 1s                 | CH <sub>3</sub> -C                     | 284.8              | 1.10      | -             |
|                      | C-O                                    | 285.7              | 1.86      | -             |
|                      | C=O                                    | 288.3              | 1.89      | -             |

Table 7. XPS analysis for NiO deposited at 14,5% of oxygen.

| Element              | Origin                                 | Peak position (eV) | FWHM (eV) | Intensity (%) |
|----------------------|----------------------------------------|--------------------|-----------|---------------|
| Ni 2p <sub>3/2</sub> | NiO                                    | 853.7              | 1.09      | 16            |
|                      |                                        | 855.4              | 3.16      | 43            |
|                      |                                        | 860.8              | 3.89      | 34            |
|                      |                                        | 863.9              | 1.80      | 3             |
|                      |                                        | 866.3              | 2.34      | 3             |
| O 1s                 | NiO                                    | 529.4              | 1.01      | -             |
|                      | hydroxide                              | 531.4              | 1.88      | -             |
|                      | abs.H <sub>2</sub> O or O <sub>2</sub> | 533.2              | 1.88      | -             |
| C 1s                 | CH <sub>3</sub> -C                     | 284.8              | 1.13      | -             |
|                      | C-O                                    | 285.8              | 1.91      | -             |
|                      | C=O                                    | 288.3              | 2.05      | -             |