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Comparison of Optical and Electrical Characteristics of SnO_2-based Thin Films Deposited by Pyrosol from Different Tin Precursors

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Abstract

Tin dioxide-based thin films have regained interest recently for applications where low sheet resistance ($< 10\,\Omega/\square$) and/or high transmission of the visible light (> 80–90%) are requested. In this work we have explored the deposition of SnO_2 films by pyrosol, which is a CVD type process operating at atmospheric pressure. Results concern the compared optical and electrical characteristics of films deposited by three different precursors. © 1999 Elsevier Science Limited. All rights reserved

Keywords: pyrosol, films, electrical properties, optical properties.

1 Introduction

Thin films of non-stoichiometric and/or doped oxides of metals such as tin, indium, zinc and their various alloys, whereby they exhibit high optical transparency (transmission of the visible light > 80–90%) while maintaining low electrical conductivity (sheet resistance $< 10\Omega/\square$) [hence the name transparent conducting oxide (TCO)], have been put to use in numerous applications.[1–4] Some of the methods frequently used to deposit the TCO films are evaporation, sputtering, reactive ion plating, the dip technique, chemical vapor deposition (CVD) processes. Among CVD techniques, the pyrosol process is interesting as it operates at atmospheric pressure[3,4] and offers a relatively inexpensive and mature technology for the deposition of oxides thin films over large areas. After describing the process, this paper compares the electrical and optical characteristics of tin dioxide based thin films deposited from different tin precursors.

2 Description of the Process

A salt of the material to be deposited is dissolved in an appropriate solvent. The usual concentrations range between 0·1 and 0·5 mol^{-1} and the solvents are alcohols or ketones. An ultrasonic excitation (800 kHz) produces an aerosol which is transported at atmospheric pressure towards a heated substrate, which can be glass, ceramic or metal. In the heated zone, the mist is pyrolyzed and film deposition occurs. The temperature has to be carefully controlled to ensure crystallization of the deposit. Usually, it ranges between 300 and 700°C. Lastly, the deposition time reported in the literature ranges between 5 min to several hours. In the present work, the deposition time is between 10 min and 1 h. The experimental conditions used in this study for deposition of crystallized tin dioxide are summarized in Table 1. The film thickness was estimated with a step profiler after chemical etching.[3] The resistivity was determined at room temperature from Van der Pauw's method and the optical transmittance in the visible range (400–800 nm) was measured.[4] Scanning electron microscopy (SEM) of the deposited films was performed with a 30 kV Hitachi 2000 electron microscope.

3 Morphological, Electrical and Optical Characteristics of the SnO_2 based Thin Films

Figure 1(a) and (b) presents micrographs of SnO_2 deposits of similar thickness, i.e. 5000 Å, deposited

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from tin dichloride, $SnCl_2.2H_2O$ [Fig. 1(a)], and tin tetrachloride, $SnCl_4$ [Fig. 1(b)], dissolved in methanol. The surface aspects are quite different. With tin dichloride, the surface of the film contains, in addition to the small crystallites, large crystallites, some of which are twinned.[3] In the case of tin tetrachloride, the crystallite size is more uniform (approximately between 0·3 and 0·8 μm). With these two mineral salts, the crystallite size increases with film thickness.[4] The films obtained with DBTDA are polycrystalline [Fig. 1(c)], the crystal size remains fairly constant with film thickness but the crystallites show less well defined edges and have a smaller average size (approximately 0·2 μm) than those obtained from $SnCl_4$.

The consequences of such morphological differences on the electrical characteristics are shown on Fig. 2. For the mineral salts, the resistance drops in both cases when the thickness increases and the sheet resistance values are one order of magnitude

Table 1. Deposited solutions, temperature and substrates

Solvent	*Salt (concentration)*	*Substrate*	*Deposition temperature*
Methanol	Tin dichloride, $SnCl_2.2H_2O$ (0·1 mol l^{-1})	Corning glass 7059 or ordinary glass coated with Al_2O_3 as a diffusion barrier[3]	450°C
Methanol	Tin tetrachloride, $SnCl_4$ (0·1 mol l^{-1})	id.	450°C
Methanol	Dibutyltindiacetate, noted DBTDA $(C_4H_9)_2Sn(CH_3CO_2)_2$ (0·1 mol l^{-1}) and ammonium fluoride (0·025 mol l^{-1})[4]	id.	500°C

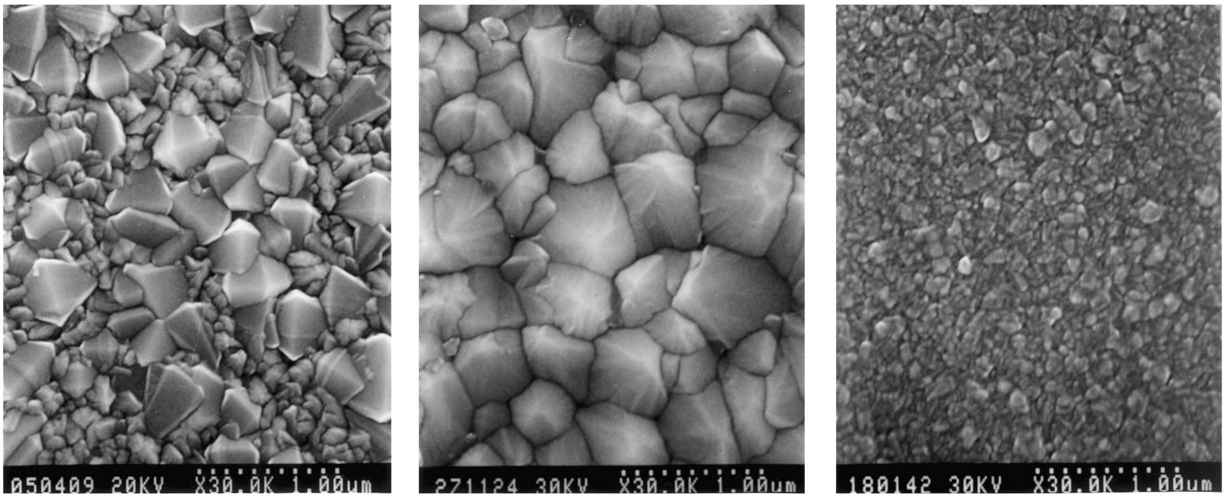

Fig. 1. Micrographs of SnO_2-based films deposited from different salts : (a) $SnCl_2.2H_2O$, (b) $SnCl_4$ and (c) DBTDA.

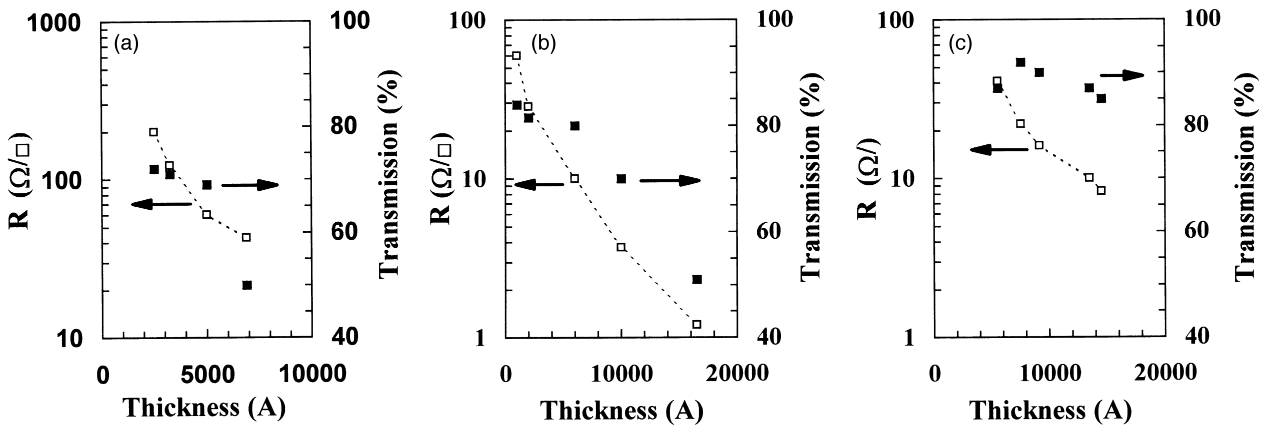

Fig. 2. Sheet resistance (□) and optical transmission of the visible light (■) as a function of thickness for SnO_2 based films deposited from different salts: (a) $SnCl_2.2H_2O$, (b) $SnCl_4$ and (c) DBTDA.

higher with $SnCl_2.2H_2O$ than with $SnCl_4$. With DBTDA, the sheet resistance is of the same order of magnitude as with $SnCl_4$. Concerning the optical characteristics, a strong drop in optical transmission with thickness is observed for deposits obtained from $SnCl_2.2H_2O$ and $SnCl_4$, while it is not the case for films obtained from the DBTDA based solutions. A rather small decrease in optical transmission of visible light with thickness between 0·8 and 1·45 μm is quite remarkable for TCO-type films. It suggests an absence of scattering for visible light in those films which present a grain size (0·2 μm) smaller than the wavelength of transmitted light (0·4–0·8 μm). In the case of mineral salts and in particular with $SnCl_4$, a strong drop in optical transmission correlates with the presence of larger grain size approximately equal to the wavelength of transmitted light; beyond a thickness of 0·7 μm, the light is probably more scattered than transmitted.

The practical implication of such results is the following : with mineral salts, though the sheet resistance can be quite low, in particular while using $SnCl_4$, the deposited thickness should be carefully controlled during the process. With DBTDA, an increase in thickness is not a debilitating factor with respect to optical transmission and allows sufficiently low electrical resistance for applications to be achieved.

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