

ON TITANIUM OXIDE SPRAY DEPOSITED THIN FILMS FOR SOLAR CELLS APPLICATIONS

Ignas VAICIULIS^{1,2}, Mihaela GIRTAN^{1,2}, Anca STANCULESCU³, Liviu LEONTIE⁴, Farid HABELHAMES⁵, Stefan ANTOHE⁶

¹ Angers University, Photonics Laboratory, Angers, France

² Vilnius University, Vilnius, Lithuania

³ National Institute of Materials Physics, Bucharest, Romania

⁴ "Al.I. Cuza" University, Faculty of Physics, Iasi, Romania

⁵ Ferhat Abas University, Faculty of Science, Setif, Algeria

⁶ Bucharest University, Faculty of Physics, Bucharest, Romania

E-mail: Mihaela.Girtan@univ-angers.fr

Titanium oxide is one of the most promising candidate for relatively low cost, simple manufacture and high-performance new generation solar cells and the recent achievements in dye-sensitized solar cells (DSSCs) efficiencies and life time confirm the fact that these new generation solar cells becomes one of the future solutions in energy conversion. In DSSCs the presence of a dense titanium oxide layer is necessary in order to avoid short circuits between electrodes. Then, the interest to have a second porous TiO₂ layer is determined by the fact that compared to a flat surface, a dye-sensitized porous surface area increase the absorption and hence conduct to the increase of solar cells efficiencies. Generally these two layers are prepared by successive depositions using two different methods. In this paper we present a simple technique to prepare both layers during the same spraying process. Films morphology and structure of titanium oxide deposited on glass and ITO substrate was investigated by AFM, SEM and XRD respectively.

Key words: titanium oxide thin films, spray pyrolysis, hybrid dye-sensitized solar cells.

1. INTRODUCTION

Renewable energy is a hot topic today due to limitations of fossil fuel and pollution problems. The 2009 World Energy Outlook, published by the International Energy Agency, predicts that world demand for oil (often used as reference for world demand for energy) will increase from 2,000 million tons of oil equivalent (mtoe) to 16,800 mtoe in 2030. The increase in worldwide energy demand is principally driving by the increase of population, the industrialisation and the globalization. Beside the other renewable energies sources: biomass, wind, hydroelectricity, the solar energy source has many advantages: is ready available, secure from geopolitical tension, available everywhere, even on isolated sites and less polluting. Although silicon based solar cells are still most popular, due to the high cost and the trapping problems in the electrical transport and phototransport [1,2] they have been challenged by new promising materials such as polymers, copolymers [3–5] and new generation organic and hybrid photovoltaic devices [6–20]. These new solar cells are based on low cost and environment friendly materials and technology. Transparent oxide thin films are widely used materials in new generation solar cells. Most of these oxides such as ZnO, AZO, ITO, or FTO are used as transparent electrodes [21–29]. Another intensively studied oxide is TiO₂ [30–34], which is the most promising candidate for relatively low cost, simple manufacture and high-performance dye-sensitized solar cells (DSSCs) [35–38]. Here the titanium oxide film doesn't act as electrode but it contributes as active layer in a process similar to the photosynthesis [39, 40]. The new advancements in the organic and hybrid solar cells performances (9.8% in 2011 for organic solar cells and 11% for hybrid DSSCs) confirm the fact that these new generation solar cells becomes one of the future solutions in energy conversion. Different methods could be employed for titanium oxide thin film deposition such as: sol-gel, sputtering, thermal oxidation or spray. Spray deposition systems [41–45] present the advantages of a large area and low cost technology.

Typical DSSCs consist on multilayer structure as follow: FTO or ITO (transparent electrode)/TiO₂(dense layer)/TiO₂(porous layer)+dye (sensitized monocrystalline TiO₂ film)/electrolyte/Pt (counter electrode). The presence of a dense titanium oxide layer is necessary in order to avoid short circuits between electrodes. Then, the interest to have a second porous TiO₂ layer is determined by the fact that compared to a flat surface a dye-sensitized porous surface area increase the absorption and hence conduct to the increase of solar cells efficiencies.

In this paper we present some of the structural and morphological properties of titanium oxide films prepared by spin coating and spray pyrolysis starting from a same precursor solution. Some technical aspects of titanium oxide thin films spray deposition and a new method of creating films divided by 'channels' into 'blocks' in order to increase the TiO₂ dye-sensitized surface area are discussed.

2. EXPERIMENTAL

The experimental setup for spray deposition is depicted in Fig. 1 and is similar to the systems described in other papers [41, 43]. The vertical distance nozzle-substrate was about 8 cm. Two nozzles of 0.2 mm and 0.5 mm diameter respectively were employed for different thin films preparation. The precursor solution consisted in titanium isopropoxide, ethanol and hydrochloric acid (1:12:1 vol%) and was atomized by a pneumatic spray system using compressed air as a carrier gas.

Glass and ITO/glass substrates were previously cleaned with ethanol and acetone in an ultrasonic bath, followed by 15 minutes UV ozone exposure.

Films were deposited on substrates heated between 150 and 350 °C by pulsed solution feed, so as to prevent substrate from cooling down at too low temperatures. Different spray and break times were tested in order to find the optimal deposition parameters. The films were subsequently heat treated for 20 min. at 350 °C followed by 20 min. at 450 °C and 20 min. at 500 °C in air.

Thin films thickness measurements were performed by profilometry and ellipsometry, using a Veeco Dektak 6M Stylus Profilometer and a Horiba Jobin Yvon ellipsometer respectively.

Films surface morphology was determined by Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM). The structural characterization was made with a Cu-K α ($\lambda = 1.5406 \text{ \AA}$) Bruker D8 Advance Diffractometer.

The transmittance spectra were recorded in the wavelength range 280–1600 nm with unpolarized light, at room temperature, using a Lambda 19 UV-Vis spectrophotometer.

3. DISCUSSION

Thin films thickness is controlled by many changeable parameters such as nozzle to substrate distance, pressure (airflow), nozzle size, substrate temperature or spray duration. Due to the big number of deposition parameters, one of the major inconvenient of spray deposition method is the control of thickness and homogeneity on larger surfaces area. One of the easiest ways to control the thickness is the spray deposition time. The measurements of thickness in function of the total spray duration indicate a linear increase of the average values with the spraying time for a given temperature. For the same total spraying duration the deposition in the temperature interval between 150 °C and 270 °C give relatively good uniform films. At 300 °C the film thickness is very inhomogeneous and if substrate's temperature during the deposition is higher than 350 °C the thickness of TiO₂ film drop to really low values (up to 6 times thinner than layers sprayed

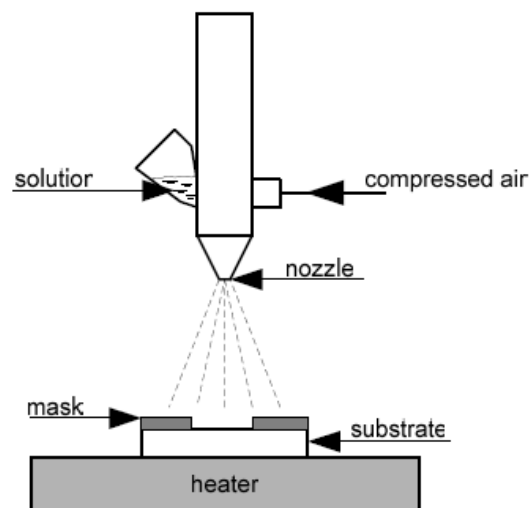


Fig. 1 – Spray deposition system.

with lower substrate temperature). This decrease is due to the fact that the solution drops evaporates before hitting the surface of substrate and then blown away by the hot airflow. Much more, for the solution drops which cannot reach the substrate, the reaction conducting to TiO_2 formation take place above the substrate and lead to the formation of solid TiO_2 nanoparticles which doesn't stick to substrate surface. The schematic representation of this effect is shown in Fig. 2.

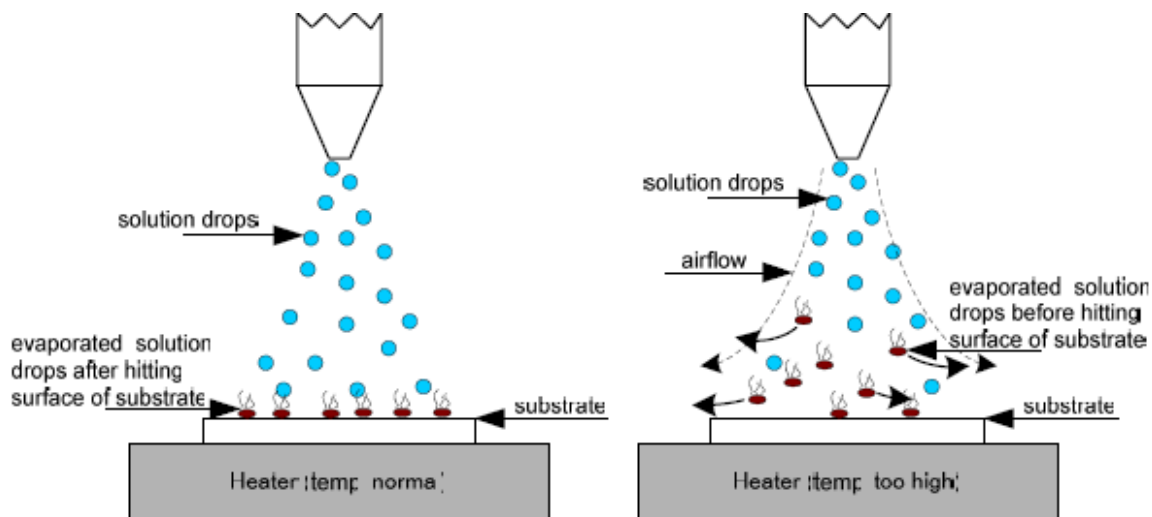
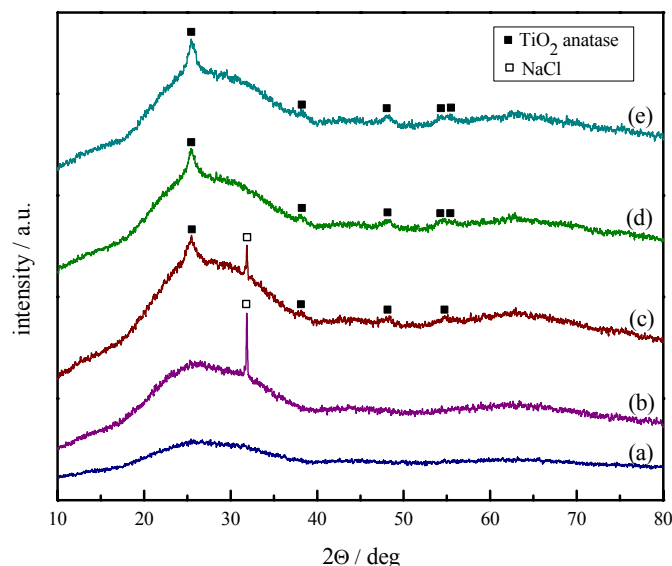


Fig. 2 – Schematic representation of layer thickness drop in high temperature effect.

The XRD patterns for as deposited films on glass and after successive annealings during 20 min at 350 °C, 450 °C and 500 °C are presented on Fig. 3. The XRD analysis on all as deposited TiO_2 films at substrate temperature ranged from 150 °C to 350 °C showed no presence of any crystalline phase.

Fig. 3 – XRD patterns of TiO_2 layer prepared by spray pyrolysis method on glass substrate; a) as deposited; b) annealed at 350 °C for 20 min.; c) again annealed at 450 °C for 20 min.; d) again annealed at 500 °C for 20 min.; e) again annealed at 500 °C for 60 min.; background of XRD pattern was not removed.



The crystalline anatase phase formation starts after 20 min. annealing at 450 °C. Further annealing procedures gave little improvement films crystallinity (Fig. 3d, e). NaCl peak in XRD patterns was observed, for some samples, after annealing at 350 °C for 20 minutes, but then it declined after annealing at 450 °C for 20 minutes and disappeared completely after 20 min. annealing at 500 °C. The presence of some NaCl crystals is due to the Na diffusion from glass substrates. These crystals could be generally easily removed from the surface by films cleaning with distilled water.

The XRD patterns for TiO_2 thin films deposited on ITO are given in Fig. 4. As previous, no crystalline TiO_2 phase was observed for as deposited films (Fig. 4a), just ITO crystalline phase peaks in XRD pattern are visible. Annealing sample for 20 minutes at 350 °C gave results of evidence that TiO_2 started to form

anatase phase (Fig. 4b). Successive annealing of samples for 20 minutes at 450 °C (Fig. 6c) and 20 minutes at 500 °C shows the increase of TiO₂ crystallinity with the increase of the annealing temperature.

As one can remark, by comparing the XRD patterns of TiO₂ films deposited on glass (Fig. 3) with XRD patterns of TiO₂ films deposited on ITO (Fig. 4), formation of anatase crystalline phase is easier on ITO than on glass. After samples annealing at 350 °C for 20 minutes, thin films deposited on glass substrate showed no phase peaks (Fig. 3b) whereas, for films deposited on ITO, we remark the apparition of anatase peaks phase (Fig. 4b). This difference of the crystals growth is due to initial ITO substrates crystalline phase as a contrast to amorphous glass substrate.

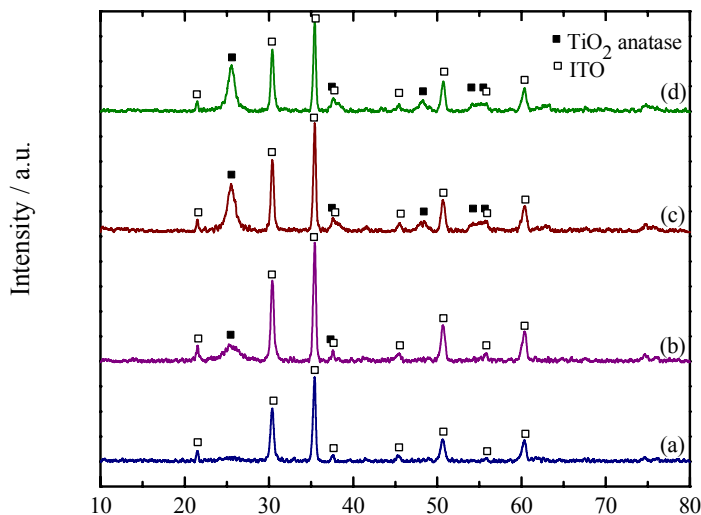


Fig. 4 – XRD patterns of TiO₂ layer prepared by spray pyrolysis method on ITO substrate: a) as deposited; b) annealed at 350°C for 20 min.; c) again annealed at 450 °C for 20 min.; d) again annealed at 500 °C for 20 min.; e) again annealed at 500 °C for 60 min.; background of XRD pattern was removed.

Studies made by AFM shows a difference in roughness multiplied by 5 for spray deposited titanium oxide thin films compared to spin coating films deposited using the same precursor solution and the same annealing procedure.

Even after annealing at 500 °C, spray deposited titanium oxide thin films are quite fragile and the upper layer can be quite easily removed by soft materials. In this experimental part, cotton wool moistened with ethanol was used for layer gently wiped. In Fig. 5 we can see layer surface pictures before and after cleaning.

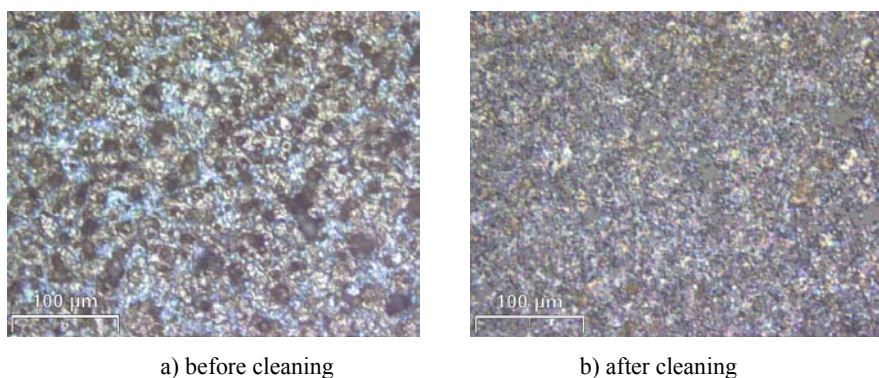


Fig. 5 – Surface morphology of titanium oxide spray deposited thin films before and after removing the porous upper layer.

Layer thickness measurements before and after surface cleaning were performed (Fig. 6) and showed that great amount of TiO₂ layer can be cleaned away leaving just rigid dense layer. The dense layer is much tougher and cannot be scratched or removed. So, thin films morphology may be represented schematically by a dense layer followed by a porous layer (Fig. 7).

Usually, in DSSCs preparation two different methods are employed for the successive deposition of the dense and then the porous layer, so, the obtained morphology by the technique and parameters presented in this work has the technological advantage of obtaining both desired layer during the same process. For the same deposition temperature, no matter the total spray duration the dense layer film has the same thickness.

As for example (as we can see from Fig. 6) for films deposited at 270 °C the thickness of the dense film is about 600–700 nm and the thickness of the porous film may vary from 2.5 μm to 5.5 μm when the total duration of spray phase vary from 30 to 52 seconds.

Fig. 6 – TiO₂ layer thickness d vs. times of spray phase before and after porous layer removing. Thin films preparation: substrate temperature 270 °C, spray phase 1 s, pause ~10 s, pressure 1.3 bar, nozzle size 0.5 mm, samples were annealed at 300 °C for 20 min and 500 °C for 20 min.

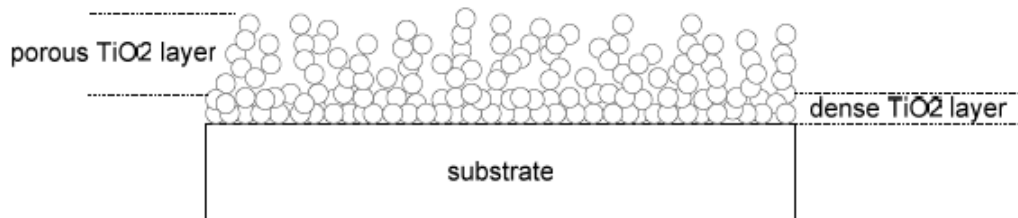
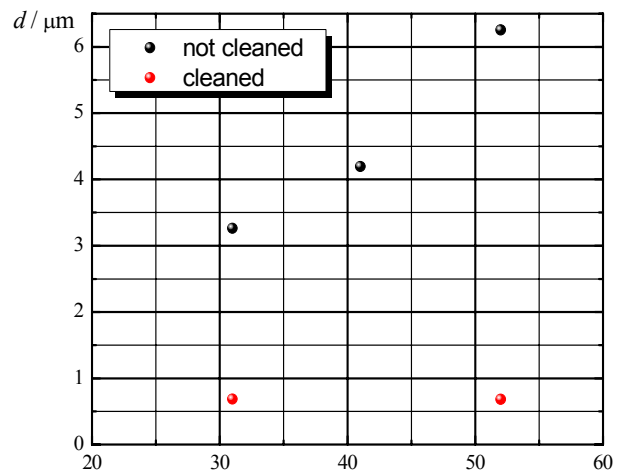


Fig. 7 – Schematic representation of TiO₂ layer deposited by spray pyrolysis method.

For porous films some improvements were reported [46] in solar cells performance due to formation of ‘channeled’ TiO₂ layer. Authors were using microwave annealing or ammonia adding techniques respectively to obtain channeled TiO₂ layer. In this work we present a simple way based only on spray technique for making films divided by ‘channels’ into ‘blocks’.

Base TiO₂ layer was prepared by spraying solution on glass for 3s with pauses of 1 minute 3 times (heating plate temperature 325 °C). After third spray phase spray, layer was left on hot plate (325 °C) for 5 minutes and then left to cool down to room temperature. The process is continued by a fourth spray phase with a 15 s continuous spraying at room temperature. Then after, the sample is placed on hot plate (540 °C) and sprayed 5 times for 1–2 s with intervals of 4–5 s with pure ethanol. After ethanol spraying, samples are left on the hot plate at 540 °C for 15 minutes.

SEM images (Fig. 8) reveal the layer morphology prepared by previously mentioned method. TiO₂ forms ‘blocs’ with average diameter ranging from 2 μm to 10 μm . Tilted image give more information about ‘blocks’ shape. This method enables to create concave TiO₂ ‘blocks’ with sintered area in the centre of the ‘block’ with base TiO₂ layer.

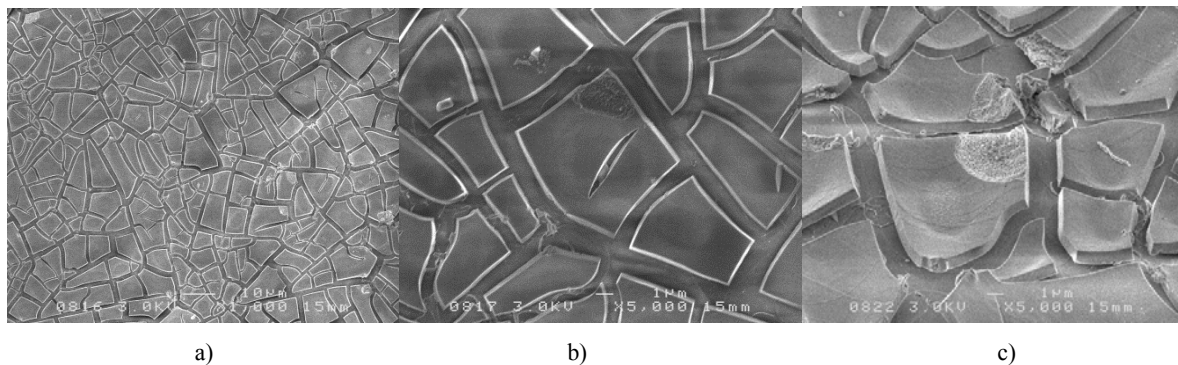


Fig. 8 – SEM images of ‘channeled’ TiO₂ layer: a) $\times 1000$; b) $\times 5000$; c) $\times 5000$ tilted image.

Titanium oxide porous films wettability is an important property for DSSCs since the pores should be filled and covered at maximum with the dye in order to increase the absorption. In this work the wettability of TiO₂ layers sprayed on glass and ITO substrate was investigated by contact angle method. Distilled water was used as a liquid source to form drops for this measurement. All samples (also after annealing) were held in atmosphere for several days.

Results of contact angle measurements are shown in Table I. Not annealed samples showed greater values of contact angle (Fig. 9.a) while annealed demonstrated lower angles (Fig. 9b). This could be attributed to anatase crystalline phase formation after annealing, previously discussed.

Table I

Water drop contact angle on the surface of different titanium oxide films deposited by spray pyrolysis at temperatures ranging between 150 and 350°C, then annealed at 350, 450 and 500°C or/and exposed to UV radiation

No.	Sample	Contact angle / deg
1.	as deposited	80 - 85
2.	after annealing	27 - 36
3.	after 30 min UV exposure	0

Titanium oxide thin films change their hydrophobic and hydrophilic characteristics when exposed to UV light [47]. This behaviour was putted in evidence for all TiO₂ studied samples after exposure to strong UV light. Contact angle measurements, done within 30 minutes, evidenced that all samples (annealed or not) became hydrophilic (Fig. 9c), with a contact angle of 0°.

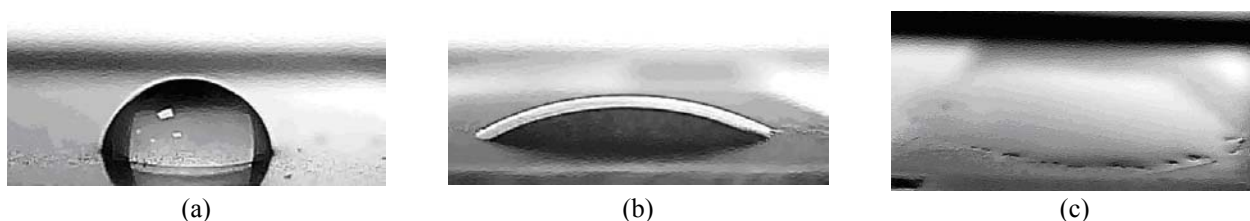


Fig. 9 – Image of water contact angle on the surface of: a) non annealed TiO₂ film; b) annealed TiO₂ film; c) annealed TiO₂ film after strong UV light exposure for 30 min.

Spectroscopy and ellipsometry methods were used to investigate TiO₂ films optical properties. It was found that annealed pyrolysed and spin-coated TiO₂ layer shared the same absorption edge wavelength of 320nm. But not annealed (amorphous) TiO₂ layer had absorption edge wavelength shift (edge 300 nm).

4. CONCLUSIONS

In this work spray pyrolysis layer deposition technique and pyrolysed TiO₂ thin films are discussed. The optimum conditions for spraying TiO₂ layers were: 0.5–1 s of spraying phase with 10 s pauses at 250–270 °C. For a fixed solution flow rate of 0.03 ml/s and a static pressure of the carrier gas of 2.5 bar, substrate variation temperature indicate that for an increasing substrate temperature up to 300 °C increases layer thickness dispersion and the substrate temperatures higher than 350 °C results in great film thickness drop.

XRD studies showed that TiO₂ films deposited between 150 and 350 °C are amorphous. Subsequent annealing during 20 min at 350 °C, 450°C or 500 °C conduct to anatase crystalline phase formation. ITO substrates favors faster crystalline phase formation compared to glass.

Thickness measurements before and after surface cleaning showed that spray pyrolysed TiO₂ films consist of two layers: an upper porous layer that could be easily wiped away and a dense and an rigid lower (next to substrate) layer, which is much more difficult to remove or scratch.

Surface morphology gave more insight of TiO₂ layer surface structure depending on spray method. It was found that subsequent ethanol spraying enables to creating TiO₂ films divided by ‘channels’ into ‘blocks’ with average diameter ranging from 2 μm to 10 μm.

Contact angle measurements were performed and showed important differences between annealed and not annealed samples. For annealed samples the contact angles ranged between 27° and 36°, while, not annealed showed hydrophobic properties with angles of 80° to 85°. After UV radiation all TiO₂ films became hydrophilic (contact angle 0°).

ACKNOWLEDGMENTS

Authors are grateful R. Mallet and G. Mabillaud from SCIAM for AFM and SEM analysis and to M. Allain and N. Mercier from PIAM for providing the necessary facilities for XRD studies. This work was founded by the European Project FILMSOLAR – ERA RUS NET and the Regional Project PERLE 2 – Pays de la Loire.

REFERENCES

1. L.A. KOSYACHENKO, *Solar Cells - Silicon Wafer-Based Technologies*, InTech Publications, 2011.
2. M.L. CIUREA, *Trapping aspects in silicon-based nanostructures*, Proceedings of the Romanian Academy, Series A, **12**, pp. 315–323, 2011.
3. F.C. KREBS, *Polymeric solar cells: Materials, Design, Manufacture*, DESTech Publications, 2010.
4. A. BALACEANU, D.E. DEMCO, A. PICH, *Responsive copolymer microgel morphology*, Proceedings of the Romanian Academy, Series A, **12**, pp. 296–301, 2011.
5. C.J. BRABEC, V. DYAKONOV, J. PARISI, N.S. SARICIFTCI, *Organic Photovoltaics: Concept and Realisation*, Springer, 2003.
6. A. STANCULESCU, M. SOCOL, G. SOCOL, I.N. MIHAILESCU, M. GIRTAN, F. STANCULESCU, *Maple prepared organic heterostructures for photovoltaic applications*, Appl. Phys. A-Materials Science&Processing, **104**, pp. 921–928, 2011.
7. D. MIHALACHE, *Recent trends in micro- and nanophotonics: A personal selection*, Journal of Optoelectronics and Advanced Materials, **13**, pp. 1055–1066, 2011.
8. A. RADU, S. IFTIMIE, V. GHENESCU, C. BESLEAGA, V.A. ANTOHE, G. BRATINA, L. ION, S. CRACIUN, M. GIRTAN, S. ANTOHE, *The influence of LiF layer and ZnO nanoparticles additions on the performances of flexible photovoltaic cells based on polymer blends*, Digest Journal of Nanomaterials and Biostructures, **6**, pp. 1141–1148, 2011.
9. S. IFTIMIE, A. RADU, M. RADU, C. BESLEAGA, I. PANA, S. CRACIUN, M. GIRTAN, L. ION, S. ANTOHE, *Influence of PEDOT:PSS layer on the performances of "bulk-heterojunction" photovoltaic cells based on MEH-PPV:PCBM (1:4) polymeric blends*, Digest Journal of Nanomaterials and Biostructures, **6**, pp. 1631–1638, 2011.
10. M. GIRTAN, M. RUSU, *Role of ITO and PEDOT:PSS in stability/degradation of polymer: fullerene bulk heterojunctions solar cells*, Solar Energy Materials and Solar Cells, **94**, pp. 446–450, 2010.
11. A.K. PANDEY, K.N.N. UNNI, J.-M. NUNZI, *Pentacene/perylene co-deposited solar cells*, Thin Solid Films, **511–512**, pp. 529–532, 2006.
12. J.-M. NUNZI, *Organic photovoltaic materials and devices*, Comptes Rendus Physique, **3**, pp. 523–542, 2002.
13. F. LIU, J.-M. NUNZI, *Enhanced organic light emitting diode and solar cell performances using silver nano-clusters*, Organic Electronics, **13**, pp.1623–1632, 2012.
14. N.S. SARICIFTCI, L. SMILOWITZ, A.J. HEEGER, F. WUDL, *Photoinduced electron-transfer from a conducting polymer to buckminsterfullerene*, Science, **258**, pp.1474–1476, 1992.
15. I-W. HWANG, J.Y. KIM, S. CHO, J. YUEN, N. COATES, K. LEE, M. HEENEY, I. MCCULLOCH, D. MOSES, A.J. HEEGER, *Bulk heterojunction materials composed of poly(2,5-bis(3-tetradecylthiophen-2-yl)thieno 3,2-b thiophene): Ultrafast electron transfer and carrier recombination*, Journal of Physical Chemistry C, **112**, pp.7853–7857, 2008.
16. F.C. KREBS, *All solution roll-to-roll processed polymer solar cells free from indium-tin-oxide and vacuum coating steps*, Organic Electronics, **10**, pp.761–768, 2009.
17. G.P. SMESTAD, F.C. KREBS, C.G. GRANQVIST, K.L. CHOPRA, X. MATHEW, I. GORDON, C.M. LAMPERT, *Priority publishing in Solar Energy Materials and Solar Cells*, Solar Energy Materials and Solar Cells, **94**, pp.1187–1190, 2010.
18. B.J. LEEVER, C.A. BAILEY, T.J. MARKS, M.C. HERSAM, M.F. DURSTOCK, *In Situ Characterization of Lifetime and Morphology in Operating Bulk Heterojunction Organic Photovoltaic Devices by Impedance Spectroscopy*, Advanced Energy Materials, **2**, pp.120–128, 2012.
19. M. SOYLU, M. GIRTAN, F. YAKUPHANOGLU, *Properties of PEDOT:PEG/ZnO/p-Si heterojunction diode*, Materials Science and Engineering B-Advanced Functional Solid-State Materials, **177**, pp. 785–790, 2012.
20. M. GIRTAN, R. MALLET, D. CAILLOU, G.G. RUSU, M. RUSU, *Thermal stability of poly(3,4-ethylenedioxythiophene)-polystyrenesulfonic acid films electrical properties*, Superlattices and Microstructures, **46**, pp. 44–51, 2009.
21. M. GIRTAN, *Comparison of ITO/metal/ITO and ZnO/metal/ZnO characteristics as transparent electrodes for third generation solar cells*, Solar Energy Materials and Solar Cells, **100**, pp. 153–161, 2012.
22. M. RUSU, G.G. RUSU, M. GIRTAN, S.D. SEIGNON, *Structural and optical properties of ZnO thin films deposited onto ITO/glass substrates*, Journal of Non-Crystalline Solids, **354**, pp. 4461–4464, 2008.
23. G.G. RUSU, M. GIRTAN, M. RUSU, *Preparation and characterization of ZnO thin films prepared by thermal oxidation of evaporated Zn thin films*, Superlattices and Microstructures, **42**, pp.116–122, 2007.

24. M. GIRTAN, A. BOUTEVILLE, G.G. RUSU, M. RUSU, *Preparation and properties of SnO₂:F thin films*, Journal of Optoelectronics and Advanced Materials, **8**, pp.27–30, 2006.
25. F.Z. GHOMRANI, S. IFTIMIE, N. GABOUZE, A. SERIER, M. SOCOL, A. STANCULESCU, F. SANCHEZ, S. ANTOHE, M. GIRTAN, *Influence of Al doping agents nature on the physical properties of Al:ZnO films deposited by spin-coating technique*, Optoelectronics and Advanced Materials-Rapid Communications, **5**, pp. 247–251, 2011.
26. M. GIRTAN, M. SOCOL, B. PATTIER, M. SYLLA, A. STANCULESCU, *On the structural, morphological, optical and electrical properties of sol-gel deposited ZnO In films*, Thin Solid Films, **519**, pp. 573–577, 2010.
27. C.G. GRANQVIST, *Transparent conductors as solar energy materials: A panoramic review*, Solar Energy Materials and Solar Cells, **91**, pp. 1529–1598, 2007.
28. C.G. GRANQVIST, *Transparent conductors for solar energy and energy efficiency: a broad-brush picture*, International Journal of Nanotechnology, **6**, pp. 785–798, 2009.
29. A.E. HAJJ, B. LUCAS, M. CHAKAROUN, R. ANTONY, B. RATIER, M. ALDISSI, *Optimization of ZnO/Ag/ZnO multilayer electrodes obtained by Ion Beam Sputtering for optoelectronic devices*, Thin Solid Films, **520**, pp. 4666–4668, 2012.
30. A. YILDIZ, S.B. LISESIVDIN, M. KASAP, D. MARDARE, *Electrical properties of TiO₂ thin films*, Journal of Non-Crystalline Solids, **354**, pp. 4944–4947, 2008.
31. D. MARDARE, N. IFTIMIE, D. LUCA, *TiO₂ thin films as sensing gas materials*, Journal of Non-Crystalline Solids, **354**, pp. 4396–4400, 2008.
32. D. MARDARE, F. IACOMI, N. CORNELI, M. GIRTAN, D. LUCA, *Undoped and Cr-doped TiO₂ thin films obtained by spray pyrolysis*, Thin Solid Films, **518**, pp.4586–4589, 2010.
33. N. IFTIMIE, D. LUCA, F. LACOMI, M. GIRTAN, D. MARDARE, *Gas sensing materials based on TiO₂ thin films*, Journal of Vacuum Science & Technology B, **27**, pp. 538–541, 2009.
34. D. CRIȘAN, N. DRĂGAN, M. CRIȘAN, M. RĂILEANU, A. BRĂILEANU, M. ANASTASESCU, A. IANCULESCU, D. MARDARE, D. LUCA, V. MARINESCU, A. MOLDOVAN, *Crystallization study of sol-gel un-doped and Pd-doped TiO₂ materials*, Journal of Physics and Chemistry of Solids, **69**, pp. 2548–2554, 2008.
35. A. HAGFELDT, U.B. CAPPEL, G. BOSCHLOO, L. SUN, L. KLOO, H. PETTERSSON, E. GIBSON, *1.21 - Mesoporous Dye-Sensitized Solar Cells*, in *Comprehensive Renewable Energy*, E.-C.A. Sayigh, Ed., Elsevier, 2012, pp. 481–496.
36. M.K. NAZEERUDDIN, M. GRÄTZEL, *Conversion and Storage of Solar Energy using Dye-sensitized Nanocrystalline TiO₂ Cells*, in *Comprehensive Coordination Chemistry II*, E.-C.J.A. McCleverty and T.J. Meyer, Eds. Pergamon, 2003, pp. 719–758.
37. K.R. MILLINGTON, *Photoelectrochemical cells/ Dye-Sensitized Cells*, in *Encyclopedia of Electrochemical Power Sources*, E.-C.J. Garche, Elsevier, 2009, pp. 10–21.
38. J. BOUCLE, J. ACKERMANN, *Solid-state dye-sensitized and bulk heterojunction solar cells using TiO₂ and ZnO nanostructures: recent progress and new concepts at the borderline*, Polymer International, **61**, pp. 355–373, 2012.
39. N.S. LEWIS, *Photosynthesis, Artificial*, in *Encyclopedia of Energy*, E.-C.C.J. Cleveland, Ed., Elsevier, 2004, pp. 17–24.
40. A. PANDIT, R.N. FRESE, *1.31-Artificial Leaves: Towards Bio-Inspired Solar Energy Converters*, in *Comprehensive Renewable Energy*, E.-C.A. Sayigh, Ed., Elsevier, 2012, pp. 657–677.
41. M. GIRTAN, G. FOLCHER, *Structural and optical properties of indium oxide thin films prepared by an ultrasonic spray CVD process*, Surface & Coatings Technology, **172**, pp. 242–250, 2003.
42. M. GIRTAN, P.O. LOGERAIS, A. BOUTEVILLE, *Substrate thermal profiles in spray-CVD reactor*, Journal of Optoelectronics and Advanced Materials, **8**, pp. 144–147, 2006.
43. M. GIRTAN, H. CACHET, G.I. RUSU, *On the physical properties of indium oxide thin films deposited by pyrosol in comparison with films deposited by pneumatic spray pyrolysis*, Thin Solid Films, **427**, pp. 406–410, 2003.
44. D. CHAPRON, M. GIRTAN, J.Y. LE POMMELEC, A. BOUTEVILLE, *Droplet dispersion calculations for ultrasonic spray pyrolysis depositions*, Journal of Optoelectronics and Advanced Materials, **9**, pp. 902–906, 2007.
45. M. GIRTAN, *Investigations on the optical constants of indium oxide thin films prepared by ultrasonic spray pyrolysis*, Materials Science and Engineering B-Solid State Materials for Advanced Technology, **118**, pp. 175–178, 2005.
46. J.N. HART, D. MENZIES, Y.B. CHENG, G.P. SIMON, L. SPICCIA, *A comparison of microwave and conventional heat treatments of nanocrystalline TiO₂*, Solar Energy Materials and Solar Cells, **91**, pp. 6–16, 2007.
47. K.-R. WU, J.-J. WANG, W.-C. LIU, Z.-S. CHEN, J.-K. WU, *Deposition of graded TiO₂ films featured both hydrophobic and photo-induced hydrophilic properties*, Applied Surface Science, **252**, pp. 5829–5838, 2005.

Received August 13, 2012