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Structural, electrical and optical properties of ATO thin films fabricated by dip coating method

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ABSTRACT

Antimony-doped tin oxide ATO thin films were prepared by dip coating method. The effect of antimony doping on the structural, electrical and optical properties of tin oxide thin films were investigated. Tin(II) chloride dehydrate ($\text{SnCl}_2 \cdot 4\text{H}_2\text{O}$) and antimony(III) chloride (SbCl_3) were used as a host and a dopant precursor. X-ray diffraction analysis showed that the non-doped SnO_2 thin film had a preferred (211) orientation, but as the Sb-doping concentration increased, a preferred (200) orientation was observed. The lowest resistivity (about $5.4 \times 10^{-3} \Omega \cdot \text{cm}$) was obtained for the 2 at.% Sb-doped films. Antimony-doping led to an increase in the carrier concentration and a decrease in Hall mobility. The transmittance of ATO films was observed to increase to 96% at 2 at. % Sb-doping, and then it is decreased for higher level of antimony doping. © 2011 Trade Science Inc. - INDIA

INTRODUCTION

Transparent conducting oxide (TCO) films are widely used in a variety of optoelectronic devices such as solar cells, displays and electrochromic devices. In recent years, there has been growing interest in the application of TCO films as electrodes in solar cell devices. Among the TCO films, the most appropriate material for the application seems to be tin oxide films, which are chemically inert, mechanically hard and heat-resistant. In addition, they exhibit low electrical resistivity and high optical transmittance. Either doped or non-doped tin oxide thin films can be fabricated by a number of techniques: chemical vapor deposition^[1], sputtering^[2], sol-gel coating^[3] and spray pyrolysis^[4-6]. The sol-gel method has such advantages as cheap cost and flexible deposition technique at hand. Such properties can be improved by doping the tin oxide with, for example, antimony (Sb), indium (In) or fluorine (F). In fact, by increasing the doping concentra-

tion (>2%) a degenerate semiconductor is formed, displaying higher σ values ($>103 \Omega^{-1} \text{cm}^{-1}$). Since this doping level is not too high, doped- SnO_2 thin films are transparent for visible light, which make them useful for a device application point of view. Then, the nature, quantity, and structural distribution of the doping are important factors for the electrical properties of SnO_2 ^[7].

The current study investigated the characteristics of Sb-doped SnO_2 thin films prepared by dip coating technique. The structural, electrical, and optical properties of the thin films were examined in relationship to the increase in the antimony amount.

EXPERIMENTAL DETAILS

The antimony-doped tin dioxide sols were prepared using the same methodology which was utilized in our previous literature^[8]. The SnO_2 solution was obtained by dissolving 2.01 g of $\text{SnCl}_4 \cdot 4\text{H}_2\text{O}$ in 25 ml of absolute

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ethanol. To achieve Sb doping, antimony trichloride (SbCl_3) was added to the precursor solution. The amount of SbCl_3 to be added depends on the desired doping concentration. The doping concentration was varied from 0–7 at. %. The solution was stirred at 70°C for 6 h in a closed container for the homogenous mixing of the solution and then aged in air for 24 h, i.e., until the solid materials had dissolved. The thin films were deposited by the dip-coating technique on glass substrates, which had been cleaned ultrasonically in acetone, rinsed in DI water, and then dried by N_2 blowing. The clean glass substrates were dipped vertically and carefully into the sol, left for a short time, and withdrawn from the bath at withdrawal speeds in the range from 1 mm/s to 10 mm/s. This was followed by drying and then sintering of the films between 400 and 550°C for periods ranging from 6 to 24 h. For obtaining higher thickness films, the sequence of dipping, drying and then dipping again was performed a number of times. However, the sintering was done only after the final dipping. The thickness of the films increased almost linearly with respect to the number of times of dipping. The films were kept at 25°C and humidity of 40% RH. All measurements were performed in the same conditions and after the final annealing. The film thickness, t was measured with a Tencor P10 Profilometer. The measurement accuracy of this equipment for the thickness measurement is 0.1 nm. The sheet resistance, R , of the films was measured by the linear four-point method. The electrical resistivity, ρ was determined by the relation $\rho = Rt$. The optical transmittance of the films was measured using a UV-visible spectrophotometer (Cary 500). Crystal structure identification and crystal size analysis were carried out by X-ray diffraction XDS 2000, Scintac Inc., USA with $\text{CuK}\alpha$ radiation source, and scan rate of $2^\circ/\text{min}$.

RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of the sol-gel ATO thin films with a 220 nm thickness deposited at 550°C as a function of Sb-doping concentration. The preferred orientation changed with Sb-doping. The non-doped SnO_2 thin films had a preferred (211) orientation. However, as the Sb-doping amount increased, the intensity of the (211) peak decreased and the (200) peak-intensity increased. Thus, the preferred (200) orientation was observed for 2-7 at.% Sb-doped films.

The preferred (200) orientation was also reported by Elangovan et al.^[9]. This behavior with Sb-doping implies that in the present case antimony incorporation in SnO_2 lattice has not affected the structural properties to a considerable extent. On the other hand, for higher dopant levels, the incorporation would take place at interstitial sites and some precipitation like antimony oxides (Sb_2O_3 , Sb_2O_4 and Sb_2O_5) could be induced^[10]. As a result, with the increase of doping concentration, the deposited films lost the crystallinity, and the preferred orientation growth of SnO_2 films may be suppressed by the precipitation. In the present case, antimony incorporation in SnO_2 lattice has not affected the structural properties to a considerable extent. It is also clear that in Figure 1 the crystallinity improves initially with antimony doping up to 7 at.% in the present case, but it decreases progressively beyond 7 at.% doping concentration, as observed by Shanthy et al.^[11].

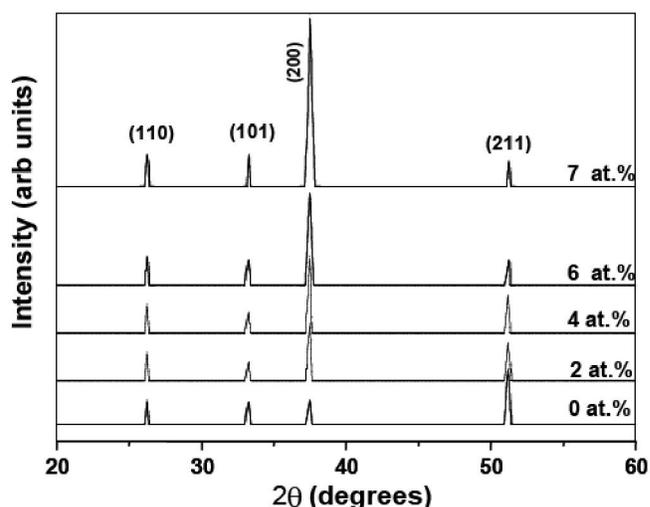


Figure 1 : XRD patterns of the sol-gel ATO thin films deposited at 550°C as a function of Sb-doping concentration.

The effect of doping on the electrical properties of ATO thin films has been investigated. Figure 2 shows the variation of the resistivity (ρ) with different Sb doping concentration (at. %). The resistivity of ATO thin films decreases initially with increase in the Sb doping concentration to about $4 \times 10^{-4} \Omega \cdot \text{cm}$ for 2 at.% of Sb, but increases again for further doping. The observed minimum is significantly less than that for pure SnO_2 thin films ($5.4 \times 10^{-3} \Omega \cdot \text{cm}$). The decrease in resistivity which may be attributed due to the substitution of Sn^{4+} by Sb^{5+} ^[11], as their ionic radii match (Sn^{4+} 0.071 nm and Sb^{5+} 0.065 nm). It is observed that this substitution increases the carrier

concentration and thereby decreases resistivity. Thus, we could obtain the thin films which have the lowest resistivity at 2 at.% Sb-doping level. The resistivity ρ is proportional to the reciprocal of the product of carrier concentration n and Hall mobility μ , as in the following equation:

$$\rho = \frac{1}{ne\mu} \quad (1)$$

As shown in Figure 3, Hall mobility decreased from 0.9024 to 0.2901 cm^2/Vs with Sb-doping. The increase in Hall mobility may be attributed to the (1) increase in the addition of antimony at the tin site and (2) a decrease in grain boundary scattering. It is known that grain boundary scattering and ionized impurity scattering are two major scattering mechanisms, determining the mobility variation of such extrinsic, doped semiconductors (102, 213).

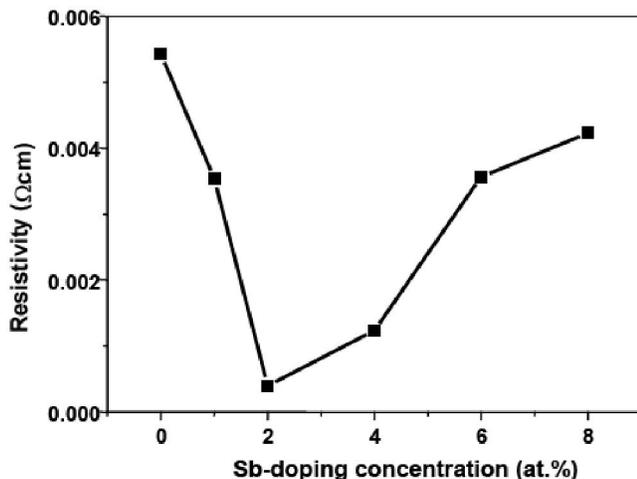


Figure 2 : Resistivity of ATO thin films with the Sb-doping concentration.

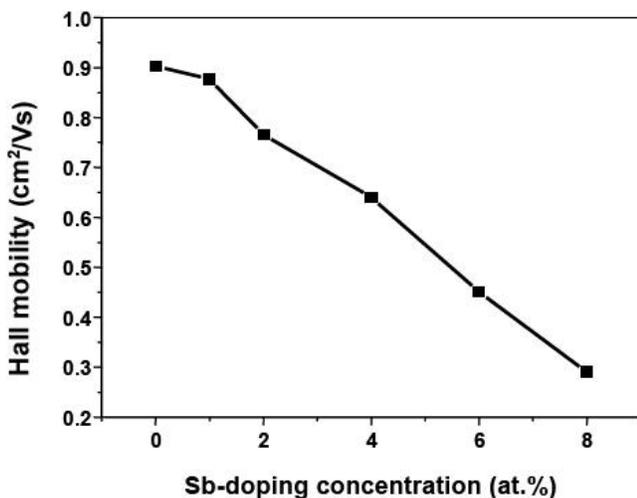


Figure 3 : Hall mobility of ATO thin films as a function of Sb-doping concentration.

The resultant mobility is given by

$$1/\mu = 1/\mu_{\text{gb}} + 1/\mu_{\text{is}} \quad (2)$$

Where μ is the resultant mobility, μ_{gb} is the mobility due to grain boundary scattering and μ_{is} is the mobility due to ionized impurity scattering. These observations are in close coincidence with E. Shanthi^[11], Chitra Agashe^[12], G.N. Advani^[13].

Figure 4 shows the carrier concentration of thin films with increase in Sb-doping concentration. The substitution of Sn^{4+} by Sn^{5+} led to increase in the carrier concentration because the radii of the two ions matched. The carrier concentration of SnO_2 thin films was $2.004 \times 10^{19} \text{ cm}^{-3}$ and the value increased continuously with Sb-doping to $6 \times 10^{19} \text{ cm}^{-3}$ at 8 at.% Sb-doping concentration.

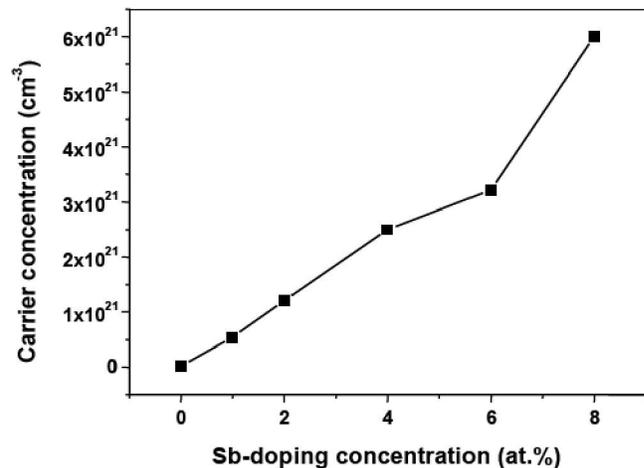


Figure 4 : Variation of carrier concentration with at. % of Sb-doping for ATO thin films.

The effect of doping on the optical properties of ATO thin films has been investigated. Figure 5 shows the transmittance spectra of ATO thin films with a thickness of 220 nm in the range 300-2000 nm. Maximum transmittance is found to be 96 % (at 502 nm) for the ATO film doped with 2 at. % of Sb, which is attributed to low scattering effect, thickness uniformity of the film due to the surface smoothness of the film. But the transmittance is found to decrease gradually if the antimony concentration is increased above 2 at.%. The decrease in transmittance with the increase in dopant concentration may be attributed to the increase in cluster size and surface roughness of the film, which promotes the diffuse and multiple reflections at the surface and increases the absorption. These observations are well in agreement with the results illustrated by J.C. Manificier^[14,15], K.L. Chopra^[16], M.Fantini^[17], S. Shanthi^[18]. In the case of heavily doped semiconductors whose carrier concentration was ap-

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proximately 10^{19} – 10^{21} cm^{-3} , the Drude model can be generally used to represent the decrease in the transmittance^[19-21]. Briefly, the model indicates that the transmittance drop in the near infrared region is associated with the plasma frequency ω_p that can be expressed as

$$\omega_p = \left[\frac{ne^2}{\epsilon_0 \epsilon_\infty m^*} \right]^{1/2} \quad (3)$$

where n is the carrier concentration, e the electronic charge, ϵ_0 the permittivity of free space, ϵ_∞ the high-frequency permittivity and m^* the conductivity effective mass. Below the plasma frequency, the films are characterized by a high reflectance, which functions as a screen of the incident electromagnetic wave^[21]. As ω_p is proportional to the square root of the carrier concentration, the increase in the carrier concentration led to the lowering of the transmittance level in the near infrared region.

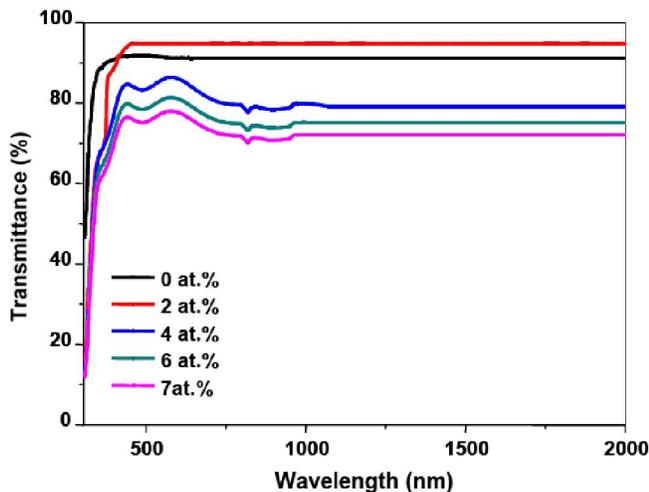


Figure 5 : Optical transmissions of non-doped SnO_2 and several Sb-doped SnO_2 thin films as a function of wavelength.

CONCLUSIONS

Transparent conducting ATO thin films were prepared by dip coating method via sol gel route. A preferred (211) orientation was observed for the non-doped SnO_2 thin films, but as the Sb-doping concentration increased, a preferred (200) orientation appeared for 3-7 at.% Sb-doped films. The polyhedron-like grains became rounder and smaller grains with the increase in the Sb-doping concentration. The carrier concentration of SnO_2 thin films was $2.004 \times 10^{19} \text{ cm}^{-3}$ and the value increased continuously with Sb-doping to $6 \times 10^{19} \text{ cm}^{-3}$ at 8 at.% Sb-doping concentration., while the Hall

mobility decreased from 0.9024 to 0.2901 cm^2/Vs . The resistivity decreased to 2 at.% Sb-doping concentration, thereafter it increased. Thus, the lowest resistivity (about $5.4 \times 10^{-3} \Omega \cdot \text{cm}$) was obtained for the 2 at.% Sb-doped films.. The most effective transparent conducting ATO thin film was the 2 at.% Sb-doped films.

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