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

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Retraction

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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, respectively. 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 $5.4 \times 10^{-3} \Omega \text{ cm}$) was obtained for Sb-doped films at 2 at.%. 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 was decreased for a higher level of antimony doping.

Keywords: Electrical properties, Optical properties, ATO, Thin films, Dip coating

Background

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 a 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. Such properties can be improved by doping tin oxide with, for example, antimony (Sb), indium (In), or fluorine (F). In fact, by increasing the doping concentration

(>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 makes them useful for a device application point of view. Also, the nature, quantity, and structural distribution of doping are important factors for the electrical properties of SnO_2 [7].

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

Methods

The antimony-doped tin dioxide sols were prepared using the same methodology 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 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 varied from 0 to 7 at.%. The solution was

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stirred at 70°C for 6 h in a closed container for the homogenous mixing of the solution and then was aged in the air for 24 h, i.e., until the solid materials dissolved. The thin films were deposited by dip coating technique on glass substrates, which had been cleaned ultrasonically in acetone, rinsed in DI water, and then dried by N₂ 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 of 1 to 10 mm/s. This was followed by drying and then sintering of the films between 400°C and 550°C for periods ranging from 6 to 24 h. To obtain higher thickness films, the sequence of dipping, drying, and then dipping again was performed a number of times. However, sintering was done only after the final dipping. The thickness of the films increased almost linearly with 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, (KLA-Tencor Corporation, Milpitas, CA, USA). 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, Agilent Technologies, Inc., Santa Clara, CA, USA). Crystal structure identification and crystal size analysis were carried out by X-ray diffraction (XRD) (2000, SCintag Inc., Cupertino, CA, USA) with a Cu-K α radiation source and a scan rate of 2°/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 SnO₂ 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 Sb-doped films at 2 to 7 at.%. The preferred (200) orientation was also reported by Elangovan et al. [6]. This behavior with Sb doping implies that in the present case, antimony incorporation in SnO₂ 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 (Sb₂O₃, Sb₂O₄, and Sb₂O₅) could be induced [9]. As a result, with the increase of doping concentration, the deposited films lose the crystallinity, and the preferred orientation growth of SnO₂ films may be suppressed by the precipitation. In the present case, antimony incorporation in SnO₂ 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 Shanthi et al. [10].

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 (atomic percentage). The resistivity of ATO thin films decreases initially with an increase in the Sb

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

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

doping concentration to about $4 \times 10^{-4} \Omega \text{ cm}$ 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 ($5.4 \times 10^{-3} \Omega \text{ cm}$). The decrease in resistivity which may be attributed to the substitution of Sn^{4+} by Sb^{5+} [10], as their ionic radii match (Sn^{4+} 0.071 nm and Sb^{5+} 0.065 nm). The variation in the resistivity of tin oxide thin films with antimony doping is explained on the basis of the presence of Sb in two oxidations states, namely Sb^{5+} and Sb^{3+} . The possible mechanism may be as follows. When SnO_2 is doped with Sb, a part of the lattice Sn^{4+} atoms are replaced by Sb^{5+} , resulting in the generation of conduction electrons and thus the decrease of resistivity [11,12]. Hence, a continuous decrease of resistivity is observed until Sb doping concentration ≤ 2 at.%. Beyond 2 at.% of Sb, the resistivity increases again (Figure 2). This is because beyond 2 at.% of Sb doping, a part of Sb^{5+} ions reduces to the Sb^{3+} state, resulting in the formation of acceptor sites and concomitant loss carriers [13-16]. The reduction of Sb^{5+} to Sb^{3+} has been verified by Terrier et al. [12] by estimation of the lattice parameter of the doped SnO_2 films. Since the ionic radius of Sn^{4+} is less than that of Sn^{3+} but higher than that of Sn^{5+} , an increase in the lattice parameter of SnO_2 phase is observed beyond 2 at.% of Sb doping. This reduction of Sb^{5+} to Sb^{3+} can be attributed to the increase in the resistivity above an optimum level of Sb doping.

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

Figure 4 Variation of carrier concentration with atomic percentage of Sb doping for ATO thin films.

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

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

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

variation of such extrinsic doped semiconductors. The resultant mobility is given as follows:

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

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 those of Shanthi [10], Agashe [17], and Advani [18]. Figure 4 shows the carrier concentration of thin films with an increase in Sb doping concentration. The substitution of Sn^{4+} by Sn^{5+} led to an 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. 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 of 300 to 2,000 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 the low scattering effect and thickness uniformity of the film due to surface smoothness of the film. However, 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 Advani et al. and Manificier [18,19], Jarzebski [20], Ambrazevičienė [21], and Shanthi [22]. In the case of heavily doped semiconductors with carrier concentration being approximately 10^{19} to 10^{21} cm^{-3} , the Drude model can be generally used to represent the decrease in the transmittance [23-25]. 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 follows:

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

where n is the carrier concentration; e , the electronic charge; ϵ_0 , the permittivity of free space; ϵ_∞ , the high-frequency permittivity; 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 [25]. 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 near the infrared region.

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 Sb-doped films at 3 to 7 at.%. With the increase in the Sb doping concentration, the polyhedron-like grains became rounder and smaller. 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 $5.4 \times 10^{-3} \Omega \text{ cm}$) was obtained for the Sb-doped films at 2 at.%. The most effective transparent conducting ATO thin film was the Sb-doped films at 2 at.%.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

NKH made the experiment on the thin films and performed tests on the samples. TMH carried out the characterization and wrote the manuscript. TMH gave the final approval of the version to be published. All the authors read and approved the final manuscript.

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TMH is a professor of Material Science in the Physics Department, Faculty of Science in Al-Azhar University, Gaza, Palestine. He got his Ph.D. (May 1998) in Solid State Physics from Moscow State University. His research interests include solid state physics, thin film coating, material science, and nanotechnology (nanoparticles, nanowires, nanorods). NKH is an assistant professor of Physical Chemistry in the Chemistry Department in Al-Quds Open University, Gaza, Palestine. He got his Ph.D. (February 2009) in Physical Chemistry from Ain Shams University, Cairo, Egypt. His main research areas are thin film coating and nanostructure and their characterizations.

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