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Microstructural, optical and electrical investigations of Sb-SnO_2 thin films deposited by spray pyrolysis

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ABSTRACT

The structural, optical and electrical properties of spray deposited antimony (Sb) doped tin oxide (SnO_2) thin films, prepared from $SnCl_4$ precursor, have been studied as a function of antimony doping concentration. The doping concentration was varied from 0 to 1.5 wt.% of Sb. The analysis of X-ray diffraction patterns revealed that the as deposited doped and undoped tin oxide thin films are pure crystalline tetragonal rutile phase of tin oxide which belongs to the space group $P4_2/mnm$ (number 136). The surface morphological examination with field emission scanning electron microscopy (FESEM) revealed the fact that the grains are closely packed and pores/voids between the grains are very few. The resistivity (ρ) and mobility (μ) are in the range of 1.512×10^{-3}–$6.624 \times 10^{-3}\ \Omega$ cm and 9.75–22.96 $cm^2\ V^{-1}\ s^{-1}$. The electron density lies between 4.11×10^{19} and $4.24 \times 10^{20}\ cm^{-3}$. A thorough electrical investigation reveals that the film's resistivity depends on carrier concentration. It is found that ionized impurity scattering is the dominant mechanism, which limits the mobility of the carriers. The transmittance spectra for as-deposited films were recorded in the wavelength range of 200–1000 nm. The transmittance of the films was observed to increase from 57% to 68% (at 800 nm) on initial addition of Sb (up to [Sb]/[Sn] = 0.5 wt.%) and then it is decreased for higher level of antimony doping ([Sb]/[Sn] >0.5 wt.%).

1. Introduction

Transparent conducting oxides (TCOs) are solid-state oxides that combine low electrical resistance with high optical transparency in the visible range of the electromagnetic spectrum [1]. These properties are sought in a number of applications; notably as electrode materials in solar cells, light emitting diodes, flat panel displays, and other optoelectronic devices where an electric contact needs to be made without obstructing photons from either entering or escaping the optical active area and in transparent electronics such as transparent field effect transistors [2–12]. Another property of TCOs is that although they are transparent in the visible light they are highly reflective for infrared light. This property is responsible for today's dominant use of TCO as an energy conserving material. TCO coated architectural windows, for instance, allow the light to transmit but keeping the heat out or in the building depending on the climate region. More sophisticated architectural windows, so-called smart windows, rely on TCOs to electrically contact electrochromic films that are changing their coloring and transparency by applying a voltage across the films [13–15].

There is a large number of TCOs, the most commonly known ones are the binary systems, i.e. SnO_2, ZnO, In_2O_3, Ga_2O_3, and CdO [16,17]. A large variety of ternary (Cd_2SnO_4, $CdSnO_3$, $CdIn_2O_4$, Zn_2SnO_4) and more complex TCO materials are being developed [18–21] and continuous efforts are being made to find p-type conducting TCOs [22] in addition to the above-mentioned n-type materials. For different applications different materials may possess advantageous properties [23]. Hartnagel et al. gave a review of properties and preparation procedures for TCOs [1]. For practical use as transparent electrodes in devices such as solar cells, flat panel displays, and light emitting diodes, a TCO must have a resistivity of less than $10^{-3}\ \Omega$ cm and over 80% transmittance in the visible range [18]. Indium tin oxide (ITO) is the current industrial standard material for transparent electrodes as thin films can be produced with resistivities of the order of $10^{-5}\ \Omega$ cm. However, due to the expense and scarcity of indium, alternatives need to be found. Among the available TCOs, SnO_2 seems to be more appropriate because they are quite stable toward atmospheric conditions, chemically inert, mechanically hard and can resist high temperature but its conductivity does not yet approach to that of ITO [24].

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Thin films of SnO_2 can be prepared by many techniques, such as chemical vapor deposition [25], sputtering [26], sol–gel [27], reactive evaporation [28], pulsed laser ablation [29], screen printing technique [30], and spray pyrolysis [31]. Among these, spray pyrolysis is the most convenient method because of its simplicity, low cost, easy to add doping materials, and the possibility of varying the film properties by changing composition of starting solution. Otherwise, this method is promising for high rate and mass production capability of uniform large area coatings in industry.

The main objective of this work is to prepare high conducting Sb doped SnO_2 thin films by chemical spray pyrolysis method with different doping levels of Sb ([Sb]/[Sn] = 0.0–1.5 wt.%) and explore its structural, morphological, electrical and optical properties.

2. Experimental details

Thin films of pure and Sb doped SnO_2 were deposited by spray pyrolysis method. The quality of these films depends on various process parameters such as spray rate, substrate temperature and the ratio of the various constituents in the solutions. Since the deviation from stoichiometry due to oxygen vacancies [32–34] makes tin oxide thin films to possess semiconducting nature, it is very essential that the complete oxidation of the metal should be avoided in order to obtain films with good conductivity. This is generally achieved by adding appropriate reducing agents. Methanol was used as the reducing agent in the present work.

The substrate temperature also plays an important role in the film formation. When the substrate temperature is below 350 °C, the spray falling on the substrate will undergo incomplete thermal decomposition (oxidation) giving rise to a foggy film whose transparency as well as electrical conductivity will be very poor. If the substrate temperature is too high (>500 °C) the spray gets vaporized before reaching the substrate and the film becomes almost powdery. Whereas at substrate temperature in the range of 350–500 °C the spray reaches the substrate surface in the semi vapor state and complete oxidation will take place to give clear SnO_2 film as a final product. Keeping these facts in mind, we optimize substrate temperature at 425 °C.

An amount of 17.529 g of $SnCl_4 \cdot 5H_2O$ (Merck purity >98%) was dissolved in 5 ml of concentrated hydrochloric acid (Merck, min 35% GR) by heating at 90 ° C for 15 min. The addition of HCl rendered the solution transparent, mostly, due to the breakdown of the intermediate polymer molecules [35]. The transparent solution thus obtained and subsequently diluted by methanol, served as the precursor. To achieve Sb doping, antimony trichloride ($SbCl_3$) was dissolved in isopropyl alcohol and 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 to 1.5 wt.%. The amount of spray solution was made together 50 ml. For each concentration the reproducibility of the films were verified by repeating the experiments several times. Microscope glass slides (2.0×2.5 cm^2), cleaned with organic solvents, were used as substrates. During deposition, the solution flow rate was maintained at 0.2 ml/min by the nebulizer (particle size 0.5–10 μm). The distance between the spray nozzle and the substrate as well as the spray time was maintained at 3.0 cm and 15 min respectively. The thickness of the films was observed to be at the range of 1–2 μm.

The gross structure and phase purity of pure and Sb doped SnO_2 films were examined by glancing angle X-ray diffraction (GAXRD) technique using a Philips X-ray diffractometer (X'Pert PRO, Model PW 3040). In the present study, all the XRD patterns of undoped and Sb doped SnO_2 thin films were recorded in the 2θ range from 20° to 60° with a 1° glancing angle, this angle was kept small (1°) to ensure that maximum signal comes from films rather than from the substrates. The experimental peak positions were compared with the data from the database Joint Committee on Powder Diffraction Standards (JCPDS) and Miller indices were assigned to these peaks. Morphologies of as-deposited films were investigated by field emission scanning electron microscopy (ZEISS-FESEM). The transmission and absorption spectra of pure and Sb doped SnO_2 films were recorded using Dual beam UV–Vis spectrometer (Cary 50) in the wavelength ranging from 200 to 1000 nm. Hall measurements were performed according to van der Pauw method to estimate the film resistivity (ρ), donor concentration (n) and carrier mobility (μ).

3. Results and discussion

Fig. 1 displays the X-ray diffraction patterns of pure SnO_2 and Sb-SnO_2 with various Sb concentration (0.5–1.5 wt.%). The analysis of X-ray diffraction patterns revealed that the as deposited doped and undoped tin oxides films are pure crystalline tetragonal rutile phase of tin oxide (JCPDS card no. 041-1445) which belongs to the space group $P4_2/mnm$ (number 136). No obvious reflection peaks from impurities, such as unreacted Sn, Sb or other oxide phases such as Sb_2O_5 or Sb_2O_3 are detected, indicating high purity of the product. It is perceptible from the XRD patterns of Fig. 1 that the undoped as well as doped tin oxide films grow along the preferred orientation of (1 1 0). The presence of other orientations such as (1 0 1), (2 0 0) and (2 1 1) have also been detected with considerable intensities for both doped and undoped tin oxide films. Evolution of the cell parameters a and c with Sb concentration is shown in Fig. 2 and Table 1. The cell parameters a and c decrease monotonously with Sb concentration, indicating the replacement of Sn^{4+} by Sb^{5+}. The lattice parameter a is observed to decrease from 4.7384 Å to 4.7295 Å, while the lattice parameter c decreases from 3.1899 Å to 3.1803 Å, both with increase in the Sb concentration from 0 to 1.5 wt.% respectively. The cell volume parameter (inset of Fig. 2) decreases from 71.6210 Å^3 to 71.1375 Å^3 with increase in the Sb content from 0 to 1.5 wt.% respectively. These results are in agreement with the fact that the difference in the ionic radius of Sb^{5+} (0.62 Å) and Sn^{4+} (0.69 Å) is rather small, leading to very small changes in the lattice constants on doping with Sb. For antimony, there are two oxidation states namely Sb^{3+} (0.76 Å) and Sb^{5+} (0.62 Å). The ionic radius of each ion in Å is given in brackets. Since the ionic radius of Sn^{4+} is lesser than that of Sb^{3+} but higher than that of Sb^{5+}, an increase in the lattice parameter of

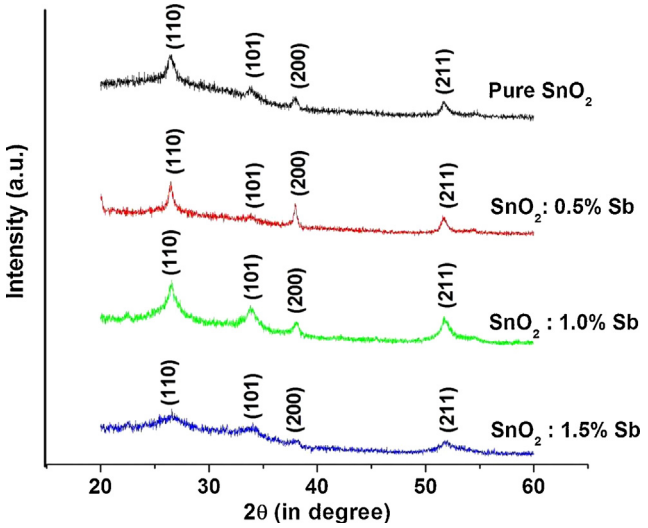

Fig. 1. X-ray diffraction pattern for Sb-doped SnO_2 films for different concentrations of dopant.