Morphology and microstructure of textured SnO₂ thin films obtained by spray pyrolysis and their effect on electrical and optical properties

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Abstract

Tin dioxide thin films on glass substrate with different Zn doping levels were obtained by spray pyrolysis. Their microstructure, preferred crystallographic orientation, electrical and optical properties were extensively studied. The characterization techniques employed were scanning electron microscopy, transmission electron microscopy, atomic force microscopy, X-ray diffraction, electrical conductivity and optical transmission measurements. It was found that the material obtained has a nano-scale texture which characteristic size and orientation strongly depend on the Zn doping level. Doping-induced variations in texture and structure modify both the electrical and optical properties of films (namely, refractive index and transparency). The results obtained are relevant for potential applications of the studied films in gas sensing and photoconductive devices.

Introduction

Tin dioxide based films are wide band gap n-type semiconductors which are attractive from the scientific and technological point of view. Several potential applications have been reported previously, such as: gas sensors[1,2], transparent electrodes [3], photochemical and photoconductive devices in liquid crystal display



[4], gas discharge display, etc. [5]. In addition, it has been pointed out that the material properties could be greatly improved in nano-structured films, especially when formed by nanorods [6]. For instance, the nano-scale texture in tin dioxide films plays an important role, improving the sensitivity of gas sensing devices based in this material [7,8]. Many techniques have been employed to produce, either doped or undoped tin oxide based coatings, such as chemical vapor deposition [9,10], ion-beam assisted deposition, radio frequency magnetron sputtering, spray pyrolysis [11], sol–gel, laser assisted metal-organic, chemical vapor deposition (CVD) [12], etc. Among these techniques, spray pyrolysis has proved to be simple, reproducible and inexpensive, as well as suitable for large area applications.

In general, the properties of textured thin films can be influenced by a specific crystallographic preferred orientation and also by the segregation of impurity atoms at grain boundaries [13]. This paper demonstrates that the spray pyrolysis technique provides a powerful tool to obtain Zn doped tin dioxide films with specific morphology where the texture, size and shape of grains depend on the pyrolysis deposition conditions. Specifically we have found that the Zn concentration in the starting solution determines the growth characteristics, composition, stoichiometry, surface morphology and microstructure of the films. It is shown that the texture has strong influence on the optical and electrical properties.

Experimental details

The samples used in this study were synthesized by the spray pyrolysis technique, which is described elsewhere [7]. The starting solution was formed by a methanol dilution of tin chloride (0.05 M) and zinc acetate, used as a dopant, the



Zn/Sn at.% was varied between 1 and 33.3, that means that the number of Zn atoms was from 1 to 33.3 for every 100 atoms of Sn. Corning 7059 ($2.5 \times 7.5 \text{ cm}^2$) glass slides were used as substrates at a fixed temperature of 773 K (\pm 5 K). Dust and oil filtered air was used as a carrier gas at a pressure and flux of 310 kPa and 4 l/min, respectively.

The spray system was attached onto a mobile stage that provides an oscillating movement to the spray nozzle. For deposition, the oscillating spray nozzle was open during one swept and then closed for the next two; this cycle was repeated for 4 times in all samples. This procedure allowed the deposited material to dry out before the next layer was applied. No structural inhomogeneities along the films were detected by the analytical tools used in the characterization of the films thickness, indicating that the fresh deposited layer followed the same growth characteristics than the layer beneath it. Using this periodic deposition process films with better optical transparency were obtained.

The thickness of films was determined from near normal reflectance spectra using a Filmetrics F-20 device. Table 1 shows the thickness and deposition rates for the samples analyzed in this report, as a function of the Zn/Sn at.% in the starting solution. The notation used for the samples was ZNOX, were X increases with the increase in the Zn/Sn at.%. For the ZNO2 to the ZNO6, X-ray energy dispersive spectrometer (EDS) was unable to detect the presence of Zn in the films; however, the gradual change in film properties suggests an increase in Zn concentration for an increase in X. Surface morphology and microstructure of the films were studied by Atomic Force Microscopy (AFM) and by Scanning Electron Microscopy (SEM).



The former was a Veeco Nanoscope IVa model, operating in a tapping mode, the cantilever resonance frequency was typically around 300 kHz and two different SEM were used, the JSM-5800LV model coupled to an X-ray energy dispersive spectrometer (EDS) and the field emission JSM-7401F operating at 2 kVand 1.5 mm of work distance. Transmission electron micrographs and selected area electron diffraction patterns (SAED) were obtained in a side entry CM-200 transmission electron microscope (TEM) working at 200 kV coupled to a scanning transmission STEM and to a parallel electron energy loss spectroscopy model DigiPEELS 766. For these studies, samples were obtained directly by floating the zinc oxide film from the substrate and mounted on a 1000-mesh copper grids. Elemental analyses of the films were performed by means of EDS using SEM and TEM electron microscopy techniques. The crystal structure of the materials was analyzed using a Philips X-Pert diffractometer operating at 40 keV and 30 mA. The X-ray diffraction (XRD) patterns were obtained using the Cu K α radiation (λ = 0.1542 nm) in the range of 20-80° in the 20 scale at intervals of 0.02°.



Table 1

Zn/Sn at.% (in starting solution), film thickness, deposition rate and Zn/ Sn at.%(in films) for SnO₂:Zn film obtained at 500 °C from alcoholic solution

Sample	Zn/Sn at.% in solution	Thickness (nm)	Deposition rate nm/min	Zn/Sn at.% in films (by EDS)
ZN01	0.0	325	84.5	ND
ZN02	1.0	467	121.3	ND
ZN03	2.9	439	114	ND
ZN04	4.8	390	101	ND
ZN05	6.5	310	85	ND
ZN06	9.1	337	88	ND
ZN07	23.8	274	71	0.5
ZN08	33.3	244	63	1

ND: Not detected by EDS.

The optical measurements, in the UV–Visible range, were carried out using a Lambda-2 Perkin-Elmer Spectrophotometer; the diameter of the optical beam was around 5 mm. The transmission data was taken with a glass sample as a reference, i.e., the reflection from the substrate was substracted. Electrical conductivity with and without illumination was measured with the standard 4-probe technique with the probe separation larger than the film thickness. The electrical conductivity (σ), in the 2dimensional approximation was calculated using the expression $\sigma = I(4.53 \text{ VD})^{-1}$ [14], *I* is the applied current, *V* the induced voltage, and *D* the film thickness. The current and the induced voltage were measured with a 485 Keithley ammeter and a 34401A HP voltmeter with input resistance N 10 G Ω , respectively.

Results and discussion

Composition and growth characteristics

The elemental analysis of all films was performed by EDS. The results show



that the Zn/Sn at.% in the solid film is much lower than that of the starting solution (see Table 1), from the analysis presented latter on in this section, there is evidence that some of the Zn forms aggregates at the grain boundaries. Film thickness was in the range of 240–470 nm, in general thinner films were obtained in samples with the highest dopant concentration (see Table 1).

Morphology and microstructure

Fig. 1 shows the SEM micrographs for two films in Table 1:

a) the undoped ZNO1 and b) the ZNO8 with the highest Zn concentration (33.3 Zn/Sn at.% in the starting solution). It is seen that the grain size in the undoped sample varies between 50 and 200 nm with an average size around 100 nm, whereas in the doped one the grain size is much more uniform, with a smaller average size of approximately 50 nm. In order to visualize more details in the microstructure, i.e., shape and size of grains, a higher magnification image of a selected area, are included at the left lower corner of Fig. 1a and b.

Fig. 2 shows the 3-dimensional AFM surface images for films with three levels of doping: the undoped ZNO1 (a), a slightly doped ZNO2 (b) and the heavily doped ZNO8 (c)





Fig. 1. SEM micrographs of: a) an undoped (ZNO1) and, b) a Zn-doped (ZNO8) SnO₂ sample.

samples. It is observed that a grain size decreases with the increase in Zn/Sn concentration ratio in the starting solution. It is in the range of 100–200 and 50 to 100 nm for the ZNO1 and ZNO2 samples, respectively. For films with the ZNO8 composition, the surface texture is more complex. The AFM images show features with elongated forms, of about 500 nm long, however, it is clear that these stripes



are composed by smaller grains with an average size in the order of 50 nm, certainly smaller than in the two previous micrographs. These results agree with the observed by SEM.

Fig. 3 shows XRD patterns for undoped (ZNO1) and Zndoped (ZNO2–ZNO8) SnO₂ samples. The top pattern corresponds to a standard SnO₂ randomly oriented polycrystalline powder pattern from the JCPDS–ICDD, 2005, with the rutile tetragonal phase. The ZNO1 film shows a XRD pattern similar to that of the standard powder, although with a slight (200) preferred orientation. The ZNO2 sample, with a Zn/Sn at.% of 1 in the starting solution, shows a pattern with a strong (200) preferred orientation. Further increase in the Zn concentration in the starting solution promotes a gradual transition in the preferred orientation from the (200) to the (101). Samples with a Zn/Sn at ratio of 23.8 or higher in the starting solution (ZNO7 and ZNO8) have already a strong (101) preferred orientation. From the XRD data the structure of the SnO₂ films corresponds to the rutile tetragonal phase.

The results presented so far provide information mainly related with the surface and the near-surface layers of the films.









Fig. 2. AFM images of films ZNO1 (a), ZNO2 (b) and ZNO8 (c).





Fig. 3. X-ray diffraction patterns, for undoped (ZNO1) and Zn-doped SnO₂ (ZNO2–ZNO8) films. Top pattern corresponds to a randomly oriented polycrystalline SnO₂ powder.

ZNO1 (a) and a Zn-doped ZNO4 (b) SnO2 samples. Here we observe significant difference in morphology as a function of doping level. In the ZNO1 sample, the crystallites are mostly spherical although some elongated with a small aspect ratio are also observed, the length of these crystallites is of about 200 nm. In the ZNO4 sample, the shape of grains is completely different, practically all grains are rod-like with a length and width of about 250 and 50 nm, respectively. As was



shown by XRD data, the ZNO4 sample shows two preferred orientations, the (200) and the (101), the former being dominant. In samples with a high Zn/Sn at ratio, the elongated crystals have their main axis along the (010) orientation. The SAED patterns, shown at the left lower corner of the TEM micrographs, confirm the XRD results, that is: all SnO2 films are single phase with the tetragonal rutile structure [15], with a preferred orientation which depends on Zn doping level.

Electrical properties

Fig. 5 shows the measured (squares) electrical conductivity as a function of the Zn/Sn at.% in the starting solution, the conductivity was measured using the 4 probe method [16] and each point is the average of 4 measurements, the estimated experimental error is less than 5%. As can be seen, it has an anomalous behavior, it first decreases more than 3 orders of magnitude with the increase of the Zn/Sn at.% to about 5 and then, for higher Zn/Sn concentrations, it increases slowly. Considering that our films are polycrystalline, we have assumed that the measured conductivity corresponds to an effective value which includes the grains and the grain boundaries conductivities. There are many approximations for the description of an effective conductivity of a two-phase system, starting from the classic Maxwell–Wagner model (see a review in [16]).





Fig. 4. TEM microphotographs for: a) an undoped (ZNO1), and b) a Zn-doped (ZNO4) SnO2 samples.





Fig. 5. Electrical conductivity versus Z/Sn at.% in the starting solution.

Brailsford and Hohnke [16] have proposed a model for the conductivity of polycrystalline materials formed by spherical grains surrounded by a shell or grain boundary. We have considered this as the most appropriate model for our materials. The effective conductivity ó obtained from this model is given by:

$$\sigma = \frac{3\sigma_{\rm G} - 2x(\sigma_{\rm G} - \sigma_{\rm GB})}{3 + x(\sigma_{\rm G} - \sigma_{\rm GB})/\sigma_{\rm GB}} \tag{1}$$

Where *x* is the volume fraction of grain boundaries, σ_{G} and σ_{GB} are the conductivities of grain and grain boundary, respectively. First we assume that, for all films, σ_{G} has the value of pure SnO₂, and that this value is measured in the undoped ZNO1 sample. Therefore, all the observed changes in the measured conductivity due to the Zn incorporation are associated with changes in the grain



boundaries conductivity (thus, we assume $\sigma_G \gg \sigma_{GB}$). Under these assumptions, the calculated grain boundary conductivity is shown in Fig. 5 (circles), which has a similar anomalous behavior but does not explain the results obtained. Therefore we conclude that Zn incorporation affects the conductivity of both the crystallites and crystallite boundaries.

Let us propose a possible explanation to the measured conductivity. Considering that both Zn and Sn have practically the same ionic radius (around 0.6 Å, whereas the oxygen ion is twice as big) and very close electronegativity values (1.96 for Sn, 1.65 for Zn and 3.44 for O), it is possible that some of the Zn is substituting the Sn into the SnO₂ lattice. Since Zn has valence 2 instead of 4 as for Sn, Zn will act as an acceptor in the *n*-type tin dioxide, and therefore, the material conductivity decreases with an increase of the doping level in samples with a Zn/Sn ratio up to 5 at.% in the starting solution. This compensating effect (i.e the reduction of conductivity by Zn doping) can be observed up to the solubility limit of Zn in SnO₂; we could not find the appropriate data for tin dioxide, but according to [17], the solubility of Zn in metallic tin is 0.24 at.%, which is probably higher then that of Zn in SnO₂. Based on our EDS data (Table 1) and on the behavior of the measured conductivity we assumed that in samples with Zn in the order or larger the corresponding to the ZNO4 film, most of the incorporated Zn atoms stays at the grain boundaries, and somehow enhance their conductivity. Thus, we attribute the increase in the effective material conductivity, in the Zn/Sn at.% range from 5 to 33, to the increasing contribution of grain boundaries conductivity.

Now we consider that σ_G (σ_{GB} . The expression (1) for this case takes the form



[15]

$$\sigma = \sigma_{\rm G} + (2x/3)\sigma_{\rm GB}.\tag{1a}$$

It is worth to note that Eq. (1a) is equivalent to the corresponding expression of the Maxwell–Wagner model, and also for the frequently used brick layer model, so that the conductivity does not depend much upon the geometry assumed. Using Eq. (1a) and taking that for the growing part of the measure conductivity curve (Zn/Sn at.% at solution \geq 5%), the value of "*x*" is approximately equal to the Zn/Sn at.% at the starting solution, we obtain that the grain boundary specific conductivity in this region has a slight variation from 1.5 to 2.5 (Ω cm)⁻¹. This value is many orders of magnitude less than the metallic Zn conductivity; thus, we propose that the grain boundaries are formed by ZnO layer.

For a rough estimation of the ZnO layer thickness, let us assume that all SnO_2 grains are spheres of the same radius *R* and all are covered with a ZnO layer of thickness *d*. Then for a certain sample volume containing *N* grains, the total tin dioxide volume is:

$$V_1 = N \frac{4}{3} \pi R^3$$

The total volume of ZnO layers can be written as $V_2 = Nd4\pi R^2$.

The volumetric ratio F, of ZnO to SnO2 phases is:

$$F = V_2/V_1 = 3 \ d/R(\approx x).$$
 (2)

Since the density of ZnO and that of SnO₂ are very close (5.6 and 6.85 g/cm³, respectively), the value of *F* defines also the ratio of masses M_2/M_1 . To get from Eq.



(2) the atomic percentage ξ of Zn in relation to Sn, the molecular weights must be taken into account (81.4 for ZnO and 150.7 for SnO₂). Therefore:

$$F = M_2/M_1 = 3 d/R = \xi 81.4/150.7 = 0.54\xi$$

From which:

$$d = 0.54 \ \xi R/3.$$
 (3)

From the minimum of experimental conductivity vs Zn/Sn at.% (Fig. 5), ξ = 0.05 and with a grain size R=50 nm, from Eq. (3) we obtain a ZnO layer thickness d = 4.5 Å. The crystal lattice of ZnO is characterized by the lattice constant a = 4.58 Å. Thus we can say that the minimum of conductivity is observed when a ZnO monolayer is formed on the grain surface. A further increase in the Zn content will evidently increase the grain surface conductivity, and therefore the total conductivity (Eq. (1a)).

To investigate the material photoconductivity, a UV lamp was used as the light source with an output power of 0.22 mW. The reason of using UV light for excitation is because the band gap of SnO₂ is around 4 eV. To characterize the effect of illumination we have chosen the so-called surface resistance, that is, the resistance of a square piece of film which does not depend on the square size and is equal to $Rs=(\sigma D)^{-1}$, σ being a specific conductivity, and *D* the film thickness.

Fig. 6 shows the change of surface resistance Rs induced by illumination (Δ Rs) measured by the 4 probe method versus Zn/Sn at.% ratio in the starting solution for two excitation wavelengths 254 nm (circle points) and 366 nm (square points). The data correspond to the stationary photoconductivity measured after 3 min of



illumination. The results are in good agreement with the dark conductivity variation: up to a Zn/Sn ratio of 5 at.% the material conductivity decreases, therefore, the response to the light increases; for a further increase in the Zn/Sn ratio, it is observed that the effect of the ZnO surface layer reduces the photoconductivity. Photons of larger energies (smaller wavelength) produce greater effects.

To show clearly the relation between the dark conductivity and photoconductivity, we did the following analysis. The dark conductivity for *n*-type semiconductor is σ = *enu* where *e* is the electron charge, *n* and *u* are the concentration and mobility of electrons, respectively. Thus the surface conductivity Rs= $(\sigma D)^{-1} = (An)^{-1}$ where A = euD = const. The illumination increases the concentration of electrons by Δn , so now the new value for the surface conductivity is Rs*= $[A(n + \Delta n)]^{-1}$.

The photoconductivity is then:

$$\Delta \mathbf{Rs} = \mathbf{Rs}^{\sim} - \mathbf{Rs}^{*} = A^{-1} \Delta n / [n(n + \Delta n)].$$
(4)

According to Eq. (4), the photoconductivity can be either inversely proportional to n^2 , when photoconductivity is relatively small (Δn b n), or to n for the case of greater light effects (Δn N n). In other words, photoconductivity increases with a decrease of the dark conductivity either following a quadratic, or a linear behavior. From Figs. 5 and 6, it is deduced that the photoconductivity in our case obeys the quadratic law which means that the photoconductivity variation is definitely larger than the dark conductivity.





Fig. 7. Optical transmission spectra.



Optical properties

Experimental transmission spectra in the range of 300 to 1100 nm for the 8 films are presented in Fig. 7. In all cases clear interference patterns are observed in the transparency region (500–1100 nm) with an average transmission of approximately 80%. From the position of the interference maxima and minima we found the material refractive index. The estimated value is around 2, in good agreement with the literature and with our transmission data (the reflection losses calculated from Fresnel formula, are of approximately 20% of the incident light). As usual, refractive index slightly decreases with an increase of wavelength.

A closer examination of the transmission curves in the transparency region, after excluding the interference effects, shows relatively small variations of transmission as function of the Zn doping level: the average transmission in the spectral range of 600–900 nm is 82% for the undoped ZNO1 sample, for the ZNO2 sample with the smallest Zn content it drops to 80%, then it goes up again to 82% for the ZNO3 and ZNO4 films.

Further increase in Zn content gradually decreases the transmission.

Fig. 8 shows an amplification of the transmission curves in the spectral range of 300–350 nm, this is the wavelength region for which the transition from absorption to transparency occurs, this amplification allow us to see the difference between the samples with different doping level. This difference is not large: for all samples transmission starts at about 300 nm (4.14 eV) which approximately corresponds to the material band gap. However, if we compare the transmission on the curves of Fig.





8 in the region of 310–330 nm, the following features can be noted.

Fig. 8. Initial parts of transmission spectra.

The transmission of the undoped sample ZNO1 at wavelength 320 nm is approximately 30%, and it has a thickness of 325 nm. The transmission of ZNO2 and ZNO3 films, at the same wavelength is very similar for both samples and has a value of 20%, which is lower than of the undoped sample. With further increase of the doping level, the transmission starts growing, reaching 25% for samples with the highest doping. Thus the effect of doping on the transmission at the short



wavelengths region has the same behavior than the observed in the transparency region. In both regions there are sharp changes at the beginning of doping, followed by variations in the opposite direction for higher doping levels. Although, the changes in transmission could be due in part to the film thickness variations, this effect alone do not explain the measured optical properties.

A closer examination of the optical properties of the films can be explained in terms of the observed structural changes as function of Zn doping. We ascribe the doping-induced variations in the transmission at 320 nm to the variations of the effective material density (and corresponding refractive index values) due to the texture changes. To have an idea how the density variations (or those of interatomic spacing in different crystallographic directions) could affect the refractive index, we recall that, according to [18], crystalline SnO₂ (Cassiterite) has an anisotropic refractive index characterized by the following values: n_{α} = 2.006, and n_{β} = 2.097; the first one refers to the light propagation along the *c*-axis, the second along the normal direction to the *c*-axis.

Thus, in undoped sample the *c*-axis is normal to the film, and the light reflection observed corresponds to the smallest refractive index value, therefore the reflection is minimal and the transmission is maximal. The initial Zn-doping changes the

With the increase of the doping level, some other factors could add other effects, such as variation of the effective material density due to the texture changes.

The doping-induced variation of the transmission at 320 nm has qualitatively the same behavior as in the transparency region, so the change of refractive index



due to different directions of light propagation in relation to crystallographic axes also explains part of the experimental observations.

Besides, electron transitions of the type "impurity-band" are active in this spectral region with the photon energy close to the band gap; this could increase the absorption which causes additional reduction of transmission.

In order to provide a better support of the assumption that the Zn doping induced changes in transmission in the transparency region, are related with the variation of refractive index, we calculated the effective refractive index on the basis of transmission data, taking as a rough approximation that transmission is equal to $T = (1 - r)^2$ where "r" is the reflection coefficient, which was calculated using the

Fresnel formula $r = [(n - 1) / (n + 1)]^2$. This approximation substitutes the two

reflective plane "tin dioxide–glass" and "glass–air" by only one plane "tin dioxide–air" which causes a small reduction in the effective refractive index. Using this approximation, we obtained for the ZNO1 undoped sample, with T = 82% a value of n = 1.89, and for the doped ZNO1 sample, with T = 80% a value of n = 1.961; the relative difference between these values is about 3.7% whereas the relative difference between the values n_{α} and n_{β} given above is 4.4%. Thus we see that our explanation is reasonable.

Conclusions

The structural, electrical and optical characteristics of transparent Zn-doped SnO₂ thin films were analyzed as a function of the Zn doping level in the starting



solution. It is shown that the growth habits in the material undergo changes in texture depending on the doping level, which greatly influence other material properties. The electrical conductivity has an anomalous behavior with the Zn doping level. Undoped samples have a conductivity larger than $10^2 (\Omega \text{ cm})^{-1}$, which decreases several orders of magnitude with the initial increase in Zn content, reaching a minimum for intermediate Zn doping levels, a further increase in Zn, results in an increase in conductivity of about one order of magnitude. The decrease in the conductivity is associated to a compensation effect due to the substitution of Sn, in the SnO₂ lattice, by Zn atoms which act as an acceptor impurity. The increase in conductivity is explained assuming that, in the high doping level, segregation of Zn to the grain boundaries takes place forming a thin layer of ZnO. The changes observed in the optical transmission are related with the changes in textural characteristics of the films. For higher Zn doping levels, the nanostructure consist of rodlike crystallites with an anisotropic refractive index, resulting in a propagation of light which depends on crystallite orientation respect to the incident light beam direction. The material photoconductivity, under UV excitation was analyzed, showing extremely high sensitivity to doping. Thus, the electrical and photoelectrical characteristics can be recommended as the appropriate indicators of the doping effect.

Acknowledgements

The authors are thankful to colleagues Enrique Torres, Daniel Lardizabal, Miguel Perez Cortes and L. Licon Padilla for highly valued collaboration and technical assistance. This work was partially supported with the CONACYT project 34310-U.



References

- Burresi, A. Fort, S. Rocchi, B. Serrano, N. Ulivieri, V. Vignoli, Sens. Actuators, B, Chem. 106 (2005) 40.
- [2] O. Wurzinger, G. Reinhardt, Sens. Actuators, B, Chem. 103 (2004) 104.
- [3] T. Fukano, T. Motohiro, Sol. Energy Mater. Sol. Cells 82 (2004) 567.
- [4] U. Betz, M. Kharrazi Olsson, J. Marthy, M.F. Escolá, F. Atamny, Surf. Coat. Technol. 200 (2006) 5751.
- [5] C.G. Granqvist, Handbook of Inorganic Materials, Elsevier, The Netherlands, 1995.
- [6] Paraguay-Delgado, W. Antunez-Flores, M. Miki-Yoshida, A. AguilarElguezabal, P. Santiago, R. Diaz, J.A. Ascencio, Nanotechnology 16 (2005) 688.
- [7] F. Paraguay-Delgado, PhD. Thesis, Centro de Investigación en Materiales Avanzados, México, 2003.
- [8] F. Paraguay, D.J. Morales, W. Estrada, L.E. Andrade, M. Miki-Yoshida, Thin Solid Films 366 (2000) 16.
- [9] V. Baranauskas, T.E.A. Santos, M.A. Schreiner, J.G. Zhao, A. Pellegrini Mamman, C.I. Zamitti Mammana, Sens. Actuators, B, Chem. 85 (2002) 90.
- [10] [10] T.-H. Fang, W.-J. Chang, Appl. Surf. Sci. 252 (2005) 1863.
- [11] F. Paraguay, D.W. Estrada, L.D.R. Acosta, N.E. Andradeb, M.MikiYoshida, Thin Solid Films 350 (1999) 192.
- [12] J. Lančok, A. Santoni, M. Penza, S. Loreti, I. Menicucci, C. Minarini, M.
- [13] Jelinek, Surf. Coat. Technol. 200 (2005) 1057.
- [14] M.A. Maki-Jaskari, T.T. Rantala, V.V. Golovanov, Surf. Sci. 577 (2005) 127.
- [15] H.H. Wieder, Laboratory Notes on Electrical and Galvanomagnetic Measurements, Elsevier Inc., Amsterdam, 1979.



- [16] Powder Diffraction File, Joint Committee on Powder Diffraction Standards, American Society for Testing and Materials (ASTM), Philadelphia, PA, 1996 card 41-1445.
- [17] J.R. Macdonald, W.R. Kenan, Impedance Spectroscopy, Wiley, New York, 1987.
- [18] F. Vnuk, M.N. Ashley, R.W. Smith, J. Mater. Sci. 16 (1981)1171.
- [19] Handbook of Physics and Chemistry, 77th edition, CRC Press, Inc., Boca Raton, 1996.

