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Influence of Solvent Volume on Solar Cell Related Electrical and Optical Properties of Antimony Doped Tin Oxide Films Synthesized using a Low-cost Spray Technique

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Abstract: Antimony Doped Tin Oxide (ATO) thin films with high optical transparency and good electrical conductivity are seem to be one of the most appropriate Transparent Conducting Oxide (TCO) layers for use in solar cells which have received significant commercialization. In the present study, ATO films were deposited on glass substrates ($T_s = 350 \pm 5^\circ\text{C}$) from the starting solutions prepared by dissolving the same amount of precursor with different volumes of solvent (10, 20, ..., 50 mL) using an inexpensive and simplified spray technique using perfume atomizer. The influence of solvent volume on the electrical, optical and structural properties was studied. A minimum electrical resistivity (ρ) of $4.4 \times 10^{-4} \Omega \text{ cm}$ is obtained for the ATO film deposited from the lowest solvent volume (10 mL), whereas the ATO film deposited from highest solvent volume (50 mL) exhibits maximum electrical resistivity of $40.96 \times 10^{-4} \Omega \text{ cm}$. Thus, the ρ value increases by nearly one order when the solvent volume increases from 10-50 mL. The predominant role of the presence of oxygen vacancies may be the reason for the lower electrical resistivity of the former case. The average optical transmittance in the visible region is 80%. The obtained optical band gap (E_g) values are found to be increased (3.66-3.88 eV) with the decrease in the solvent volume. From the XRD patterns it is revealed that, all the films show the preferential orientation along the (110) plane irrespective of the solvent volume.

Key words: Transparent conducting oxides, tin oxide films, spray pyrolysis, optoelectric applications, X-ray diffraction

INTRODUCTION

The development of transparent conducting oxides for solar cells, sensor devices and heat reflectors lead to an increasing demand in the fabrication and characterization of these materials. Tin oxide (SnO_2) is a wide band gap (3.6-4.0 eV) semiconductor material with versatile applicability in a large number of physicochemical procedures. Doped tin oxide thin films have been widely used in many optoelectronic devices such as photovoltaic cells, flat panel displays, gas sensors etc. (Tesfamichael *et al.*, 2003; Chen *et al.*, 2009; Lin *et al.*, 2010; Akhtar *et al.*, 2009; Macedo *et al.*, 2008). Due to its unique combined properties such as high transparency in the visible region, high reflectivity for infrared light, low electrical resistivity, high chemical stability and high mechanical hardness.

Different routes of manufacturing methods have been developed such as spray pyrolysis, chemical vapour

deposition, thermal oxidation, vacuum evaporation, pulsed laser deposition, electro-deposition etc. (Russo and Cao, 2008; Chopra *et al.*, 1983; Fang and Chang, 2003; Laghrib *et al.*, 2008; Stanimirova *et al.*, 2005; He *et al.*, 2005). Compared to these methods, the advantages of spray pyrolysis include simplicity, reproducibility, flexible for process modification and low cost, particularly useful for large area applications. The different deposition parameter such as precursor concentration, deposition temperature, doping level and other operation conditions are fixed to enhance the optical, electrical and morphological properties of thin film.

There are numerous investigations well reported (Ravichandran *et al.*, 2009; Shanthi *et al.*, 1999) on the influence of concentration of the precursor solution on the properties of antimony doped tin oxide films, but in this study, to the best of our knowledge, for the first time the effect of solvent volume on the physical properties of ATO films have been investigated and reported.

MATERIALS AND METHODS

Antimony doped tin oxide films were deposited on glass substrates by simplified spray pyrolysis technique using perfume atomizer. Tin (2) chloride [SnCl₂.2H₂O] (1 g) was used as a host precursor and antimony chloride [SbCl₃] was used as dopant precursor (0.02 g). Doubly deionized water was used as solvent. Different sets of SnO₂: Sb films were deposited from starting solutions having different solvent volumes (10, 20, ..., 50 mL). The substrate temperature was fixed at 350±5°C in all cases and it was maintained by a temperature controller with chromel-alumel thermocouple. Each spray cycle followed in the deposition process is consisting of a spray and a 10 s interval. Before starting the deposition cycles, all the substrates were cleaned ultrasonically using organic solvents. To confirm the reproducibility of the films, the experiment is repeated for several times.

Electrical studies were carried out using four-point probe and the transmission spectra of the films were obtained by PerkinElmer (Lambda 35 model) UV-Vis-NIR double beam spectrophotometer. X-ray diffraction patterns were obtained using PANalytical PW 340/60 X'pert PRO X-ray diffractometer which was operated with CuKα (λ = 1.5406 Å) radiation. Thickness of the films is estimated using the profilometer (Surf Test SJ-301).

RESULTS AND DISCUSSION

Electrical studies: The variation in the sheet resistance (R_{sh}) of the ATO films as a function of the solvent volume is shown in Fig. 1. The plot clearly shows that the R_{sh} increases gradually as the solvent volume increases. When the solvent volume is 10 mL, the R_{sh} is minimum (6.79 Ω sq.⁻¹) and the R_{sh} becomes maximum for the highest solvent volume (50 mL). This variation in R_{sh} can be explained on the basis of the following facts which generally cause the creation of free electrons in the SnO₂ lattice:

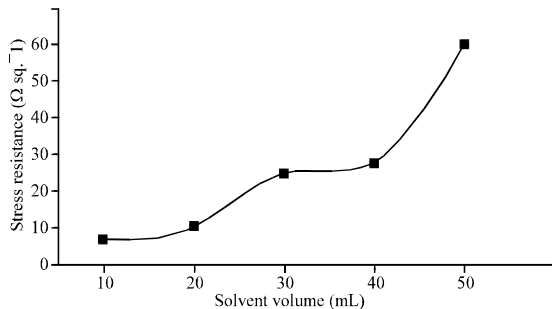


Fig. 1: Variation in sheet resistance (R_{sh}) of ATO films as a function of solvent volume

- The presence of oxygen vacancies in the system
- The interstitial incorporation of Sn⁴⁺ ions in the SnO₂ lattice
- The substitutional incorporation of Sb⁵⁺ ions into the Sn⁴⁺ sites and
- The interstitial incorporation of Sb⁵⁺ ions in the SnO₂ lattice

When, the solvent volume is minimum, the number of oxygen vacancies created in the SnO₂ lattice are larger due to the below mentioned mechanism. For minimum solvent volume, the spray flux density is maximum which causes the number of Sn species reaching the hot substrate in each spray high. Hence, there is a deficiency in the number of oxygen atoms to form a stoichiometric SnO₂ lattice. Each of these oxygen vacancies contributes a pair of free electrons to the system resulting in an increase in the carrier density which in turn reduce the R and the resistivity of the film. In addition to that, the large number of Sn and Sb species in the spray flux results in the incorporation of interstitial Sn⁴⁺ and Sb⁵⁺ in the SnO₂ matrix which also donate more free electrons to the system causing a remarkable decrease in the R_{sh}. But when the solvent volume increases, the flux density decreases correspondingly.

Consequently, the number of oxygen vacancies decreases, along with the gradual fall in the Sn⁴⁺ and Sb⁵⁺ interstitials. Even though, the substitutional incorporation of Sb⁵⁺ in the Sn⁴⁺ sites enhances with the increase in the solvent volume because of the comparatively slower growth rate (Rodriguez-Baez *et al.*, 2006), the net carrier density becomes lesser due to the lesser number of the oxygen vacancies and interstitial Sn⁴⁺ and Sb⁵⁺ ions which play predominant role in reducing the R_{sh}. The electrical resistivity (ρ) values of ATO films for different solvent volumes are tabulated in Table 1.

Structural properties: The X-ray diffraction patterns of the ATO films deposited from different solvent volumes are shown in Fig. 2. The X-ray diffraction profiles clearly showed that the preferential growth is along the (110) plane for all the films irrespective of the solvent volume. The preferred orientation factor f(hkl) of a given diffraction plane which represents the predominance of a particular plane over the others present

Table 1: Electrical and optical parameters of ATO films

| Solvent volume (mL) | Electrical resistivity (ρ)×10 ⁻⁴ (Ω cm) | Optical band gap (E _g) (eV) |
|---------------------|--|---|
| 10 | 4.48 | 3.88 |
| 20 | 7.00 | 3.78 |
| 30 | 16.06 | 3.72 |
| 40 | 19.23 | 3.70 |
| 50 | 40.96 | 3.66 |

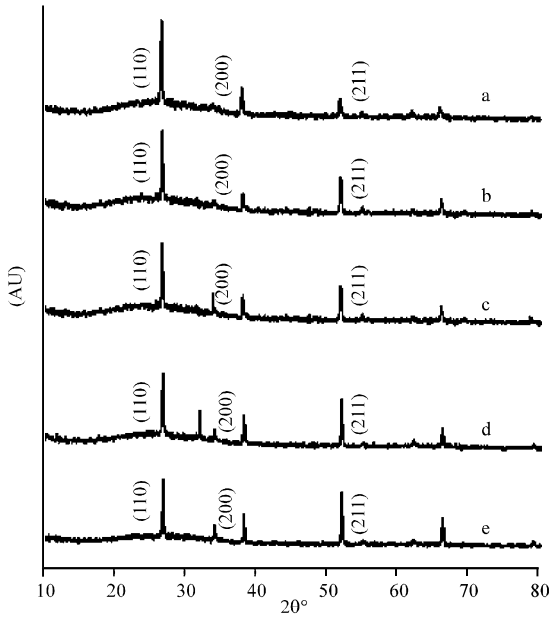


Fig. 2: XRD patterns of the ATO films deposited from a: 10, b: 20, c: 30, d: 40 and e: 50 mL of solvent volume

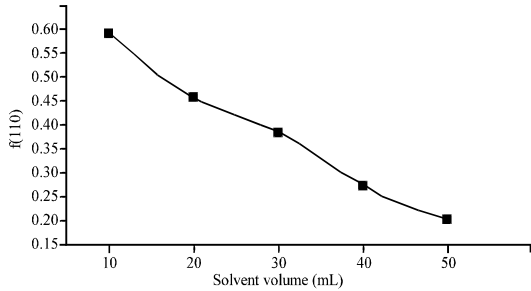


Fig. 3: Variation in f(110) of ATO films as a function of solvent volume

in the pattern can be obtained by estimating the fraction of intensity of the given plane over the sum of the intensities of all the peaks obtained within the 2θ range of $20\text{-}80^\circ$ (Ravichandran and Philominathan, 2009).

The preferential orientation factor is given by the relation:

$$f(hkl) = \frac{I(hkl)}{\sum I(hkl)} \quad (1)$$

In the present study, preferred orientation factor of the (110) plane $f(110)$ gradually decreases (Fig. 3) and the growth along (211) tends to increase which is noted from the increase in (211) peak intensity in the XRD pattern. This structural reorientation may be the reason for the

increase in the R_{sh} when the volume of the solvent increase. Shanthi *et al.* (1999) observed a degradation in the electrical property when the predominance of (110) plane is decreased.

The lattice constants a and c are calculated using the relation (Ravichandran *et al.*, 2010) and the average crystallite size (D) of SnO_2 was determined using Scherrer formula (Sivalingam *et al.*, 2011).

$$1/d^2 = (h^2+k^2)/a^2+(l^2/c^2) \quad (2)$$

$$D = k\lambda/\beta \cos\theta \quad (3)$$

where, k is the shape factor (0.94), λ is the wavelength of $\text{CuK}\alpha$ radiation, β is Full Width at Half Maximum (FWHM) of the most intense diffraction peak and θ is the Bragg angle. The calculated structural parameters are given in Table 2.

The values of a and c are found to be lesser than the standard values (JCPDS card No. 41-1445). These reduction in a and c values may be due to the incorporation of Sb^{5+} ions into the Sn^{4+} sites. This is because of the well known fact that the ionic radius of Sb^{5+} is lesser (62 pm) than that of Sn^{4+} (71 pm). This result confirms that the incorporated Sb atoms are only in the +5 oxidation state rather than 3^+ oxidation state, as the ionic radius is much higher (76 pm), in the case of Sb^{3+} state. By an estimation of the lattice parameters of the SnO_2 : Sb film, Elangovan and Ramamurthi (2003) confirmed the reduction of Sb^{5+} - Sb^{3+} when the doping level of Sb is greater than the critical doping level. Therefore, from these observations we can also conclude that the doping level employed in the present study is below the critical doping limit.

Optical studies: The optical transmission spectra recorded of the ATO films are shown in Fig. 4. The optical Transmittance (T) in the visible range is found to oscillate between 75% and 85%. The oscillatory nature of the spectra is an indicator for the uniformity in the thickness of the films. All the films have sharp absorption edge irrespective of the solvent volume suggesting the good crystallinity of the films. The optical band gap (E_g) of the films are estimated using the plots drawn for the first derivative of the transmittance with respect to the wavelength ($dT/d\lambda$) against average wavelength (λ_{avg}) (Fig. 5) and the values are presented in Table 1. The E_g value is 3.88 eV for 10 mL of solvent volume and the value gradually decreases and attains a minimum (3.66 eV) when the volume of the solvent is maximum. The higher E_g

Table 2: Structural parameters of ATO films

| Solvent volume (mL) | Lattice constant (Å) | | Crystallite size (D) (nm) | No. of crystallites per unit area $N \times 10^{15}$ | Dislocation density $\delta \times 10^{14}$ (lines m^{-2}) | Preferential orientation factor f(110) |
|---------------------|----------------------|-------|---------------------------|--|---|--|
| | a | c | | | | |
| 10 | 4.713 | 3.189 | 59.38 | 6.0282 | 2.836 | 0.5904 |
| 20 | 4.714 | 3.185 | 50.89 | 6.7010 | 3.836 | 0.4557 |
| 30 | 4.713 | 3.183 | 67.86 | 2.5580 | 2.172 | 0.3843 |
| 40 | 4.72 | 3.182 | 54.28 | 5.7123 | 3.394 | 0.2722 |
| 50 | 4.721 | 3.180 | 27.26 | 3.7340 | 1.345 | 0.2043 |

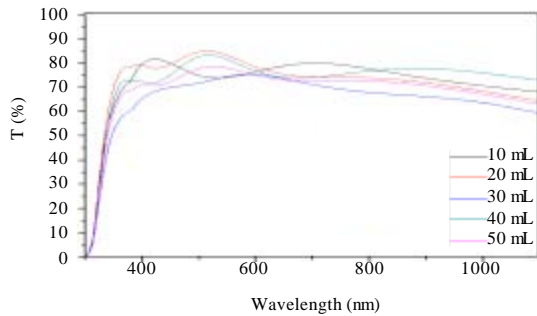


Fig. 4: Transmission spectra (T) of ATO films deposited with different solvent volume

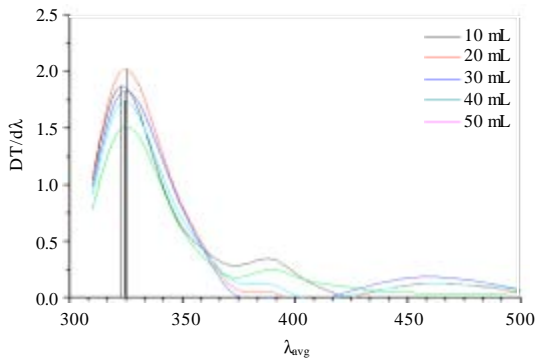


Fig. 5: Plots of $dT/d\lambda$ vs. λ_{Avg} deposited with different solvent volume

value in the case of lower solvent volume may be attributed to the Moss-Burstein effect (Muruganatham *et al.*, 2011).

CONCLUSION

Thin films of antimony doped tin oxide were fabricated successfully from starting solutions having different solvent volumes and their electrical, structural and optical properties were studied. The preferred growth of the film is along the (110) plane for all solvent volumes. The electrical resistivity is found to be minimum ($4.48 \times 10^{-4} \Omega \text{ cm}$) and the optical bandgap is maximum (3.88 eV) when the solvent volume is minimum. From the results, we can conclude that the film prepared from

lowest solvent volume has good transparent conducting properties suitable for transparent electrode applications.

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