

## Growth and characterization of $\text{SnO}_x$ :F thin films prepared by pyrolysis of $\text{SnCl}_2$

V. DE LA GARZA-GUADARRAMA, A. SANCHEZ-JUAREZ

*Solar Materials Department, Energy Research Center-UNAM, P.O.Box 34, 62580 Temixco, Morelos, Mexico*  
 E-mail: *asj@mazatl.cie.unam.mx*

A. TIBURCIO-SILVER

*Div. de Estudios de Posgrado, Instituto Tecnológico de Toluca-SEP, P.O.Box 890, 50000 Toluca, Edo. Mex., Mexico*  
 E-mail: *atsilver@prodigy.net.mx*

A. ORTIZ

*Materials Research Institute (IIM)-UNAM, D.F., Mexico*

Metal oxides such as  $\text{ZnO}$ ,  $\text{In}_2\text{O}_3$  and  $\text{SnO}_2$  (undoped and doped) are very interesting materials because of their electrical and optical properties. They are known as transparent conductors due to their high electrical conductivity and optical transmittance. This allows the use of such materials either as a transparent front contact in optoelectronic devices, thin film resistors, heat reflecting coatings, transparent conducting coatings in solar cells, etc. These oxides can be obtained by several techniques; vacuum evaporation, sputtering, chemical vapor deposition (CVD) and spray pyrolysis among them. Among these techniques, spray pyrolysis has demonstrated that thin films with very good properties can be elaborated in a reproducible manner. Furthermore, this technique is very compatible with mass production of thin films. Of the three compounds,  $\text{ZnO}$  is the cheaper to obtain by spray pyrolysis; however, its electrical properties are at present not very good.  $\text{In}_2\text{O}_3$  has the better electrical and optical properties but it is costly (mainly due to the cost of raw materials).  $\text{SnO}_2$  is a good compromise between good electrical and optical properties and production costs. The aim of this study is to try to obtain good  $\text{SnO}_2$  thin films reducing production costs by using industrial raw materials. Results are compared with those obtained by using standard reagent grade compounds, in order to assess their effect on the growth and structure of the FTO thin films.

The  $\text{SnO}_x$  (undoped and fluorine-doped) thin films were deposited onto glass by spray pyrolysis, using  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{NH}_4\text{F}$  as precursors, and several alcohols ( $\text{CH}_3\text{OH}$ ,  $\text{C}_2\text{H}_5\text{OH}$ , either reagent or industrial grade) as solvents. The solution was sprayed onto Pyrex glass substrates heated by a tin bath. The experimental set-up is as described in reference [1]. Air was used as carrier gas. Since our main goal was to reduce production costs, we used  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  because it is cheaper than the  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  compound commonly used in spray pyrolyzed  $\text{SnO}_2$  thin films (cost of  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  is a fifth than that of  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ ). In addition, industrial grade alcohols are more than a half cheaper than their reagent grade counterparts. Then, we studied the influence of different alcoholic solvents, molar concentration of the precursors, F/Sn atomic ratio in the start-

ing solution, and the substrate temperature ( $T_s$ ), on the growth and structural properties of the films obtained. Molar concentrations ranged from 0.05 to 0.2 M. F/Sn atomic ratio was varied from 0.0 to 0.9 in 0.1 steps. The substrate temperature was changed from 375 to 500 °C in 25 °C steps. The solution flow rate,  $F_s$ , was varied from 3 cc/min to 11 cc/min in odd values. The gas flux rate,  $F_g$ , was kept constant at  $F_g = 10$  l/min. The deposition time was fixed at 10 min.

The crystallographic properties of the samples were performed by using X-ray spectroscopy on a Siemens D-500 diffractometer having a Cu cathode with  $\lambda_{\text{K}\alpha 1} = 1.5405$  Å. Layer thickness was measured by an Alpha Step 100 profilometer from Tencor Instruments, and confirmed later by an analytical method developed by Manificier *et al.* [2], based on the spectral evolution of the optical transmittance of the films. Optical spectra were obtained from wavelength measurements on the 300–2500 nm range made with a double beam UV-3101PC NIR-VIS-UV spectrophotometer from Shimadzu.

It is expected that the growth rate of the films increases with the molar concentration of the solution, to an extent. In order to fix the upper limit of molar concentration that could be used without hazing the films, we deposited undoped  $\text{SnO}_2$  thin films at a fixed substrate temperature high enough to assure the complete pyrolysis of the  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  (it is expected that a substrate temperature higher than 400 °C will lead to the thermal decomposition of this compound, as we can find in the literature). Haze on films must be avoided because its presence indicates a homogeneous reaction taking place well over the substrate, and not a heterogeneous reaction on the substrate surface, as desired. Then, fixing the substrate temperature at 450 °C we deposited undoped  $\text{SnO}_2$  thin films from different starting solutions (different solvents and molar concentrations). As a result, we found that even if the growth rate increases as the molar concentration increases—regardless of the solvent—the quality (in terms of haze) of films decreases. Subsequently we used a molar concentration of 0.05 M (the lower limit before films become hazed) for our studies.

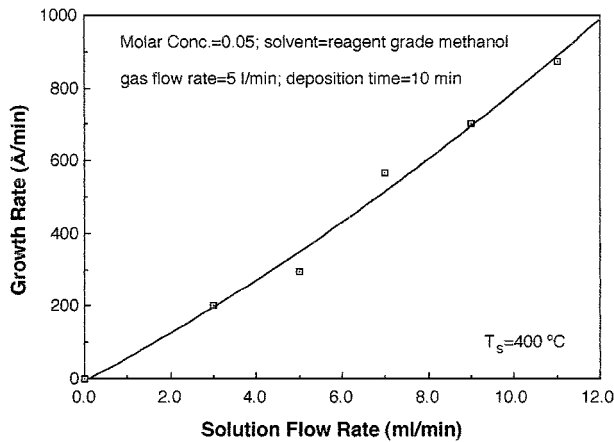


Figure 1 Solution flow rate effect on the growth rate of undoped SnO<sub>2</sub> films deposited at  $T_s = 400^\circ\text{C}$  and from a 0.05 M reagent-grade methanol-based solution.

As Fig. 1 shows, for undoped SnO<sub>2</sub> films deposited from a 0.05 M methanol-based solution, the growth rate increases almost linearly with the solution flow rate, leading to thicker films in very short times. However, on increasing the growth rate, the films become very rough, reducing their optical transmittance due to diffuse reflection on the surface of the films. The roughness of films affected their quality when prepared at flow rates far from 5 cc/min, whichever solvent was used.

Fig. 2 depicts the effect of different solvents on the time dependence of the thickness for undoped SnO<sub>2</sub> films. Thicker films are obtained from an industrial grade solvent. This is an unexpected effect that could be very important from the technological point of view, in reducing production costs of SnO<sub>2</sub> thin films: industrial grade alcohols are more than a half cheaper than their reagent grade counterparts.

Because the use of industrial grade methanol as a solvent seems to lead to some very interesting results, in Fig. 3 we present the temperature dependence of the growth rate for undoped SnO<sub>2</sub> thin films deposited from a 0.05 M solution prepared with this solvent. Growth

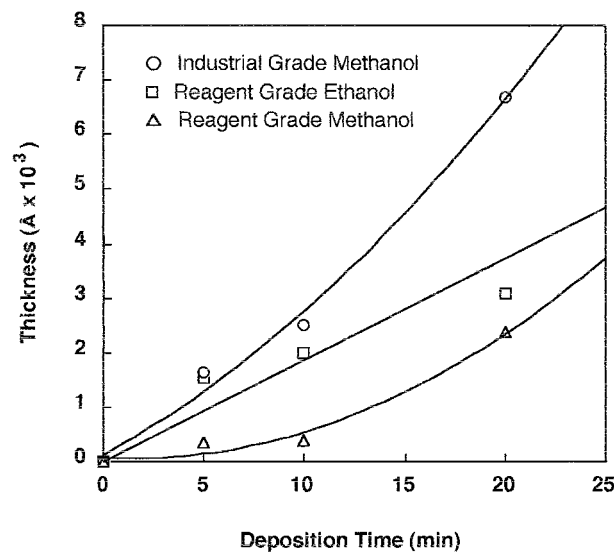


Figure 2 Influence of different solvents on the time dependence of the thickness for undoped SnO<sub>2</sub> films prepared from a 0.05 M-based solution and at  $T_s = 400^\circ\text{C}$ . [ $F_s = 5\text{ cc/min}$ ].

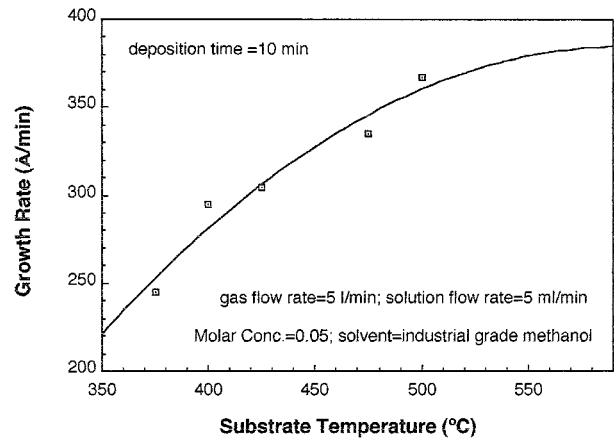


Figure 3 Temperature dependence of the growth rate for undoped SnO<sub>2</sub> thin films deposited from a 0.05 M industrial-grade methanol-based solution. [ $F_s = 5\text{ cc/min}$ ].

rates reach the mass-transport limited kinetics at substrate temperatures higher than 500 °C for these deposition conditions. As expected for SnCl<sub>2</sub> · 2H<sub>2</sub>O (lower oxidation degree of Sn), the growth rates are lower than those obtained for undoped SnO<sub>2</sub> thin films deposited from solutions prepared with SnCl<sub>4</sub> · 5H<sub>2</sub>O (higher oxidation degree of Sn) [see ref. 3].

The effect of the solution flow rate on the X-ray diffraction patterns of undoped SnO<sub>x</sub> thin films obtained at 400 °C, and using methanol industrial grade as solvent, is shown in Fig. 4 (for these films the

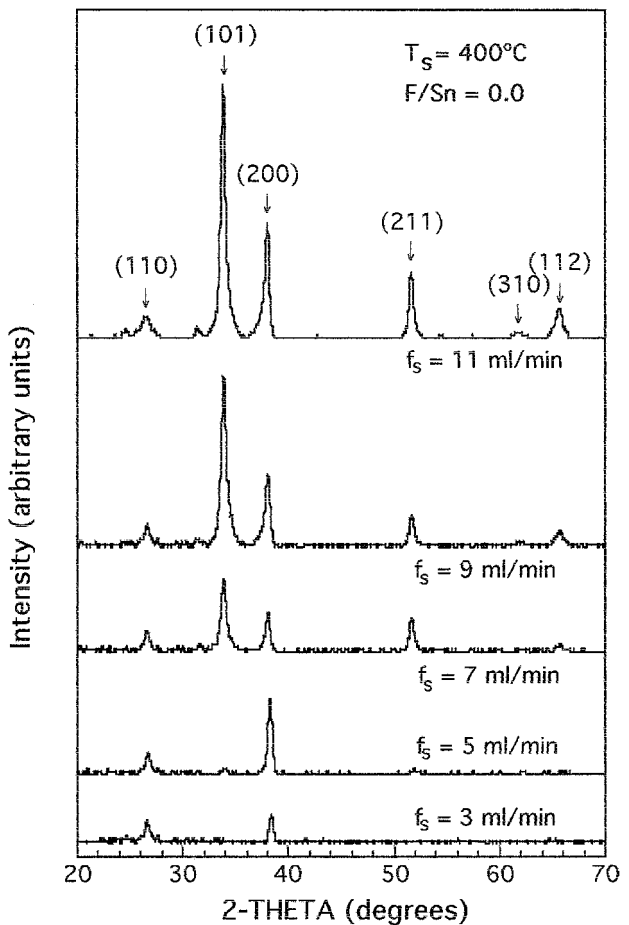


Figure 4 Effect of the solution flow rate on the X-ray diffraction patterns for undoped SnO<sub>x</sub> thin films obtained at 400 °C, and from a 0.05 M industrial-grade methanol-based solution (thickness  $\approx 0.25\ \mu\text{m}$ ).

400 °C substrate temperature was chosen because the undoped samples present a good optical transparency and the best photoresponse). The X-ray diffraction patterns show well defined peaks usually associated with the tetragonal rutile structure of SnO<sub>2</sub> [4]. As we can see, our films have a preferred orientation. The degree of preferred orientation on the undoped SnO<sub>x</sub> films changes with solution flow rate. While at a lower solution flow rates crystallites in the films shows a strongly oriented growth with (200) planes of crystallites being parallel to the surface of the substrate, this behavior become less pronounced with increasing solution flow rate. According to Kim and Chun [5], this may be ascribed to a difference on the growing mode of the films. In the CVD growth process, generally the nucleation rate is reduced as the reactant partial pressures are decreased [6]. Then, following the study of Kim and Chun, at lower solution flow rates the preferred orientation on our films may be due to oriented overgrowth because of preferred nucleation on the growing surface. A decrease in the crystalline orientation as the solution flow rate increases may be explained by the occurrence of homogeneous nucleation, resulting from a random sticking of homogeneous nuclei on the growing surface.

Bélangier *et al.* [7] and Agashe *et al.* [8] calculated the trap densities along various crystal orientations. After these studies, only the (200) planes are free of surface traps. Then, by choosing experimental conditions that leads to films with most of crystallites having (200) planes oriented parallel to the surface of the substrate, we can expect to have the best electrical transport properties across the films. Following our results for undoped SnO<sub>x</sub> films, we deposited a series of doped films from a methanol industrial grade solution, at  $T_s = 400\text{ }^\circ\text{C}$  and  $F_s = 5\text{ ml/min}$ . Fig. 5 shows the measured X-ray diffraction patterns, having a F/Sn atomic ratio in the solution as a parameter, for SnO<sub>x</sub> (undoped and fluorine-doped) thin films obtained at  $T_s = 400\text{ }^\circ\text{C}$  and  $F_s = 5\text{ ml/min}$ , and using methanol industrial grade as solvent. For all the samples, most of crystallites in the films grow with their (200) planes strongly oriented parallel to the substrate surface; we may note that the preferred orientation becomes less pronounced for F/Sn = 0.5. It seems that the sticking of homogeneous nuclei on the growing surface becomes slightly random for this particular fluorine concentration, leading to a partial homogeneous nucleation of crystallites. As Bruneaux *et al.* [9] have shown, fluorine doping increases the density of structural defects inside the individual grains. This could explain the loss of preferred orientation as the F/Sn atomic ratio in the solution increases, but cannot account for the subsequent improvement of the textured growth of films. The reasons for this behavior remain unclear. (Bruneaux's studies were performed using only a ratio F/Sn = 0.7 in the solution kept constant). We may then expect that the crystalline orientation behavior for doped samples will have a significant effect on their electrical and optical properties. These studies are in progress and the overall results will be reported in a forthcoming paper (although preliminary results can be seen in reference [10]).

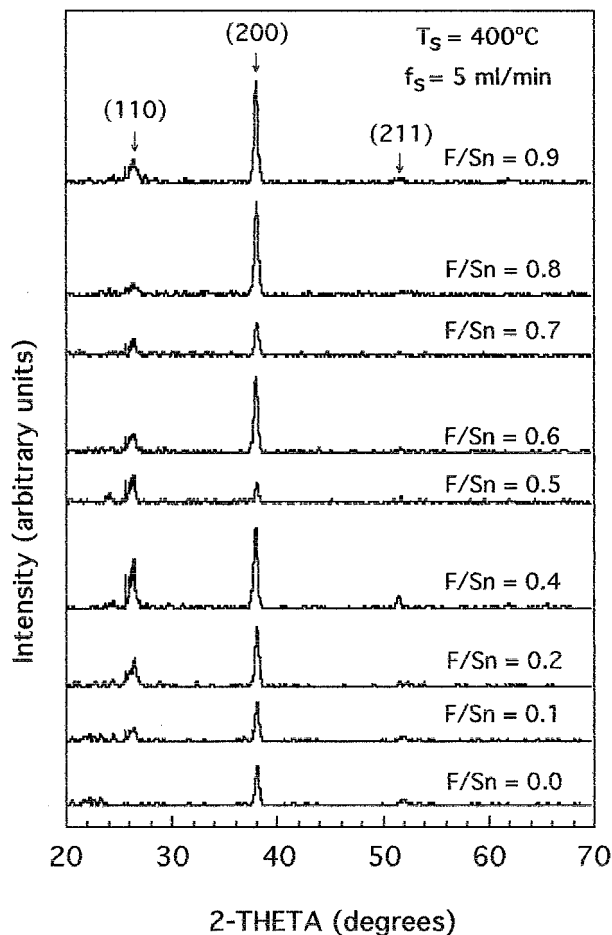


Figure 5 Influence of F/Sn atomic ratio in the solution on the X-ray diffraction patterns for undoped and fluorine-doped SnO<sub>x</sub> thin films obtained at 400 °C and 5 ml/min, and from a 0.05 M industrial-grade methanol-based solution (thickness  $\approx 0.25\text{ }\mu\text{m}$ ).

### Acknowledgment

The authors are much indebted to Mrs. L. Baños for the X-ray diffraction patterns.

### References

1. J. ARANOVICH, A. ORTIZ and H. BUBE, *J. Vac. Sci. Technol.* **16**(4) (1979) 994.
2. J. C. MANIFACIER, J. P. FILLARD and J. GASLOT, *J. Phys. E* **9** (1976) 1002.
3. A. TIBURCIO-SILVER, A. MALDONADO, A. ESCOBOSA, E. SAUCEDO, J. M. MONTOYA and J. A. MORENO, *Appl. Surf. Sci.* **70/71** (1993) 746.
4. Powder Diffraction File No. 21-1250, JCPDS (Center for Diffraction Data, Swarthmore, PA, 1990).
5. K. H. KIM and J. S. CHUN, *Thin Solid Films* **141** (1986) 287.
6. N. S. MURTY and S. R. JAWALEKAR, *ibid.* **102** (1983) 288.
7. D. BÉLANGIER, J. P. DODELET, B. A. LOMBOS and J. I. DICKSON, *J. Electrochem. Soc.* **132** (1985) 1398.
8. C. AGASHE, M. G. TAKWALE, B. R. MARATHE and V. G. BHIDE, *J. Mater. Sci.* **24** (1989) 2628.
9. J. BRUNEAUX, H. CACHET, M. FROMENT and A. MESSAD, *Thin Solid Films* **197** (1991) 129.
10. V. DE LA GARZA-GUADARRAMA, A. SÁNCHEZ-JUAREZ, A. TIBURCIO-SILVER and A. ORTIZ, in Proc. 2nd World Conf. & Exhib. Photovoltaic Solar Ener. Convers., 6-10 July 1998, Vienna, Austria, in press.

Received 6 June  
and accepted 16 August 2000