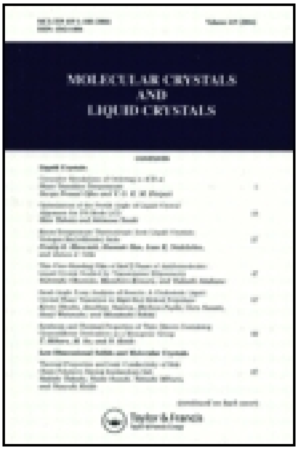

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Optical and Electrochemical Properties of SnO_2:Sb Thin Films Prepared by the Sol-Gel Process

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The sol-gel route offers the advantages of large area deposition in controlling the microstructure of films and producing films containing multiple cations. Tin oxide semiconductors with metal and/or oxide dopants and additives are widely used as transparent-electronically conductive electrodes in electrochromic devices (ECD). The aim of this research is to improve the ion storage capacity of the SnO_2 film by adding antimony. The Sn-doped SnO_2 solutions were prepared using $SnCl_2 \cdot 2H_2O$ and $SbCl_3$ as precursor materials. The films were dip-coated at speed of 12 cm/min and thermally treated at 500°C for 5 min. The electrochemical responses of the films were determined from the cyclic voltammetry and chronoamperometry measurements using $LiClO_4$ in propylene carbonate (1.0 M) as electrolyte. X-ray diffraction (XRD) technique was used to analyze the structure of the prepared film.

Keywords: counter-electrode; SnO_2:Sb film; sol-gel

INTRODUCTION

Due to its excellent physical properties (transparency and conductivity) tin oxide (SnO_2) is an interesting material for various technological applications, such as gas sensor [1], white-pigmented

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conductive paint coating [2] and optical-conductive coating for solar cells [3]. Among the various techniques used for their manufacture is the sol-gel route in combination with dip-coating technique. The latter is particularly very attractive, as it is possible to tailor the properties of the final oxide already at the beginning of the production process, i.e., in solution [4].

A counter electrode requires the ability to store ions driven across the ionic conductor by the potential pulse from the active cathodically or anodically coloring EC films. Its practical use in EC devices is accentuated by being highly transparent in the as-deposited state, and because the insertion of charge followed by ion insertion does not significantly alter their optical transparency. The first investigation of electrochromic and insertion/extraction properties of SnO_2 films was made by Coogan *et al.* [5], who observed a decrease in the redox capacity of fluorinated SnO_2 films after cycling between 0.5 and 3.0 V (vs. Li^+/Li) in a 1 M $LiClO_4$/propylene carbonate (PC) electrolyte. Olivi *et al.* [6] prepared SnO_2 films from the sol obtained by the esterification reaction between citric acid, ethylene glycol, and tin citrate. The authors reported the characteristic behavior of these films as being a reversible electrochemical process in 0.1 M $LiClO_4$/acetonitrile electrolyte. However the resultant inserted/extracted charge was only 4 μC/cm^2. An improvement in the insertion properties was obtained by Orel *et al.* [7], who made electronically conductive Sb:SnO_2 films prepared from aqueous colloidal solutions based on $SnCl_4$. The porous structure of the films exhibited ion-storage capacities of up to 8 mC/cm^2.

Issidorson *et al.* [8] made a systematic investigation of sputtered SnO_2 films in 1 M $LiClO_4$/PC electrolyte. From combined studies of the film electrochemical and optical properties and from Mössbauer spectra, they showed the existence of three different lithium insertion mechanisms at different intercalation levels (x).

Further the effect of the Sb and Mo dopant on the SnO_2 film was studied by Orel *et al.* [9]. The charge capacity of about 11 mC/cm^2 was found for films composed of SnO_2:Sb(7%):Mo(10%) and SnO_2:Mo(10%). On the basis of these experiences the same authors decided to add a higher content of Mo improving the electrochemical properties [10].

EXPERIMENTAL

The Sb-doped SnO_2 solutions were prepared using the same route used by Terrier *et al.* [11]. The SnO_2 solution was obtained by dissolving 8.37 g of $SnCl_2{\cdot}2H_2O$ in 100 ml of absolute ethanol. The antimony solution was simultaneously prepared from a given amount of $SbCl_3$ dissolved in 20 ml of absolute ethanol. The mixture was stirred and heated in a closed vessel. Then the vessel was opened and the solutions were again stirred and heated until the solvent had completely evaporated. Finally, the obtained powder was mixed in 50 ml of absolute ethanol and finally stirred and heated at 50°C for 2 hours. The same procedure was used to obtain the antimony solution and the final doping of the Sb in the solution was 3.5% v/v.

The coatings were deposited by dipping ITO coated glass substrates (Delta, 14Ω/□) previously cleaned. The substrate was immersed into the solution in ambient atmosphere (RH $<$ 50%) and withdrawn at a rate of 12 cm/min. The uniform gel films were then thermally treated at 500°C for 5 min. The resulting coatings with a thickness of about 80 nm per 1 dip were transparent and homogeneous without any visual cracking. The electrochemical measurements were taken using a Solartron 1286 analyzer and a conventional three-electrode cell. The counter electrode was a platinum foil of 1 cm^2 area and the quasi-reference electrode was a silver wire. The electrolyte was a 1.0 M solution of $LiClO_4$ dissolved in propylene carbonate (PC).

RESULTS AND DISCUSSION

Figure 1 shows the effect of the number of layer of SnO_2:Sb films on the cathodic/anodic charge density response for Li^+ intercalation/deintercalation process, for intervals of 30s at potentials of -1.3V and $+1.5$V, respectively. In this figure it can be observed that the increase in the number of layers promotes an increase in the charge density. The maximum value of 40 mC/cm^2 was achieved for the 5-layer film, which was later utilized in this research for the electrochemical characterization.

Cyclic voltammetry (CV) was employed to investigate the effectiveness of the SnO_2:Sb film as a counter electrode for electrochromic devices. The CV of the 10th cycle of the SnO_2:Sb with 5 layers ($\sim$400 nm) is shown in Figure 2, where one can observe the evolution of reduction/oxidation process during the potential sweep from $+1.5$ V to -1.3 V. After the negative potential application an increase was observed in the cathodic current, indicating the oxide reduction promoted by lithium ions intercalation. During the reduction process a slightly blue coloration was also observed in the investigated coating. After the reversal of the potential at -1.3 V, the anodic current started to flow, corresponding to the deintercalation process with an anodic band potential with the maximum at $+0.3$ V.

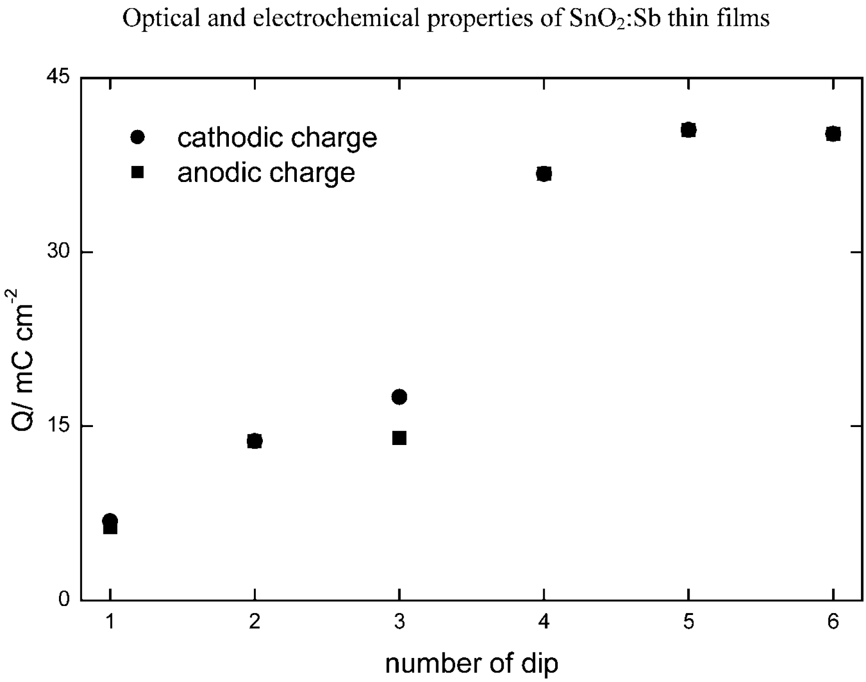

FIGURE 1 Cathodic and anodic charge density of the SnO_2:Sb film as a function the number of layer.

Figure 3 shows the cathodic and anodic charge densities for the SnO_2:Sb film with 5 layers obtained by chronoamperomtry during a potential step at intervals of 30 s between -1.3 V (insertion process) and $+1.5$ V (extraction process). From the Q versus t curve it can be seen that the rate for charge increase is slightly faster than for a thinner film (not shown here), but the charge storage capability is larger for a thicker film. The response time for the system was about 80% of the total charge stored in a half of the intercalation process and the ratio of the coulombic efficiency of the SnO_2:Sb film was about 1.0, showing that the process is reversible.

Figure 4a shows the transmission spectra of the SnO_2:Sb film in the UV-Vis region of electromagnetic spectra (from 350 to 1100 nm), registered in situ at a fixed potential of -1.3 V (insertion process) and $+1.5$ V (extraction process).

The SnO_2:Sn film shows a slight coloration representing the transmittance variation of 8%. The changes of the optical density ΔOD were calculated by equation $\Delta OD = \log(T_b/T_c)$, where T_b and T_c are

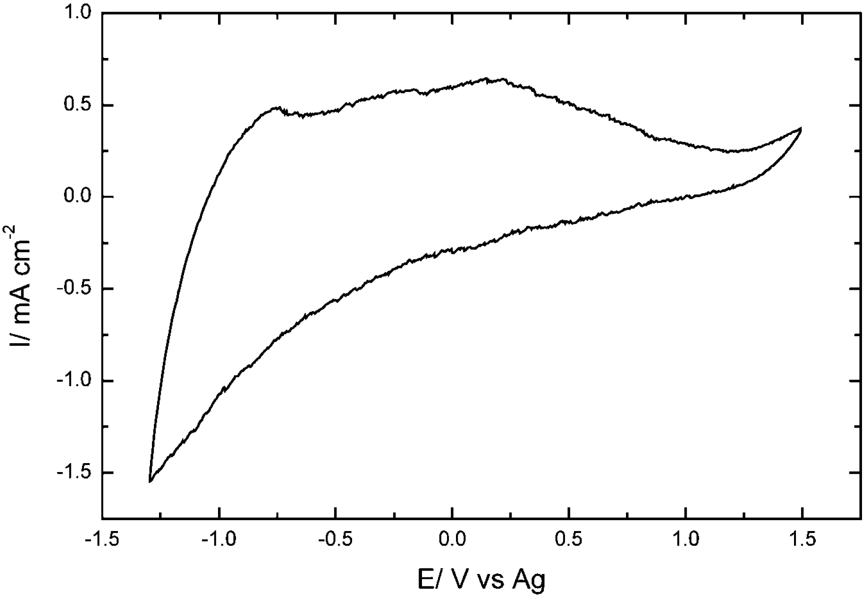

FIGURE 2 Cyclic voltammogram of the SnO_2:Sb film. Potential scan rate of 50 mV/s.

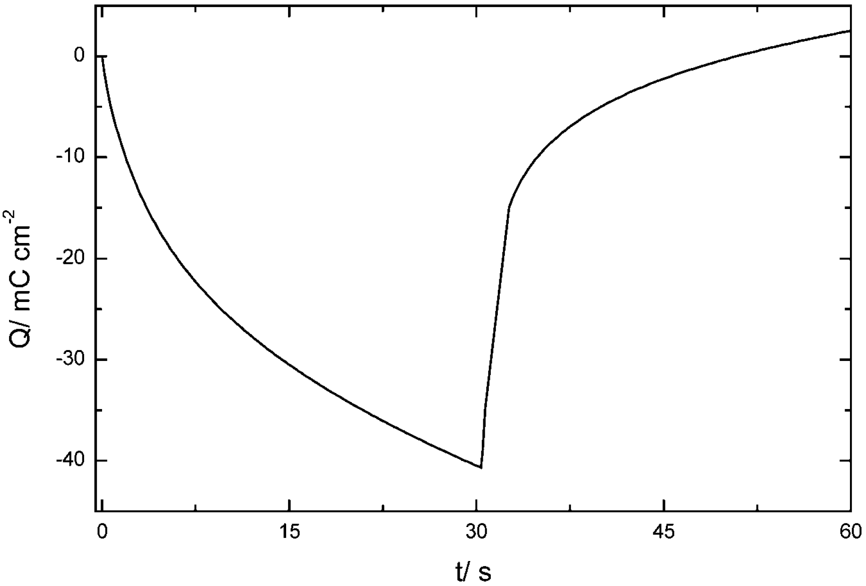

FIGURE 3 Cathodic and anodic transient charge density for SnO_2:Sb 5-layer film; charged at $E = -1.3\,V$ and discharged at $E = +0.7\,V$.

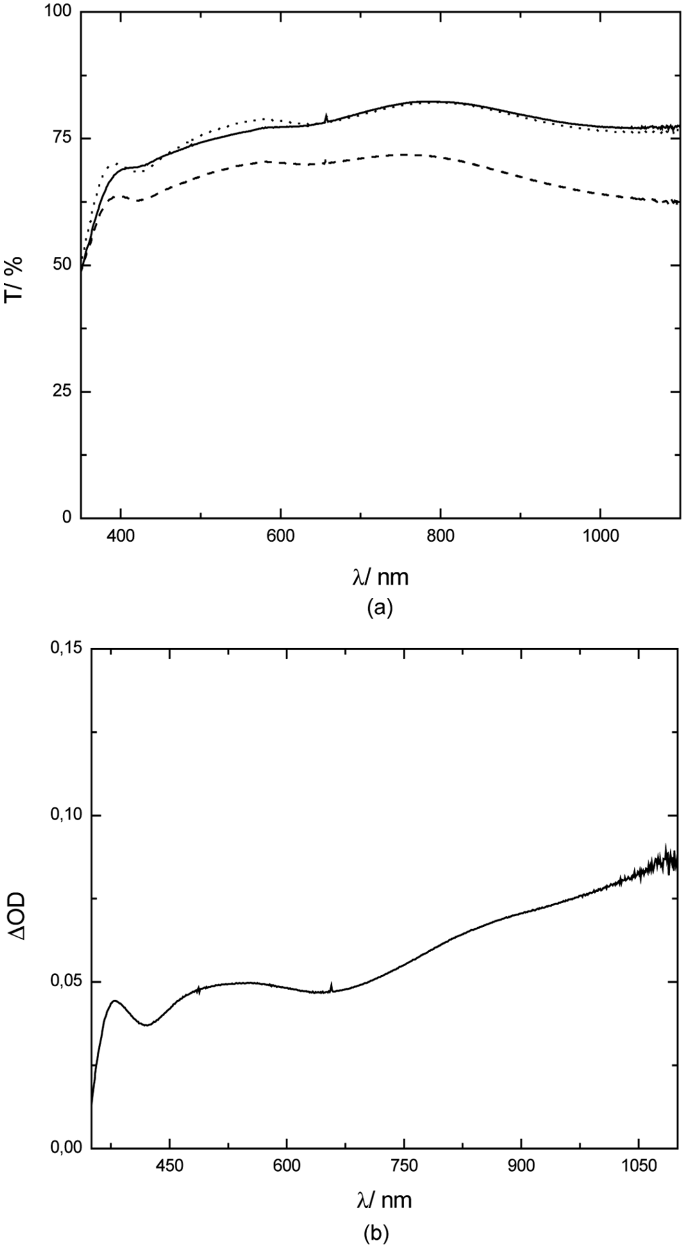

FIGURE 4 (a) Transmittance (UV-Vis) spectra of SnO_2:Sb film with 5-layers, (———, as deposited); (- - -, E = −1.3 V) and (⋯, E = 1.5 V). (b) Optical density of the SnO_2:Sb film.

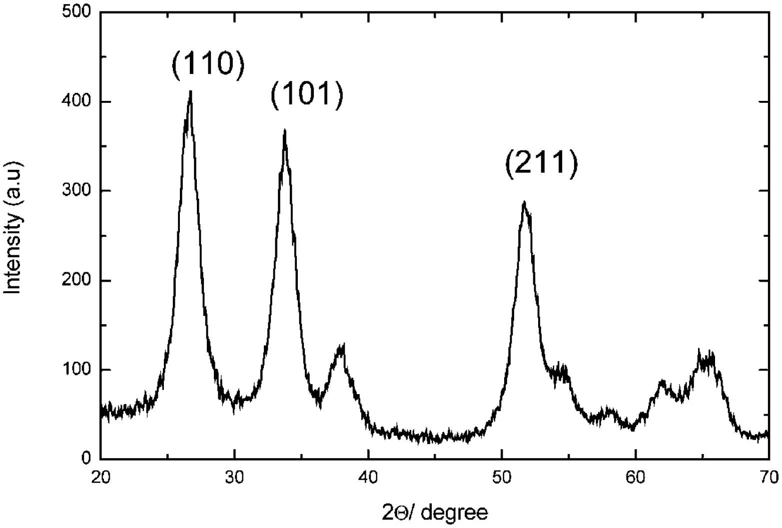

FIGURE 5 X-ray diffraction pattern of the powder of SnO$_2$:Sb.

the transmittance in the bleached and colored processes, respectively (Fig. 4b). The optical density calculated at $\lambda = 550\,\text{nm}$ for the SnO$_2$:Sb film was found to be 0.05 and the coloration efficiency ($\eta = \Delta\text{OD}/\text{Q}$) expressed as the change in optical density (ΔOD) per inserted charge (Q) in C/cm^2 of the film was low. In our case the value obtained was 1.24.

The X-ray diffraction patterns of SnO$_2$:Sb are depicted in Figure 5. The XRD measurements of SnO$_2$:Sb xerogel prepared at a temperature of 500°C revealed several peaks confirming its crystalline state. The spectra were superimposed with the spectra of the International Center for Diffraction Data (JCPDS) library and the best match was found. The significant feature is the large width of the cassiterite (110), (101), and (211) planes, which are clearly observed in the diffraction pattern of SnO$_2$:Sb.

CONCLUSION

The sol-gel route was succesfully used for the preparation of SnO$_2$:Sb film. The 5-layer film obtained from this sol exhibited a good electrochemical and optical properties, with charge density of 40 mC/cm^2 and a variation of the transmittances of 8% between the reduced and oxided state. The X-ray diffraction revealed that the xerogels thermally treated at 500°C are crystalline and show the cassiterite (110), (101), and (211) planes. All the results presented suggest the possible use of the SnO_2:Sb counter-electrode films as ion storage in electrochromic devices.

REFERENCES

[1] Radecka, M., Przewoznik, M., & Zakrzewska, J. (2001). *Thin Solid Films*, *391*, 247.

[2] Jimenez, V. M., Mejias, J. A., Espinos, J. P., & Gonzales-Elipe, A. R. (1996). *Surf. Sci*, *366*, 545.

[3] Liu, P. Y. & Ye, H. (2001). *Vac. Sci. Technol B*, *19*, 1085.

[4] Brinker, C. J. & Scherrer, G. W. (1990). *Sol-Gel Science, The Physics and Chemistry of Sol-Gel Processing*, Academic Press: San Diego.

[5] Cogan, S. F., Andersson, E. J., Plante, T. D., & Rauh, R. D. (1985). *App. Opt.*, *24*, 2282.

[6] Olivi, P., Pereira, E. C., Longo, E., Varela, J., & Bulhões, L. O. S. (1993). *J. Electrochem. Soc.*, *140*, L81.

[7] Orel, B. & Lavrencic Stangar, U. (1994). *J. Electrochem. Soc.*, *141*, L127.

[8] Isidorsson, I., Stromme, M., Gohlin, R., Niklasson, G. A., Granqvist, C. G., & Haggstrom, L. (1995). *Ionics*, *1*, 400.

[9] Orel, B., Lavrencic Stangar, U., Opara, U., Gaberseck, M., & Kalcher, K. (1995). *J. Mater. Chem.*, *5*, 617.

[10] Opara, U., Orel, B., Hocevar, S., & Musevic, I. (1997). *J. Electrochem. Soc.*, *144*, 3398.

[11] Terrier, C., Chatelon, J. P., Berioan, R., & Roger, J. A. (1997). *Thin Solid Films*, *263*, 37.