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# Characterization of SnO<sub>2</sub> Films Prepared Using Tin Tetrachloride and Tetra Methyl Tin Precursors

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**Abstract.** We have investigated the effect of deposition conditions of SnO<sub>2</sub> films, deposited by chemical vapor deposition using tin tetrachloride and tetramethyltin precursors, on the film properties. The type of precursor and the deposition temperature affect the morphology of the films. The structure of the films is determined by the deposition temperature: films deposited at low temperatures show a mixed SnO and SnO<sub>2</sub> phase. The processing temperature and type of substrate determine the impurity content in the films. Electrical properties (e.g. the carrier mobility) and optical properties of the films are affected by the structure and the impurity content in these layers.

## INTRODUCTION

SnO<sub>2</sub> film doped with fluorine is one of the most commonly used transparent conducting oxides because of its ease of fabrication, low cost, and adequate performance. These films are usually deposited by chemical vapor deposition (CVD). For laboratory use, a tetramethyltin (TMT) precursor is used with oxygen, whereas industry uses a tin tetrachloride (SnCl<sub>4</sub>) precursor in the presence of water vapor. In solar cells, SnO<sub>2</sub> is used as a front contact, because it allows most of the solar spectrum through because of its high bandgap. The properties of the films must be tailored to the particular type of device. In the case of amorphous silicon solar cells, SnO<sub>2</sub> films with a high degree of surface texture are necessary to enhance the device performance through light trapping. In the case of CdS/CdTe solar cells, SnO<sub>2</sub> films with minimum roughness are essential to allow the thinnest CdS layers for optimal device performance (1). The deposition conditions must be adjusted to optimize the properties of SnO<sub>2</sub> films for each type of application. To obtain smoother SnO<sub>2</sub> films, growth temperature must be reduced, which, in turn, affects other properties of the films.

In this paper, we present data on the characterization of SnO<sub>2</sub> films prepared by the CVD technique using TMT and SnCl<sub>4</sub> precursors, deposited at different temperatures. Films deposited on borosilicate 7059 substrates and soda-lime substrates (which are used in commercial solar cells) are included in this study. The electro-optical properties of these samples vary, and we have therefore investigated the factors that control these properties.

## EXPERIMENTAL

SnO<sub>2</sub> samples used in this study were all deposited using the CVD technique. Films were deposited on borosilicate 7059 substrates at growth temperatures of 550° and 600°C using TMT as the Sn precursor and O<sub>2</sub> with CBrF<sub>3</sub> as the fluorine dopant source. The thickness of these layers were 0.47 μm and 1 μm, respectively. Films using SnCl<sub>4</sub> as the precursor and water vapor as the source of O<sub>2</sub> were deposited on borosilicate glass and soda-lime substrates at growth temperatures of 450°C and 650°C, respectively. The thickness of these layers were 1 μm and 0.4 μm respectively.

The surface morphology of these films was studied using atomic force microscopy (AFM); the crystal structure was analyzed by X-ray diffraction (XRD); composition analysis was carried out using secondary ion mass spectrometry (SIMS); optical analysis was done by spectrophotometry; and the electrical properties were measured using temperature-dependent Hall and resistivity measurements.

## RESULTS

AFM images of SnO<sub>2</sub> films deposited by the SnCl<sub>4</sub> process and TMT process on borosilicate glass are shown in Fig. 1. The morphology of these films is strongly influenced by the type of precursor used for deposition. Films deposited using TMT precursor have elongated grains, whereas the films deposited using the SnCl<sub>4</sub> precursor result in more rounded grains. The grain size of the films is a function of the type of precursor and the growth temperature. Average grain size and surface roughness data for the films are given in Table I. Grain size increases with growth temperature, and the TMT process gives relatively larger grains. Surface roughness of the films is a function of the morphology of the films, and the roughness of the films is higher for the films deposited by the SnCl<sub>4</sub> process. Surface roughness also increases with growth temperature as a result of the increase in the grain size.

Table I – Average grain size of the films

Substrate type	Growth conditions	Grain size (nm)	RMS Surface roughness (nm)
Borosilicate, 7059	SnCl <sub>4</sub> process, 450°C growth	60	14.7
Soda-lime	SnCl <sub>4</sub> process, 650°C growth	120	30.3
Borosilicate, 7059	TMT process, 550°C growth	100	11.1
Borosilicate, 7059	TMT process, 600°C growth	120	12.8

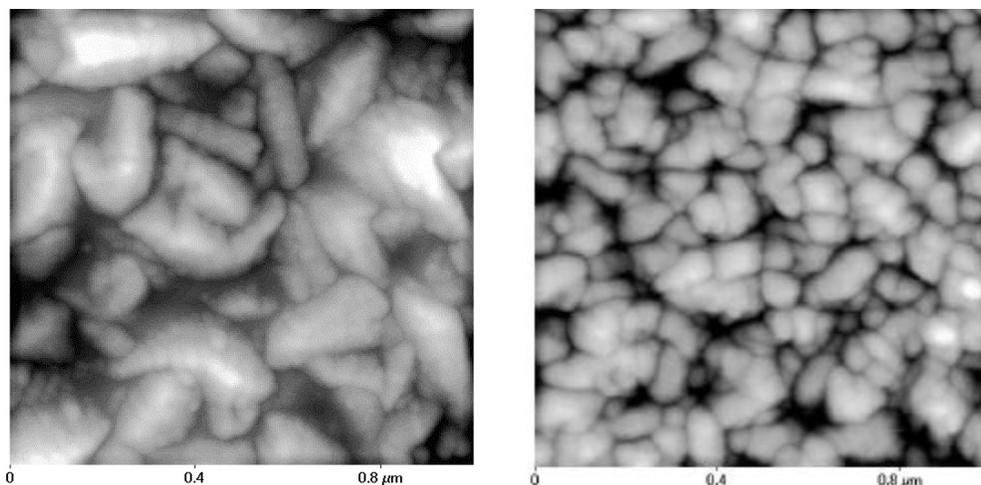


Fig.1 (a) SnO<sub>2</sub> deposited by TMT process on borosilicate 7059 substrate

(b) SnO<sub>2</sub> deposited by SnCl<sub>4</sub> process on borosilicate 7059 substrate

Structural analysis of the samples was carried out using standard  $\theta$ - $2\theta$  X-ray diffraction analysis. XRD data for representative samples are shown in Fig. 2. All films deposited at temperatures  $\sim 550^\circ\text{C}$  with both types of precursors show the presence of single-phase SnO<sub>2</sub>. But there is a difference between the preferred orientation of the films. The preferential orientation of these films is a function of the precursor used and the growth temperature. In comparison, the film deposited at  $450^\circ\text{C}$  using the SnCl<sub>4</sub> precursor has a completely different structure. This film is largely composed of the SnO phase with only a small amount of the SnO<sub>2</sub> phase.

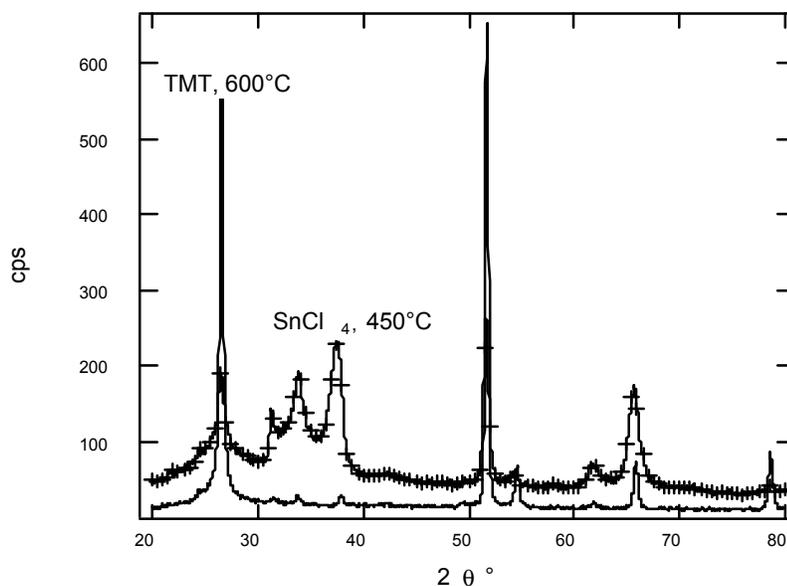


Fig. 2- XRD data for SnO<sub>2</sub> deposited at low and high temperatures

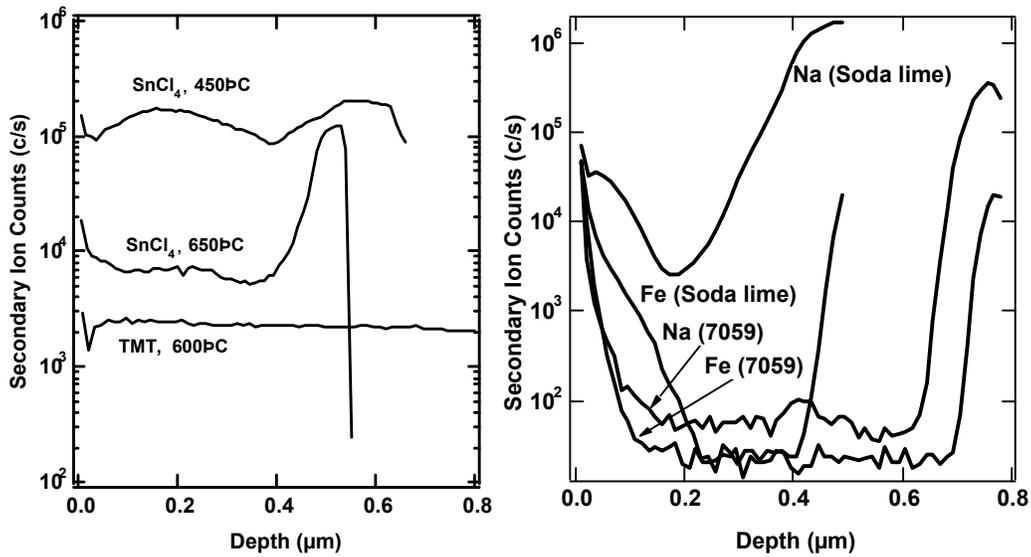


Fig. 3 (a) SIMS data for Cl in SnO<sub>2</sub> films

(b) SIMS data for SnO<sub>2</sub> deposited on sodalime and 7059 borosilicate substrates

SIMS analysis of the samples was carried out to determine the impurities present in these samples. SIMS depth profiles are presented in Fig. 3. Samples deposited using the SnCl<sub>4</sub> precursor show higher levels of Cl as compared to the TMT samples. The sample deposited at 450°C using SnCl<sub>4</sub> has Cl counts an order of magnitude higher than the sample deposited at 650°C. In addition, the 450°C sample also has F counts that are 2-3 times higher than other samples. The sample deposited on the soda-lime substrate shows significantly more Na and Fe in the bulk of the film than for borosilicate substrate.

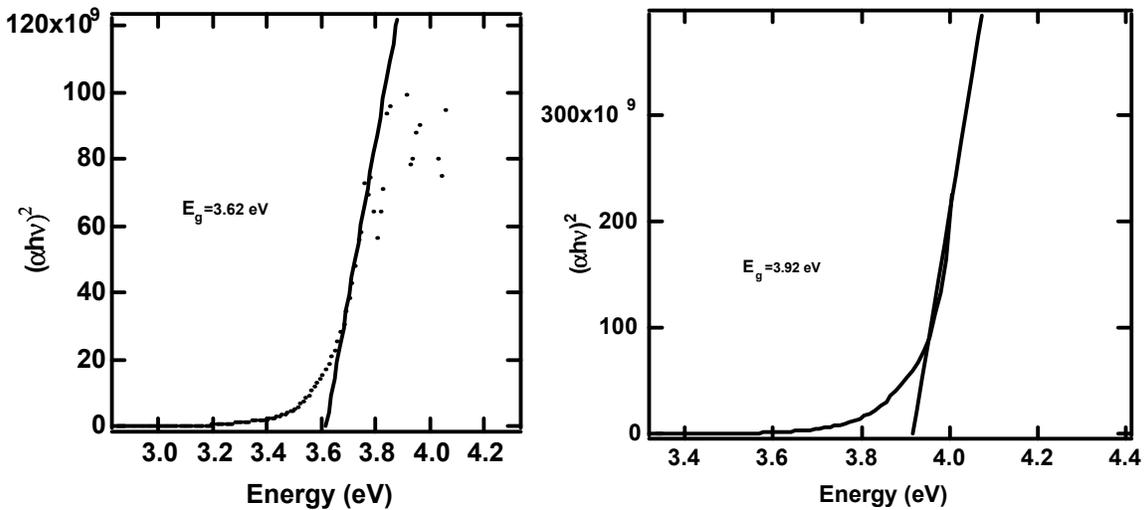


Fig. 4 (a) Optical data for SnO<sub>2</sub> film deposited at 450°C by SnCl<sub>4</sub> process

(b) Optical data for SnO<sub>2</sub> film deposited at 600°C by TMT process

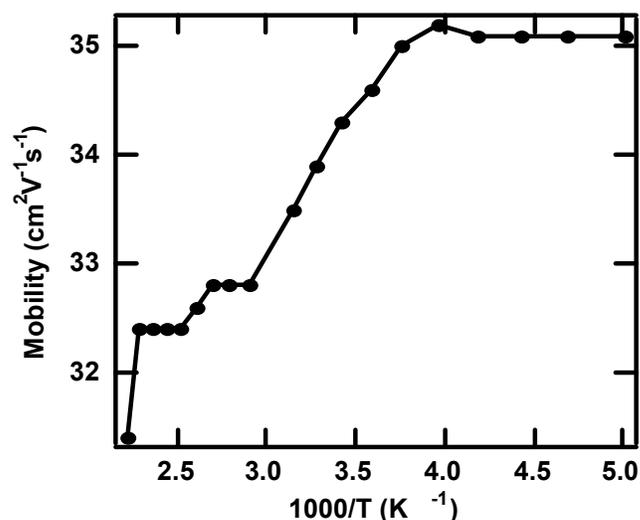


Fig.5 – Hall Mobility vs temp. data for SnO<sub>2</sub> film deposited by TMT process at 600°C

Optical analysis of the samples was carried out to calculate the bandgap. The results are shown in Fig. 4. The bandgaps for the samples deposited at growth temperatures ~ 550°C prepared using both precursors range from 3.92-4.0 eV, whereas the bandgap of the sample deposited at 450°C is considerably lower (3.62 eV). Samples deposited using the SnCl<sub>4</sub> precursor show comparatively higher optical losses at sub-bandgap energies. The sample deposited on the soda-lime substrate has a higher optical loss than the sample deposited on the borosilicate 7059 substrate.

Analysis of the electrical properties of the samples was performed by temperature-dependent Hall measurements in conjunction with resistivity measurements. Room-temperature mobilities of the 450°C sample (SnCl<sub>4</sub>) is 13 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>, the 550°C sample (TMT) is 33 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>, the 600°C sample (TMT) is 35 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>, and the 650°C sample (SnCl<sub>4</sub>) is 28 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>. The temperature dependence of Hall mobility of a representative sample is presented in Fig. 5. For samples deposited at high temperatures (~ 550°C), the mobility remains constant at low temperatures, and it starts to decrease as the temperature increases. For the film deposited at 450°C, the mobility decreases continuously from low temperature to high temperature.

## DISCUSSION

The electrical and optical data of the samples indicate that the properties of the samples grown at higher temperatures (~ 550°C) are similar, whereas the properties of the sample deposited at 450°C are quite different. XRD data show that the growth at higher temperatures ensures complete reaction, resulting in single-phase SnO<sub>2</sub>. The growth at 450°C results in a mixed phase of SnO and SnO<sub>2</sub>. The presence of the SnO phase reduces the bandgap to 3.62 eV, compared to the 3.92-4.0 eV range for the single-phase SnO<sub>2</sub> samples deposited at higher temperature.

Hall mobilities of the TMT samples grown at temperatures  $\sim 550^\circ\text{C}$  on borosilicate substrate are the highest in this set of samples. SIMS analysis shows that these samples contain lower levels of impurities such as Na, Cl, and Fe. The  $\text{SnCl}_4$  sample deposited at  $650^\circ\text{C}$  on a soda-lime substrate shows the presence of Na and Fe impurities as the result of out-diffusion of impurities from the substrate during growth and the presence of Cl due to the precursor. These impurities may cause enhanced carrier scattering thereby reducing the mobility. The  $\text{SnCl}_4$  sample grown at  $450^\circ\text{C}$  has the highest levels of Cl and F as a result of lower-temperature growth. In addition, this sample also contains mixed  $\text{SnO}$  and  $\text{SnO}_2$  phases. Both of these factors result in enhanced scattering of carriers in the sample, thereby reducing the mobility of the film.

Temperature-dependent Hall mobility measurements show that the mobility of the samples grown at  $\sim 550^\circ\text{C}$  is constant at low temperatures. This may be the result of carrier scattering dominated by neutral-impurity scattering and grain-boundary scattering (2). At higher temperatures, the mobility of these samples starts to decrease, possibly due to the contribution from lattice scattering. The data for the sample deposited at  $450^\circ\text{C}$  are noisy and indicate a decrease in the mobility from low to high temperatures. This may be the result of higher levels of impurities, the presence of mixed phases, and the smaller grain size of this sample.

## CONCLUSIONS

The electro-optical properties of  $\text{SnO}_2$  films are determined mainly by the structure of the films and, to a minor extent by the impurity content in these films. Films containing mixed phases of  $\text{SnO}_2$  and  $\text{SnO}$  show reduced bandgaps and reduced carrier mobilities. The phase of tin oxide is determined mainly by the growth temperature and possibly by the precursor used for deposition of the films. Films deposited on soda-lime substrates show the presence of Na and Fe impurities due to out-diffusion of these impurities from the substrate. Films deposited on borosilicate 7059 substrate using the TMT precursor at higher growth temperatures have better electro-optical properties.

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