



464 - Novel solar absorber surfaces with organic pigments

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Abstract

This paper presents results of application of natural and synthetic organic pigments in selective solar absorber coatings. Some of these photo excite pigments were tested like solar radiation absorber pigments in paint coatings and others as a form to increase the absorption of solar radiation in titanium oxide monolayer selective coatings produced by reactive magnetron sputtering. Morphologic aspects and optical properties are discussed as a function of deposition parameters and of formulation parameters. The main goal is to prepare solar absorber surfaces as a tandem of TiOx thin films, organic pigment using a conductive substrate or of paint with organic and/or inorganic pigments and conductive substrate, all reaching great photo thermal conversion efficiency, high durability and low costs to the ending product and stability at medium range temperatures (120-150°C). The best optical properties for titanium oxide sputtered films were 88% for solar absorption, with 7% of emissivity for deposition parameters of: pulsed frequency 200kHz, reverse time of 0.4μs, discharge current of 0.7A, argon flow rate of 50ml/min and oxygen flow rate changing from 0 to 2.5ml/min. The results obtained with paints were not satisfactory. The best couple values for solar absorption and emissivity were respectively 94%, and 74%.

1. Introduction

In this paper we present some results of organic pigment application in selective solar absorber coatings developed within a Portuguese research project [1], obtained as a tandem of TiOx thin films, organic pigment and conductive substrate, described elsewhere [2, 3]. This idea is a spin off of the work done by members of the research team in the field of TiOx thin films deposition by reactive magnetron sputtering in DC or pulsing DC mode over conductive substrate [4], and of synthesis and characterization of [60] and [70] fullerene-coumarin dyads [5, 6], in a parallel way as that done to develop dye-sensitized nanocrystalline TiO₂ thin films for PV applications [7], and to develop paints with inorganic or organic pigments [8, 9, 10].

Although many and good work has been done in the area of selective solar absorber surfaces, still subsists interest to develop selective solar absorber surfaces, with high durability, low costs and thermal and environmental stability, to apply in solar thermal conversion, mainly for higher values of medium range temperatures (120-150°C). Our idea is that titanium oxide films could be a good stake, because of high stability, no toxicity and possibility of wide range of refraction index variation [11-12].

It's known that optical properties of materials are dependent of factors like the composition (electrons distribution in atomic external energy levels, minimum energy necessary to change for places of higher energy, type of link between atoms and molecules, minimum energy to cause inter or intra-molecular vibrations), the structure (that determine the strength of link between atoms and molecules and consequently the movement of more external electrons), the morphology (interfaces



between columns or grains could be scattering places of radiation, and shape, size and orientation relatively to incident radiation are also determinants in scattering effects and radiation interference phenomena's, the same happens with defects, displacements, discontinuities, holes and their shape and size), the surface topography (adequate roughness could be motive of multiple reflections of incident radiation, with some absorption at each incidence and also forcing radiation to come into material) and the presence of different layers with their interfaces (which could cause interference phenomena's motivated by adequate conjugation of thickness with composition layer and level of package, determinant in values of refraction indices, being optical thickness equal to physical thickness multiplied by refraction index, etc [13]).

Having in attention described topics, titanium oxide films obtained by magnetron sputtering seems to be adequate option for selective solar absorption coatings once that refraction index can be changed with adequate control of deposition parameters, between certain limits, to control composition, package, thickness, number of different layers, structure, morphology and topography of coatings [13-17].

2. Experimental details

2.1. Oxide titanium thin films with organic pigment

Titanium oxide films were deposited on glass and metallic substrates with dc magnetron sputtering and also with pulsed dc magnetron sputtering at room temperature from 7.5mm titanium target with 99.995% purity, in reactive atmosphere with mix of argon and oxygen gas. The sputtering was carried out using a 5kW power supply, with possibility to change pulsed frequency from 5 to 350 kHz, and reverse time from 0.4 to 5 μ s, and reverse voltage 10% of operation voltage.

The gas argon was fed to the chamber independent of the reactive oxygen. Flows for both, argon and oxygen were regulated using Bronkorst mass flow controller, operated by Bronkorst control unit. Pressure monitoring in the sputtering chamber was made by Balzers penning and pirani with TPG 300 monitor unit.

All experiments were performed with target to substrate distance of 6cm, and depositions were started after pumping the chamber to a base pressure of 1×10^{-6} mbar. Reflexion data were taken on a Perkin Elmer Lambda 9 NIR/UV/VIS Spectrophotometer and solar absorption was evaluated to be in account solar spectrum (AM1, 5) partition in 20 wavelength ranges of equal energy. Thermal emissivity was measured with an AE emissometer of Seivics & Services at an equilibrium temperature of 82°C and after adequate calibration. Optical properties values were evaluated with an uncertainty not exceeding $\pm 1\%$.

First experiments had in consideration the already known dependence of film morphology relatively to deposition parameters, and allowed to narrow the possible range of values variation for deposition parameters, with the final objective to reach highest as possible solar absorber selectivity [3]. Some coatings were prepared with constant oxygen flow rate and others with oxygen flow rate increasing gradually from the beginning to the end of deposition. Pulsed dc frequency and reverse time were also parameters taken in consideration.

2.2. Paint with organic and inorganic pigments

Required compatibility with fullerene pigment, high as possible transmittance to infrared radiation, heat resistance and good mechanical behaviour lead to select epoxy silicone resin as binder which, with adequate additives to confer enough strength and durability to the final paint, forms the paint base.

The paints were prepared from epoxy silicon resin that was previously mixed with charges and additives. Three types of pigments were used: a mix of C₆₀/C₇₀ fullerenes, copper powder (particle size 63 and 90 μ m), and stainless steel powder with particle size of 3 μ m. The introduction of the pigments in the initial base paint was made with the admixing of the pigments in a solution of the resin and n-butyl acetate in a rotating disperser at a constant speed of 700rpm min⁻¹ until a



granulometry of 12 μ m was reached. The paints were applied to a copper substrate by a draw bar coater and by a spray technique in order to achieve thin coatings with lower thickness.

Some painted samples with paint including organic pigments, were submitted to accelerate aging tests, with exposure to UV radiation, in humidity conditions with accordance of ASTM G 154 standard and also of strength to humidity following the standard NB ENISO G 270-1.

3. Results and discussion

Nanostructured multilayer thin films with titanium oxide already were subject of our work [4], but to avoid multilayer production complexity and eventually atomic diffusion between layers with time, at high temperatures, one of our present goals is to optimise optical properties of monolayer titanium oxide thin films with adequate thickness, composition and morphology, complemented in terms of absorption increment by organic pigment impregnation. For impregnation adequate pigments have to be selected in order to have absorption peaks located in solar spectrum and preferentially in wavelength range where our optimised titanium oxide film have less absorption.

On the basis of this strategy we prepared pigment-adsorbed single-layer TiO_x thin films using a natural dye extracted from *Sambucus nigra* L.[3] (a mixture of anthocyanins) with an absorption maximum of 530nm. Anthocyanins belong to a group of natural dyes found in fruits, flowers and leaves of plants. Because anthocyanins show the color in the range of visible light from red to blue, it is prospected to become a high efficient sensitizer for a wide bandgap semiconductors. Due to the carbonyl and hydroxyl group presented on anthocyanin molecule [3], it can be bound to the surface of titanium dioxide porous film to produce sensitized TiO₂ thin films for dye-sensitized solar cells (DSSC) applications [18].

However applied chemically over optimised titanium oxide coating, didn't improve significantly solar absorption, but best titanium oxide coating, with one layer, graded in terms of oxygen content, have 88% of absorption and 7% of thermal emissivity, and we hope that absorption could be improved with a final very thin layer with less refractive index.

Pursuing the objective of low cost, easy application, high solar absorption and durability, with a minimum possible of thermal emissivity, work was also done with formulation of paints with organic pigments (C₆₀/ C₇₀) and with organic and inorganic pigment (Cu and steel), having epoxy silicon resin as binder, with higher transmittance to thermal infrared radiation. The paints obtained showed emissivity values sensitive to the thickness, with the best couple values for absorption, emissivity of 96%, 74% respectively, these achieved for paint with organic pigment and average thickness coating of 4 μ m, the minimum thickness attained by spray application over copper substrate.

3.1. Oxide titanium thin films with organic pigment

First experiments done showed and bibliographic information is in accordance [19], that pulsed dc frequency and deposition power have implications on solar absorption, interfering with the energy of involved species and consequently affecting level of package, surface roughness of titanium oxide films and deposition rates. Best absorption values were obtained at pulsed dc frequency of 200kHz and in dc mode [3], but results obtained by dc reactive mode are not so reproducible as those obtained by pulsed dc at 200kHz.

To reach our goal, it was necessary to decide which would be the best working range for oxygen flow rate and for such it was important to analyse, for our apparatus, the voltage and deposition rate behaviour versus oxygen flow rate, and consequently oxygen partial pressure. Figure 1 shows one of obtained graphs.

Figure 1 shows that, with target current of 0.75A, the measured dependence of cathode voltage and thickness rate with oxygen flow rate for titanium target, have characteristic shapes that are not coincident in case of oxygen flow increase and decrease.

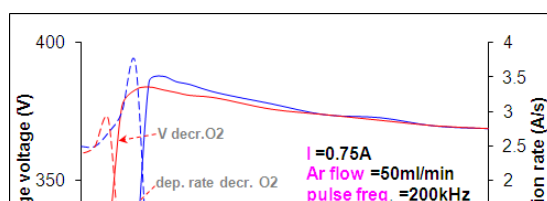




Fig.1. Variation of discharge voltage and deposition rate with oxygen flow rate, in modes of increase and decrease oxygen flow with constant: discharge current (0.75A), argon flow rate (50ml/min), pulsed dc frequency (200 kHz) and reverse time (0.4 μ s).

When, in rising oxygen flow rate mode, at zero oxygen flow, the target surface is essentially bare and in that case, metallic titanium is sputtered. Increasing oxygen flow rate, titanium oxide will be increasingly deposited over the growing film and also formed over the target (target becomes increasingly poisoned), the growing film and all surfaces in contact with it, with increasing titanium oxide formation. Secondary electrons emission increase also and consequently, to maintain discharge current constant, we have a decrease in voltage, which happens until the target becomes completely poisoned. At that point, the voltage increases sharply to maintain discharge current constant [20-22], and with such conditions, according to some authors [13, 23], will form stoichiometric titanium oxide, but a very low deposition rate.

In the backward cycle (decreasing of O₂ flow rate) the curve shows some displacement relatively to the curve referring to O₂ increase, the maximum in backward cycle occur near 2ml/min of O₂ flow rate while in forward cycle it happens between 2.5 and 3ml/min. This hysteresis is considered as the results of the residual O₂ on the target surface [24].

Relatively to the thickness rate, this has a maximum a little bit before the point, in oxygen flow, where voltage increases sharply.

Having the above understanding in consideration, it was decided that, for our films, the final oxygen flow must be situated between 2 and 3 mbar, in order to form TiO₂ films for the chemical adsorption of the pigment to be used (Fig. 2). This fact, together with the need to have adequate deposition rate, in order to obtain both high solar absorption (which implies decrease of refraction index from the substrate to the top of the film, with a decrease in oxygen content from the substrate to the top of the film) and low emissivity, it was decided to increase the oxygen flux with film growing, beginning from zero until values between 2 and 3 ml/min, with adequate slope to oxygen flow.

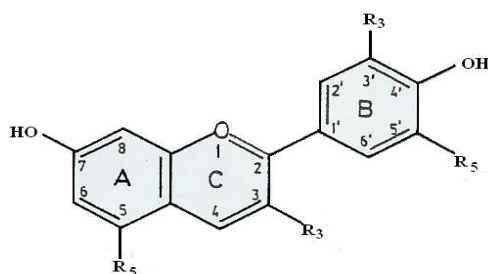


Fig.2. Chemical structure of anthocyanin.

Optimisation work, in terms of adequate values of deposition parameters to get an absorption value as high as possible, with as lowest emissivity, resulting in a maximum absorption of 88%, with 7% of emissivity.



Subsequent increment in solar absorption of these titanium oxide films will be obtained by their immersion into anthocyanin solution. Immersion was done at room temperature and at 40°C and also with different immersion times. Until the moment, when applied to optimised coatings over copper substrate, no significant increment was observed in solar absorption and this is evident in Figure 3, that show absorption variation with wavelength for two samples, with and without immersion in antocyanin solution. Each sample was obtained at different total and partial oxygen pressure. It must be noted that the increment reported elsewhere [3] was obtained with a non optimised coating over a glass substrate.

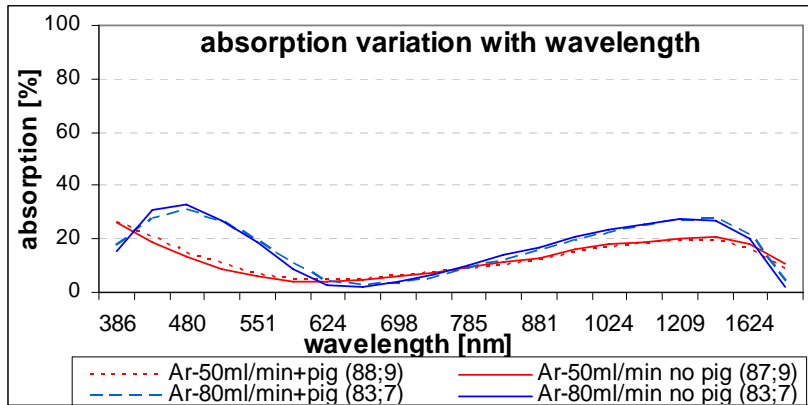


Fig. 3. Absorption variation with wavelength for two samples with titanium oxide films deposited with different argon flow, one at 50ml/min and other at 80ml/min and dash and continuum curves refer respectively sample after pigment solution immersion and before immersion.

With SEM and AFM analysis, it was possible to identify, in the titanium oxide films deposited over glass substrate in dc and also pulsed dc mode, microstructures of columnar type. With SEM cross section analysis of the thin film it was possible to observe columns distributed perpendicularly to substrate surface, which seems to be continuous along of thickness of the film (Fig.4), and in majority without transversal crack, what can mean low strength between columns which favours radiation absorption.

AFM image (Fig. 5) shows surface topography, where it is possible to visualise the top of columns. Evaluated average roughness of the films over glass substrate is low, changing between 0.5 to 1.7nm, depending of deposition parameters, but this would be expectable once that the observed films were very thin (90 to 200nm of thickness), following substrate roughness.

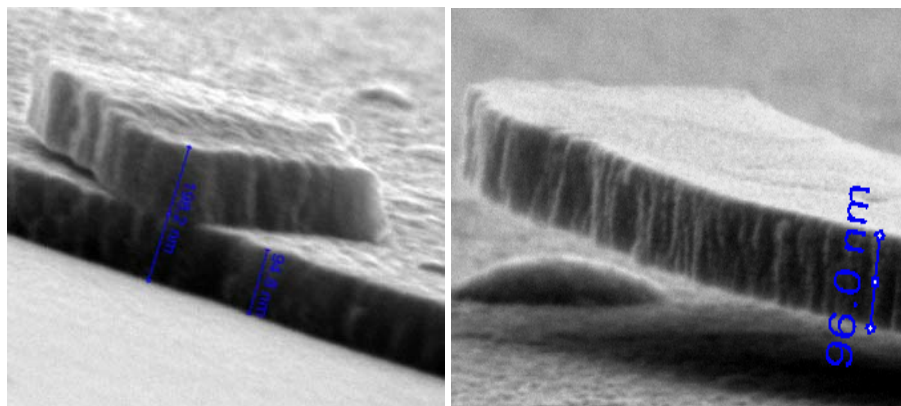


Fig.4. Morphology of titanium oxide films, over glass substrate, by SEM analysis, for a sample deposited in the conditions of: dc mode, $I=0.75A$, argon flow rate=50ml/min, O_2 flow rate changing from 0.8 to 1.5ml/min and total pressure between 6.5×10^{-3} to 6.8×10^{-3} mbar.

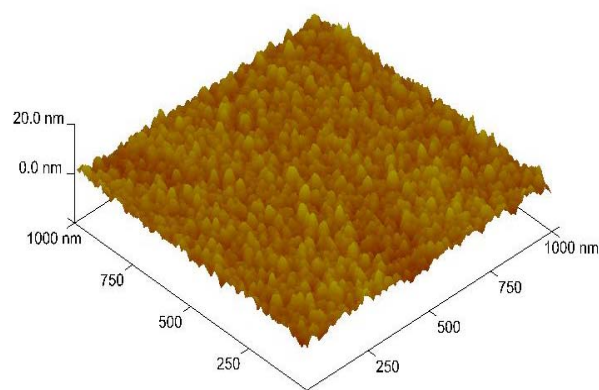


Fig.5. Topography of titanium oxide films, over glass substrate, by AFM analysis, for a sample deposited in the conditions of: dc mode, $I=0.75\text{A}$, argon flow rate= 50ml/min , O_2 flow rate changing from 0.8 to 1.5 and total pressure between 6.5×10^{-3} to 6.8×10^{-3} mbar and with average roughness of 1.1nm .

3.2- Coatings with paint

Figure 6 shows a summary of the work done to produce selective paint. It is possible to observe high solar absorption values, but undesirably also high thermal emissivity. The paints obtained until the moment are not selective.

In the initial work with paints, the objective was to get good optical properties for paint with the organic pigment $\text{C}_{60}/\text{C}_{70}$. High solar absorption (95% and 96%) was reached. The problem was the emissivity, which is strongly dependent on coating thickness. With the coil method adopted for coating, the lower thickness achieved was $7\mu\text{m}$, with 80% of emissivity and 95% of solar absorption. To reduce the thickness and consequently the emissivity, spray technique was tested and it was possible to achieve $4\mu\text{m}$ of thickness and emissivity of 74%, with 96% absorption.

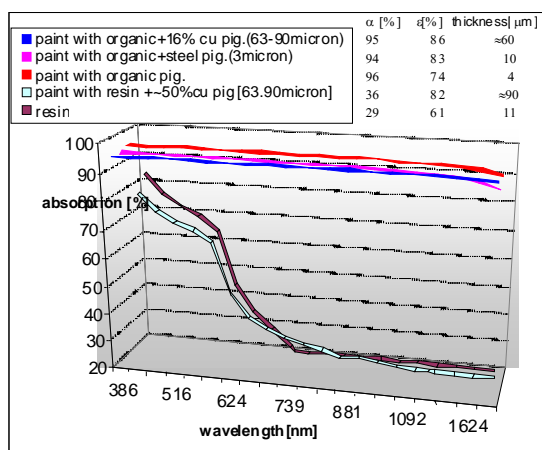


Fig. 6. Absorption variation with wavelength for different paint samples.

Without the possibility to reduce thickness to lower values with methods of easy application, it was also tested the incorporation of metallic pigments in the paint with 16% CVP of $\text{C}_{60}/\text{C}_{70}$ pigment, considering that the thermal conductivity of metallic pigments would lower the emissivity values. Both copper pigment with average grain size between 63 and $90\mu\text{m}$ and stainless steel with average grain size of $3\mu\text{m}$ were tested. The mix was done adding 16% of metallic pigment weight to the already prepared paint with $\text{C}_{60}/\text{C}_{70}$ pigment. Figure 6 shows that this did not improve the paint behaviour in relation to emissivity.

Adding higher quantity of metallic pigment, about 50%, to the base of paint, without use of organic pigments, hoping to increment thermal conductivity of the coating and obtain lower emissivity,



independently of thickness coating, also did not improve the emissivity and, without organic pigment, the absorption decreased to 36%. The fact that the metallic pigment used, was stored for a long time (surface highly oxidized) could cause the observed behaviour. Also the surface shape of used pigments could explain the observed behaviour, since the surface contact area between metallic particles and the metallic substrate was not adequate to increment conductivity. These aspects will be explored in near future.

Topography of paint with organic pigment obtained by SEM (Fig.7.a) allows us to identify a granular morphology, with grains agglutinated by resin. It is visible agglomerates of small grains; which rough surface that can improve absorption.

Figure 7.b shows one photo of the surface of paint with organic and inorganic pigment (grain average size of 63 to 90 μm) obtained by optic microscope with magnification of 45x (Fig. 7.a has magnification of 30 000x) and also it is notorious the presence of grains, but in this case bigger than of paint without inorganic pigment, what it is expectable once that Cu pigments have bigger size than granulometry (12 μm) when compared with the granulometry measured in paint with only organic pigments. The fact that copper has low solar absorption didn't decrease significantly solar absorption (95% compared to 96% for paint only with organic pigment).

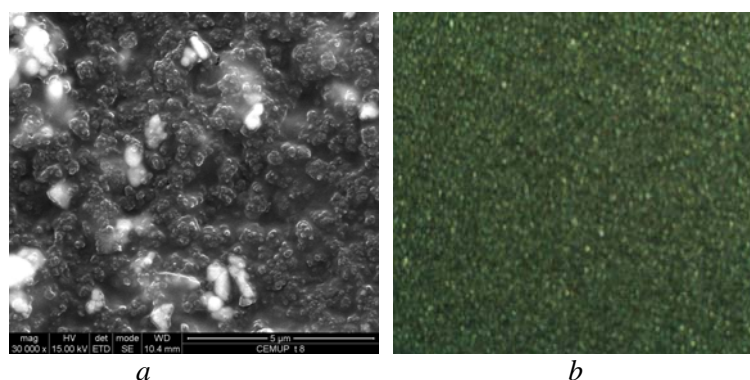


Fig. 7. a) SEM (30000x) surface micrograph of paint with organic pigment. b) Surface photography by optic microscope (45x) of paint with organic and Cu grains.

4- Conclusions

Optical properties of titanium oxide are strongly dependents of deposition parameters, and some of these are interrelated, which become very difficult to relate optical properties with change of each parameter, but it is possible to conclude that best values of absorber selectivity were obtained in dc mode and in pulsed dc mode with 200kHz, with oxygen flow rate changing between 0 and 2.5ml/min with adequate slope. Adequate slope depends of deposition rate which depends of deposition power, total pressure, oxygen partial pressure and pulsed frequency and all of these parameters are important, once that for solar absorber selectivity the final thickness and oxygen gradient concentration along of the film thickness are determinants. Best optical properties for oxide titanium sputtered films were 88% for solar absorption, with 7% of emissivity for deposition parameters of: pulsed frequency 200kHz, reverse time of 0.4 μs , discharge current of 0.7A, argon flow rate of 50ml/min and oxygen flow rate changing from 0 to 2.5ml/min. The morphology of oxide titanium films is columnar, with columns oriented in direction of growing film, which seem to be continuous from the substrate to the top of the film. Subsequent immersion in solution with antocyanin didn't show to improve solar absorption.

For paints, the results obtained until the moment weren't satisfactory. The best couple values for solar absorption and emissivity were respectively 94%, and 74%. Emissivity is dependent on thickness of coatings and with the used application techniques, the minimum thickness reached was 4 μm , not low enough to obtain infrared transparency. The effort to reduce emissivity of paints adding metallic particles were unfruitful, at least using for the shapes and sizes of metallic particles used. Surface topography shows grains agglutinated with binder.



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References

- [1] Project POCTI/ENR/62660/2004 “Development of new spectrally selective coatings with organic pigments for absorbers of solar collectors”, Fundação para a Ciência e Tecnologia.
- [2] M.J. Brites, C. Nunes, S. Vieira, D. Quintino, Lopes Prates, J. Alexandre, V. Teixeira, M.J. Carvalho, Proceedings of CIES 2006–XIII Iberic Congress, and VIII Iber American Congress of Solar Energy, Lisboa, Portugal, 9-10 November 2006.
- [3] A. J. Martins, C. Nunes, M. J. Brites, M. Lopes Prates, V. Teixeira, M. J. Carvalho, Journal of Nanoscience and Nanotechnology, Vol. 8, 1-5, 2008.
- [4] C.Nunes, V.T eixeira, M.L.Prates, N.P .Barradas, and A.D. Sequeira, *Thin Solid Films* 442, 173 (2003).
- [5] M.J.Brites, C.Santos, B.Gigante, S.Nascimento, H.Luftmann, A.Fedoro v, and M.Berberan-Santos, *New J. Chem.* 30, 969 (2006).
- [6] S.Nascimento, M.J.Brites, C.Santos, B.Gigante, A.Fedoro v, and M.Berberan-Santos, *J. Fluoresc.* 16, 245 (2006).
- [7] K.Hara, Y.T achibana, Y.Ohga, A.Shinpo, S.Suga, K.Sayama, H.Sugihara, and H.Arakawa, *Sol. Energy Mater. and Sol. Cells* 77, 89 (2003).
- [8] M.K.Gunde, Z.C.Orel, and M.G.Hutchins, *Sol. Energy Mater Sol. Cells* 80, 239 (2003).
- [9] Z.C.Orel, *Sol. Energy Mater. Sol. Cells* 68, 131 (2000).
- [10] Z.C.Orel, *Sol. Energy Mater. and Sol. Cells* 68, 337 (2001).
- [11] K.Zakrzewska, M.Radecka, A.Kruk, W.Osuch, *Solid State Ionics*, 8404 (2002).
- [12] S.G.Springer, PE.Schmid, R.Sanjines, F.Levy, *Surface and Coating Technology* 151-152 (2002) 51-54.
- [13] J.Y. Kim, EBarnat, E.J. Rymaszewski, T.M. Lu, *J. Vac. Sci. Technology A* 19(2), 429-434, Mar/Apr 2001.
- [14] V.Vancoppenolle, P.Y.Juan, M.Wautelet, J.P.Douchot, M.Hecq, *Surface and coating technology* 116-119 (1999) 933-937.
- [15] S.G.Springer, PE.Schmid, R.Sanjines, F.Levy, *Surface and Coating Technology* 151-152 (2002) 51-54.
- [16] P.S. Henderson, P.J.Kelly, R.D.Arnell, H.Backer, J.W. Bradley, *Surface and Coating Technology* 174-175 (2003) 779-783.
- [17] R.D. Arnell, P.J. Kelly, J.W. Bradley, *Surface and Coating Technology* 188-189 (2004) 158-163.
- [18] N. J. Cherepy, G. P. Smestad, M. Gratzel, J. Z. Zhang, *J. Phys. Chem B* 1997, 101, 9342-9351.
- [19] H.Backer, P.S. Henderson, J.W.Bradley, P.J.Kelly, *Surface and Coating Technology* 174-175 (2003) 909-913.
- [20] A. Belking, Z. Zhao, D. Carter, L. Mahoney, G. McDonough, G. Roche, R. Scholl, H. Walde, Society of Vacuum Coaters, 43rd Annual Techn. Conf. Proc.-Denver, April 15-20, 2000.
- [21] Jindrich Musil, Jan Lestina, Jaroslav Vlcek, Tomás Tolg, *J. Vac. Sci. Technology A* 19(2), 420-424, Mar/Apr 2001.
- [22] I. Safi, *Surface and Coatings Technology*, 127 (2000) 203-219.
- [23] P.J. Kelly, C.F. Beevers, P.S. Henderson, R.D. Arnell, J.W. Bradley, H. Backer, *Surface and Coating Technology*, 174-175, 795-800, 2003.
- [24] Sang-Wong Park, Jae-Eun Heo, *Separation and Purification Technology* 58 (2007) 200-205.