Synthesis of TiO₂ thin films by the SILAR method and study of the influence of annealing on its structural, morphological and optical properties

Síntesis de películas delgadas de TiO₂ por el método SILAR y estudio de la influencia del recocido en las propiedades estructurales, morfológicas y ópticas

F. N. Jiménez-García¹ B. Segura-Giraldo² E. Restrepo-Parra³ G.A. López-López⁴

Recibido 6 de marzo de 2014, aceptado 19 de diciembre de 2014 Received: March 6, 2014 Accepted: December 19, 2014

ABSTRACT

Preparation and characterization of TiO_2 films were made. Films were synthesized on glass substrates by the SILAR (Successive Ionic Layer Adsorption and Reaction) method. The preparation consisted of 150 cycles of a successive and alternate immersion of substrates in the precursor solution and in distilled water at 353 K. Growing was conducted at two conditions of the precursor solution which contained TiCl₃ and NH₂CONH₂: at room temperature and at 343 K. After the growth, films were annealed at 723 K for 2 hours. Regarding characterization, samples were studied using XRD, SEM and UV-Vis. Structural characterization results showed that, in general, the films presented an amorphous crystalline structure except those which were grown with precursor solution at 343 K and thermally treated after the growths, which presented an anatase crystalline structure. Concerning their morphology, a granular structure and a random distribution of a flower-like structure were observed. Grain sizes did not change significantly after annealing. The optical study was carried out taking into account an indirect transition allowed determining the band gap energy to be around 3.1 eV. This value, which is typical for TiO₂, decreases after annealing, usual for this type of films.

Keywords: TiO₂, anatase, SILAR, XRD, SEM, UV-Vis.

RESUMEN

Se prepararon y caracterizaron películas de TiO₂ sobre sustratos de vidrio por el método SILAR (del inglés Successive Ionic Layer Adsorption and Reaction, adsorción y reacción iónica en capas sucesivas). La preparación consistió en una inmersión sucesiva y alternada de los sustratos en una solución precursora y en agua destilada a 353 K durante 150 ciclos. Se hicieron crecimientos a dos condiciones de la solución precursora, la que contenía TiCl₃ y NH₂CONH₂: a temperatura ambiente y a 343 K. Después de los crecimientos, las películas se trataron térmicamente a 723 K durante dos horas. En relación con la caracterización, las muestras fueron estudiadas empleando XRD, SEM y UV-Vis. Los resultados de la caracterización estructural mostraron que las películas, en general, presentaron una estructura cristalina amorfa excepto aquellas que crecieron con solución precursora a 343 K y que fueron tratadas térmicamente después del crecimiento, las que presentaron la fase cristalina anatase. En cuanto a la morfología, se observó una estructura granular y una distribución aleatoria tipo flores cuyos tamaños de grano no cambiaron significativamente con el tratamiento térmico. El estudio óptico se llevó a cabo teniendo en cuenta una transición indirecta permitida, lo que permitió determinar una energía de la

¹ Departamento de Física y Matemática. Universidad Autónoma de Manizales. Colombia. E-mail: francy@autonoma.edu.co

² Departamento de Electrónica. Universidad Autónoma de Manizales. Colombia. E-mail: bsegura@autonoma.edu.co

³ Departamento de Física y Química. Universidad Nacional Sede Manizales. Colombia. E-mail: erestrepopa@unal.edu.co

⁴ Grupo de Investigación en Física y Matemáticas con énfasis en la formación de ingenieros. Universidad Autónoma de Manizales. Colombia. E-mail: gandreslopez@autonoma.edu.co

brecha prohibida alrededor de 3.1 eV; este valor, típico para TiO_2 , disminuyó con el tratamiento térmico, lo que es común para este tipo de películas.

Palabras clave: TiO₂, anatase, SILAR, XRD, SEM, UV-Vis.

INTRODUCTION

Titanium dioxide (TiO₂) is a material of high technological interest because of its excellent chemical, electrical and optical properties such as nontoxicity, wide band gap energy, and transparency in the visible light, good insulating properties, high refractive index and electrochemical stability [1], among others, which may be used in a wide range of applications. Titanium dioxide has been used in photocatalysis, photovoltaic and gas sensing applications, among others, [2-5] and in the field of alternative energy where porous TiO₂ electrodes are used in dye-sensitized solar cells (DSSC) due to their high conversion efficiency [6]. The possibilities for uses of this material in the applications mentioned above, however, are strongly related to their cost of production and their performances. Therefore, the search for low-cost production technologies is an important factor in the future development of these applications [7].

Most of the known thin film production methods have been applied in the synthesis of TiO₂ films, using different methods such as magnetron sputtering [20], sol-gel process [8], electrodeposition [9-10], chemical bath deposition and its modified version, the SILAR (Successive Ionic Layer Adsorption and Reaction) method [11-16]. SILAR is based on immersion of the substrate into separately placed cations and anions follows by a rinsing after each reaction, which enables heterogeneous reaction between the solid phase and the solvated ions in the solution. The SILAR method is ideal for making uniform, compact and crystalline thin films. Due to its simplicity, SILAR exhibits a great number of advantages: compared with other techniques, SILAR does not require a target nor it does require vacuum at any stage of the process; the deposition rate and the thickness of the film can be easily controlled over a wide range by changing the deposition cycles number; it is a very easy way to dope films; although there are no restrictions on substrate dimensions is very convenient in the case of large area deposition.

Even though the SILAR method has been successfully employed for obtaining selenides, sulfide, tellurides and oxides of some metals, only in 2006 a work presenting the deposition of TiO₂ thin films by the SILAR method was reported. This work showed the production of an amorphous structure, even after applying an annealing process at 723 K during 6 hours [13, 14]. In 2009, other report was published regarding to the deposition of TiO₂ thin films using different precursor solutions and carrying out some changes in immersion times and washing times in each solution; nevertheless, the amorphous structure of TiO₂ was remained, even after annealing [15-16]. Therefore, many researches were focused on producing TiO₂ with crystalline structure by using simple and low cost techniques such as the SILAR method.

The aim of this work is to present results of TiO_2 thin films obtained by the SILAR method, with crystalline structure after applying an annealing process. The structural, morphological and optical characterization of as-deposited and annealed films was performed in order to study the influence of the thermal treatment on the films properties.

EXPERIMENTAL DETAILS

In order to obtain TiO₂ thin films by the SILAR method, glass substrates were used. Glass substrates were previously treated before growth following the next procedure: First, glass substrates were washed with detergent. Then, they were immersed in a dilute H₂SO₄ solution (1:10 vol) at the boiling point for one hour, in order to activate the substrate and generate better adherence; they were washed with an ethanol and acetone solution (v/v = 1:1) during 30 minutes and, finally, they were stored in distilled water before being used. The precursor solution used for film growth was prepared by mixing 6 ml of TiCl₃ (15% P.S in HCl approx 10%) with 50 ml of distilled and deionized water. This solution was stirred for 15 minutes at room temperature for obtaining a homogenous solution. The pH of the precursor solution was adjusted by slowly adding a urea solution of 0.2 M (for 1 hour) and constantly stirring until a final pH solution of 0.5 was obtained.

The SILAR method used for the growth consisted of a successive immersion of substrates in three solutions: the precursor solution as the first solution, the second solution was the distilled and deionized water at 353 K and the third solution was the distilled water at room temperature as a rinsing solution. Rotzinger and Gratzel [17] have reported on the kinetics of decomposition of TiCl₃ solution. Reaction of Ti (III) with O₂ is the rate determining step in TiO_2 formation where peroxotitanium (IV) (TiO^{2+}) is formed. The mechanism of TiO₂ film formation by SILAR method can be explained as follows, accordingly to this report. The 0.1M TiCl₃ solution is a source of Ti³⁺, hot water is a source of oxygen, initially this Ti³⁺ is reduce to peroxotitanium (1V) by the next equation:

$$4 Ti^{3+} + O_2 + 2 H_2 O \rightarrow 4 TiO^{2+} + 4 H^+$$
(1)

It is important to note that peroxotitanium (IV) is believed to exist as $Ti(O^{2+})$ in acid solution (pH <1) because is more stable than (TiO^{2+}). An approximation of this reaction is presented next:

$$TiO^{2+} + H_2O_2 \Leftrightarrow Ti(O_2)^{2+} + H_2O \tag{2}$$

Finally, the substrates are then immersed in hot H_2O to convert the peroxotitanium (IV) into TiO_2 by the reactions:

$$TiO^{2+} + OH^- \rightarrow TiO_2 + H^+$$
 (3)

Two conditions of growing were study, In the first one, precursor solution was maintained at room temperature and in the second one at 343 K; this allowed studying which condition generate crystalline films.

This procedure was performed during 150 cycles. Each cycle consisted of the immersion of the substrates in each solution during 10 seconds, employing the next sequence: first the precursor solution, second hot water and finally cold water.

After the growth process, samples were washed with distilled water and dried in air at room temperature

during one hour. Then, several samples were annealed in air following a heating rate of 7 K/min until reaching a temperature of 723 K that was remained constant for two hours. The growth conditions of films and their identification are shown in Table 1.

Table 1. Growth conditions of films

Sample	Precursor solution	Thermal
Identification	temperature	Treatment
M1a	Room Temperature	Without
M1b	Room Temperature	At T=723 K
M2a	At T=353 K	Without
M2b	At T=353 K	At T=723 K

Each growth was performed twice in order to determine their reproducibility; the results obtained were similar in both cases.

The structural, morphological and optical characterization of as-deposited and annealed films was carried out in order to study the property changes caused by the thermal treatment. The structural analysis of the samples was carried out with X-Ray Diffraction (XRD) technique using a diffractometer Siemens D5000. These diffractograms were taken within a range of diffraction angles (2θ) between 15 degree and 80 degree, employing a step of 2deg/ min at room temperature, with CuKa radiation by using a Siemens D5000 diffractometer ($\lambda = 1.5406$ Å). The morphological study was carried out using a Scanning Electron Microscope (SEM) Jeol JSM-6060 LV, Japan. The optical adsorption was measured with a Ultra Violet (UV-Vis) spectrophotometer (Perkin Elmer) in order to determine the band gap energy. These measurements were made at room temperature within a wavelength range between 300 and 500. A glass substrate without coating was measure in order to estimate the measurement correction and obtain only the absorption of films.

RESULTS AND DISCUSSION

Structural Studies

XRD patterns of as-deposited and annealed films for both procedures are shown in Figure 1.

In the case of as-deposited films (M1a and M2a), no crystalline phases of TiO_2 were observed with any of both conditions, which indicate that the asdeposited coating was amorphous in nature. Even the procedure with precursor solution al 343 K is



Figure 1. X-ray diffraction patterns for TiO₂ film: M1a, M1b, M2a, M2b.

not sufficient to promote the crystallinity of the film without thermal treatment as it can be seen in Figure 1 (M2a). Moreover, a wide shoulder around 25° was observed being a typical feature of the glass employed as substrates. In diffractograms belonging to the samples after the annealing process (M1b and M2b) is observed that films obtained with condition one remained amorphous, while those obtained with the second one presented crystalline structure. Some researchers have reported no improvements in the crystalline nature of TiO₂ films when chemical and electrochemical methods were employed [14-18].

For film M2b a polycrystalline structure with peaks (100), (004), (200), (105), (211) and (204) can be observed. These peaks correspond to the tetragonal crystalline structure of the anatase phase in agreement with to the JCPDS standard (#65-5714). In addition to the above mentioned peaks, no other phases of TiO_2 were found. Initially, the film cristallinity was very poor; nevertheless after the annealing process, the sample showed a transformation in the crystalline nature. The crystallinity improved perhaps due to the formation of larger crystallites.

When micro-strains can be neglected, the coherently diffracted domain size can simply be evaluated by the Sherrer's equation [19] given for $D=0.9\lambda/\beta\cos\theta$, where D is the mean diameter of crystallites, λ is the wavelength of the X-ray radiation, β is the average width at half-maximum intensity of the peak (FWHM) after the correction and θ is the angle corresponding to the maximum of diffraction. The value of the average crystallite size was calculated taking into account all the peaks of the difractograms's M2b and based on the data of the Lorentzian deconvolution as shown



Figure 2. Lorentzian deconvolution of XRD pattern for M2b film.

in Figure 2. The value of the average crystallite size for this sample was of 11.72 ± 2 nm. This value is lower that it reported by TiO₂ produced by different techniques like DC reactive magnetron sputtering technique (73 nm) [20] and by sol-gel (around 38 nm) [21]. Nevertheless, values reported in this work are close to those presented by other authors that employed electrochemical methods as Mao-Sung Wu [22] (15, 18, and 22 nm). It could be concluded that chemical and electrochemical methods allow producing films with lower crystallite size. The lower crystallite size of the films grown using chemical and electrochemical methods can be attributed to the low temperature of the growing process, compared with other methods such as magnetron sputtering [20]. Normally, the high temperature favors the atoms mobility on the surface and their nucleation, producing greater grain and crystallite size.

Hereinafter, it will be shown the results for the films obtained with precursor solution at 343 K.

Morphological Studies

Figures 3, 4 and 5 show SEM images of as-deposited and annealed TiO_2 films obtained with precursor solution at 343 K. Figure 3 shows the images taken with 20,000 magnifications, while Figures 4 and 5 were acquired with 10,000 magnifications. SEM images were taken at two different sample regions. The aim of this procedure was to find more general information about their morphology. Then, two formations of representative structures for each sample are shown.

According to Figure 3 (a) and (b), films show a basic morphology of semispherical grains presenting

different sizes combined with a flower-like random formation. Flower-like formations can be due to grain coalescence which makes them grow and, therefore, a larger size structure appears. This type of structures has been reported by different researchers for this material [13, 18] and has also noted in other semiconductors such as the ZnO grown by this method [23].



Figure 3. SEM images of TiO₂ film grown with condition two at 20,000 magnifications a) as-deposited (M2a) b) after annealing (M2b).

From the SEM images shown in Figures 4 and 5, a statistical analysis of grain size distribution was performed for each as-deposited film (Figure 4) and annealed film (Figure 5). A normality test was performed using the modified Saphiro Wilk test. It was found that the grain size distribution does not exhibit a normal behavior. For this reason, goodness-of-fit tests for Gamma distribution were performed using the Kolmogorov-Smirnov Test. It was observed that the grain sizes of as-deposited



Figure 4. a) SEM images of TiO_2 as-deposited film (M2a) grown with condition two of at 10,000 magnifications, b) grain size distribution.



Figure 5. a) SEM images of TiO₂ annealed film (M2b) grown with condition two at 10,000 magnifications, b) grain size distribution.

and annealed films followed a Gamma distribution. From these analyses, the average grain size for the as-deposited film was of 228 ± 94.6 nm, while for the annealed film was of de 203 ± 90.5 nm. This decrease in the grain size can be due to water evaporation with annealing. No visible changes were observed in the grain size.

Optical Studies

In Figure 6, the optical absorption spectra are shown for the as-deposited and annealed TiO_2 films obtained with precursor solution at 343 K, which were examined between 300 and 500 nm. In these spectra, a sudden increase in absorption at wavelengths below 400 nm appeared. Tauc [24] and Mott [25] separately proposed an equation (4) for determining E_g :

$$\alpha h v = B \left(h v - E_g \right)^m \tag{4}$$

Where m=1/2 for a direct allowed transition, m=3/2 for a direct prohibit transition, m=2 for an indirect allowed transition and m=3 for an indirect prohibit transition. *B* is a constant, α is the absorption coefficient and hv is the incident energy. From this equation, the value of E_g can be obtained by correlating the amount $(\alpha hv)^{1/m}$ with hvand extrapolating the linear part to its intersection with the energy axis.



Figure 6. Absorbance spectrum versus wavelength for as-deposited (M2a) and annealed TiO₂ films (M2b) grown with condition two.

Since the absorption coefficient can be calculated as α =2,303 *A/d*, where *d* is film thickness and *A* is the absorbance which can be directly obtained from the measurement performed in the spectrophotometer, it is possible to find the value of E_g using equation (5):

$$Ahv = K \left(hv - E_g \right)^m \tag{5}$$

Where *K* is a constant related to *B* and film thickness. In this case, the correlation is made between $(Ahv)^{1/m}$ with hv and also, the linear part is extrapolated to its intersection with the energy axis.

In the case of TiO_2 , several authors have reported that, for the anatase phase as bulk material, the transition is an indirect allowed transition with a gap of 3.2 eV, while for the colloidal particles with dimensions less than 3 nm the transition was a direct allowed transition with a gap of 3.6 eV [26]. In this study, according to the XRD results, crystallite sizes were around 11 nm. Therefore, fits should be made taking into account an indirect allowed transition (m=2).

Figure 7 shows the respective fits which allowed determining the band gap of films taking into account the absorption spectra. This figure shows that the band gap energy decreases from 3.16 eV to 3.05 eV after the annealing process, being in agreement with the value reported for TiO_2 [26,3]. Many researchers have reported a decrease in the band gap after annealing for chemically deposited metal oxide thin films [27- 28].



Figure 7. Linear adjustment to obtain the band gap energy for M2a y M2b films.

The above mentioned results can explain the differences found in reports of different authors [15-16]. Reports indicate that the gap of films showed values around 3.6 eV, these values were calculated for amorphous films by adjustments of $m=\frac{1}{2}$ which would correspond to colloidal particles. For our results, the band gap around 3.2 eV were calculated for crystalline structure by adjustment

with m=2, which correspond to the films crystallite size of 11 nm.

CONCLUSIONS

 TiO_2 thin films, grown on glass substrates by the SILAR method, showed an amorphous structure of as-deposited films by two procedures. After annealing at 723 K during two hours, the structure of films grown with precursor solution at room temperature was amorphous, while for the obtained with precursor solution at 343 K the anatase crystalline phase was evidenced.

The morphological study revealed that TiO_2 films showed a soft structure with semispherical grains of random sizes and a good coverage of the exposed area of glass substrate. No visible changes were observed in the grain size.

Due to the fact that the crystallite size is around 11 nm, the material shows an optical behavior represented by an indirect allowed transition. Taking into account this type of transition, a decrease in the band gap energy for as-deposited films was observed after annealing.

REFERENCES

- U. Diebold. "The surface science of titanium dioxide". Surface Science Reports. Vol. 48, pp. 53-229. 2003.
- [2] K.D. Darlin. "Progress in Inorganic Chemistry". John Wiley and Sons. Vol. 44. 1997.
- [3] B. O'Regan and M. Gratzel. "A low-cost, high-efficiency solar cell based on dye sensitized colloidal TiO₂ films". Nature. Vol. 353, pp. 737-740. 1991.
- [4] R.L. Pozzo, M.A. Baltanas and A.E. Cassano. "Supported titanium oxide as photocatalyst in water decontamination: state of the art". Catalysis Today. Vol. 39, Issue 3, pp. 219-231. 1997.
- [5] N. Savage, B. Chwieroth, A. Ginwalla, B.R. Patton and S.A. Dutta. "Composite n-p semiconducting titanium oxides as gas sensors". Sens. and Actuators B: Chem. Vol. 79, pp. 17-27. 2001.
- [6] N.G. Park, K.M. Kim, M.G. Kang, K.S. Ryu, S.H. Chang and Y.-J. Shin. "Chemical

sintering of nanoparticles: a methodology for low-temperature fabrication of dye-sensitized TiO_2 films". Adv. Mater. Vol. 17, pp. 2349-2353. 2005.

- [7] E. Vigil, L. Saadoun, R. Rodriguez-clemente, J.A. Ayllon and X. Domenech. "TiO2 thin films grown using microwave-activated solutions". J. Mater. Sci. Lett. Vol. 18, pp. 1067-1069. 1999.
- [8] R. Espinosa, I. Zumeta, J.L. Santana, F. Marinez-Luzardo, B. Gonzalez, S. Docteur and E. Vigil. "Nanocrystalline TiO₂ photosensitized with natural polymers with enhanced efficiency from 400 to 600 nm". Solar. Eng. Mater. Solid Cells Vol. 85, pp. 359-369. 2005.
- [9] Z. Wang, U. Helmersson and P.O. Kall. "Optical properties of anatase TiO₂ thin films prepared by aqueous sol–gel process at low temperature". Thin Solid Films. Vol. 405, pp. 50-54. 2002.
- [10] C.D. Lokhande, B.O. Park, H.S. Park, K.D. Jung and Oh-Shim Joo. "Electrodeposition of TiO₂ and RuO₂ thin films for morphology-dependent applications". Ultramicroscopy. Vol. 105, pp. 267-274. 2005.
- [11] H. Abdullah, A. Amalina and S.Shaari. Solid State Science and Technology. "Study the morphology of tio2 thin films prepared by chemical bath deposition". Vol. 18, Issue 1, pp. 150-154. 2010.
- [12] A. Samuel. Darko, Ebony Maxwell and S. Park. "Photocatalytic activity of TiO₂ nanofilms deposited onto polyvinyl chloride and glass substrates". Thin Solid Films. Vol. 519, pp. 174-177. 2010.
- [13] S.S. Kale, R.S. Mane, H. Chung, M.Y. Yoon, C.D. Lokhande and S.H. Han. "Use of successive ionic layer adsorption and reaction (SILAR) method for amorphous titanium dioxide thin films growth". Applied Surface Science. Vol. 253, pp. 421-424. 2006.
- [14] H.M. Pathan, Sun-Ki Min, J.D. Desai, Kwang-Deog Jung and Oh-Shim Joo. "Preparation and characterization of titanium dioxide thin films by SILAR method". Materials Chemistry and Physics Vol. 97, pp. 5-9. 2006.
- [15] A.M. More, J.L. Gunjakar, C.D. Lokhande and Oh-Shim Joo. "Fabrication of hydrophobic

surface of titanium dioxide films by successive ionic layer adsorption and reaction (SILAR) method". Applied Surface Science. Vol. 255, pp. 6067-6072. 2009.

- [16] U.M. Patil, K.V. Gurav, Oh-Shim Joo and C.D. Lokhande. "Synthesis of photosensitive nanograined TiO₂ thin films by SILAR method". Journal of Alloys and Compounds. Vol. 478, pp. 711-715. 2009.
- [17] F.P. Rotzinger and M. Gratzel. "Characterization of the perhydroxytitanyl(2+) ion in acidic aqueous solution. Products and kinetics of its decomposition". Inorg. Chem. Vol. 26, 3704-3708. 1987.
- [18] L. Zhou, R.C. Hoffmann, Z. Zhao, J. Bill and F. Aldinger. "Chemical bath deposition of thin TiO_2 -anatase films for dielectric applications". Thin Solid Films Vol. 516, pp. 7661-7666. 2008.
- [19] L. Borgese, E. Bontempi, M. Gelfi, L.E. Depero, P. Goudeau, G. Geandier and D. Thiaudiere. "Microstructure and elastic properties of Atomic Layer Deposition TiO2 anatase thin film". Acta Materialia. Vol. 59. pp. 2891-2900. 2011.
- [20] V. Senthilkumar, M. Jayachandran and C. Sanjeeviraja. "Preparation of anatase TiO2 thin films for dye-sensitized solar cells by DC reactive magnetron sputtering technique". Thin Solid Films. Vol. 519, pp. 991- 994. 2010.
- [21] N.N. Dinh, N.Th.T. Oanh, P.D. Long, M. C. Bernard and A.H.L. Goff. "Electrochromic properties of TiO₂ anatase thin films prepared by a dipping sol–gel method". Thin Solid Films. Vol. 423, pp. 70-76. 2003.
- [22] M.S. Wu, M.J. Wang, J.J. Jow, W.D. Yang, C.Y. Hsieh and H.M. Tsai. "Electrochemical fabrication of anatase TiO₂ nanostructure as an anode material for aqueous lithiumion batteries". Journal of Power Sources. Vol. 185, pp. 1420-1424. 2008.
- [23] S.M. Pawar, K.V Gurav, S.W. Shin, D.S Choi, I. K. Kim, C.D. Lokhande, J.I. Rhee and J.H. Kim. "Effect of Bath Temperature on the Properties of Nanocrystalline ZnO Thin Films". Journal of Nanoscience and Nanotechnology. Vol. 10, pp. 3412-3415. 2010.
- [24] J. Tauc and R. Grigorovici. "Optical Properties and Electronic Structure of Amorphous Germanium". Vancu, Phys. Stat. Sol. Vol. 15, pp. 627-637. 1966.

- [25] N.F. Mott and E.A. Davis. "Electronic Processes in Non-Crystalline Materials". Clarendon Press. Oxford. 1979.
- [26] S. Monticone, R. Tufeu, A.V. Kanaev, E. Scolan and C. Sanchez. "Quantum size effect in TiO₂ nanoparticles: does it exist?". Applied Surface Science. Vol. 162-163, pp. 565-570. 2000.
- [27] V.R. Shinde, C.D. Lokhande, R.S. Mane and S.-H. Han. "Hydrophobic and textured ZnO

film deposited buy chemical bath deposition: Annealing effect". Appl. Surf. Sci. Vol. 245, pp. 407- 413. 2004.

[28] S. Karuppuchamy, K. Nonomura, T. Yoshida, T. Sugiura and H. Minoura. "Cathodic electrodeposition of oxide semiconductor thin films and their application to dye-sensitized solar cells". Solid State Ionics. Vol. 151, pp. 19-27. 2002.