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Transport properties in Sb-doped SnO_2 thin films: Effect of UV illumination and temperature dependence

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ABSTRACT

Films of Sb-doped SnO_2 were deposited by dip-coating technique. The morphology analysis showed that the microstructure of the samples exhibits many shaped nano-sized crystallites homogenously dispersed on the surfaces. The roughness varies with Sb-content, implying that doping has an important effect on the surface morphology of the films. Raman and FTIR-ATR investigations revealed that the films exhibit a vibration mode at 564 cm^{-1} ascribed to the amorphous phase overlapping the crystallites. Thus, the selection rule ($k = 0$) is relaxed because of disorder and reduced crystallites size to nanoscale by Sb-doping, which may explain the broadening and shift of the lattice modes. The vibration of sub-bridging oxygen atoms seems to be significantly affected by oxygen vacancies and Sb-derived surface mode has been identified at 578 cm^{-1}. The optical band gap is red-shift due to the introduction of localized states in the SnO_2 bulk associated to Sb-doping and oxygen defects. The refractive index varies due the enhanced grain boundaries effect and surface disorder induced by Sb incorporation in the crystal lattice. The photoconductivity (σ_{ac}) shows a dispersion pattern with two regions, corresponding to extrinsic and intrinsic conductivities. Under UV-illumination, the electrical charge transport mechanism changes from multi-hopping to single-hopping at higher temperatures.

1. Introduction

SnO_2 thin films have potential applications in the areas of solar cells [1], gas sensor materials [2], catalysis [3], architectural windows [4] and optoelectronic devices (light emitting diodes [5] and transparent field effect transistors [6]), due to high optical transparency in the visible range, low electrical resistance and high reflectivity for infrared light. In most applications, substitution or doping modify the oxide properties, and antimony is the common n-type dopant for SnO_2 [7–9]. The addition of Sb shifts the Fermi level upon substitution of Sn cations and increases the charge carriers concentration [10]. Accordingly, Mishra et al. [11] have reported that because of the lower binding energy of the impurity dopant, the modification of the band structure occurs by hybridization of the donor states and valence band levels of the host lattice.

Moreover, Sn atoms possesses a dual valence attaining an oxidation state of 2 or 4 and the charge neutrality of the surface is preserved by changing the surface from Sn(IV) to stable Sn(II)-bulk terminations [12]. Thus, a slight blue coloration is often observed on deposited transparent films. The non-stoichiometry and surface defects are more pronounced to modify the electronic structure by formation of derived states that lie deep within the band gap, thus mediating the charge transport and/or electronic exchange [13,14]. In our previous study [15], we have studied the charge transport properties in Sb-doped SnO_2 thin films. The dark conductivity measurements at room temperature, showed that the conduction mechanism change at high frequencies from single to multi-hopping. The present study, deals with the characteristics of the electrical conduction under UV illumination and the conduction is analyzed as temperature dependent at constant frequency. The effect of Sb-doping on both the microstructure and optical properties of the films was also investigated.

2. Materials and methods

The films were deposited by dip-coating technique on glass subtracts (Silicon subtracts were used for the infrared measurements). The sol-gel solutions were synthesized from ($SnCl_2{\cdot}2H_2O$), $SbCl_3$ as dopant precursor $\left(\frac{[Sb]}{[Sn]}\right)$ and anhydrous ethanol (C_2H_5OH). The dopant concentrations were 2.5%, 5% and 10% wt. After drying, the amorphous films were introduced in pre-heated oven at 500 °C, for 15 min.

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The surface morphology of the films was analyzed by SEM (VEGA3-TESCAN) equipped with an energy dispersive spectrometer (EDS). The roughness of the surface was measured using AFM (JSPM-5200) instrument in taping mode. The average crystallite size of the samples was determined with the Cu-K_α ($\lambda = 1.5406$ Å) radiation, using D8-advance Alpha Bruker X-ray diffractometer. The vibration of the lattice was investigated using Horiba Raman microscope with 532 nm laser as an excitation source in the range (200–85 cm^{-1}) and Alpha Bruker FTIR-ATR (Fourier transform infrared Attenuated Total Reflectance) spectrometer. The optical transmission of thin films was recorded at room temperature by dual beam UV–Vis spectrophotometer (UV-1650 Shimadzu). The electrical ac-conductivity was recorded using the two-probe method with GW-Instek 821–LCR-Meter in the temperature range (285–490 K). Ohmic contacts were fabricated *via* thermal vacuum evaporation of aluminum (99.9999%; 6 N) and then, the nature of the co-planar contacts was tested using current-tension (I-V) measurements. The photoconductivity of the films was recorded under ultraviolet excitation using UV-Mercury lamp (125 W; 365 nm).

3. Results and discussions

3.1. Morphology analysis

Fig. 1 shows the SEM images of Sb-doped SnO_2 films. The surface morphology of the films is significantly modified by Sb-doping. The undoped film is homogenous, smooth without cracks and exhibits a nano-porous structure. The pore radius varies in the range (0.4–0.9 µm). On the contrary, the microstructure of doped films shows many shaped aggregation of nanosized crystallites homogenously dispersed on the surface, thus confirming the Sb-doping effect on the microstructure of the films. The EDS (Fig. 1) spectra confirm the presence of Sb, Sn and O elements in the samples, which suggests that Sb ions were incorporated in the SnO_2 lattice structure.

The AFM micrographs (Fig. 2) indicate that the films surface is smooth, compact and crack-free with a granular character. The roughness (Table 1) varies with Sb-doping and nanocrystals islands are seen as white spots due to their heights that exceeds 5 nm in the undoped sample and 8 nm in the doped sample (10% Sb). The histograms of peaks height profile reveal that the peaks spread in a short range of height less than 6 nm; whereas the peaks in the doped film are normally distributed in height and most fraction of peaks height lies in the range (4–8 nm).

3.2. Raman analysis

Fig. 3 shows the room temperature Raman spectra of Sb-doped SnO_2 films deconvoluted in the range (200–850 cm^{-1}). In Table 2, we have listed the position of different modes of vibration. The peak at 632 cm^{-1} is assigned to A_{1g} generated mode of in-plane lattice oxygen vibration [16]. The width of this band is correlated with the crystallite size and oxygen defects [17], which may explain the slight red-shift and the decrease of the broadening as Sb concentration increases in the host matrix.

The peak at 560 cm^{-1} (which is shifted to 559 and 563 cm^{-1} in doped samples), is ascribed to the amorphous phase of SnO_2. Yu et al. [18] showed that the Raman spectrum of amorphous films depicts two features: a strong peak at 566 cm^{-1} and a weak band at 788 cm^{-1} related to the expansion and contraction of Sn-O vibrating bonds. This vibration band contributes by 37%, and leads to assume that the films are mainly formed by highly amorphous grain boundaries, overlapping the crystallites. B_{2g} vibration mode is observed at 789 cm^{-1} for undoped SnO_2 and 796 cm^{-1} in Sb-doped samples [19,20]. This mode corresponds to the contracting vibration of Sn–O bonds in a plane perpendicular to *c*-axis. The broadening of the peak and the blue-shift are indicative of significant structural modifications resulting from the substitution of Sb ions in the Sn^{4+} sites [21]. The broadening of the bands varies with the Sb out-diffusion from the matrix observed for high doping levels (> 2%), which decreases the surface crystallinity due to the formation of Sb^{3+} ions [22].

The peak at 460 cm^{-1} is attributed to E_g degenerate mode [17], which is the result of two sub-bridging oxygen atoms vibrating parallel to *c*-axis in opposite directions. It is more sensitive to bulk vacancies and non-stoichiometry compared to other modes [23]. The greater broadening varies from 90 to 135 cm^{-1}, indicating an increase of oxygen vacancies defects with increasing the Sb-concentration. The contribution of this band to the lattice vibration reaches its maximum (40%) in the film doped at 10% Sb. The peaks located at 248, 297 and 376 cm^{-1} are assigned to the triply degenerate mode (E_u) [24], which results from both Sn and O atoms vibrating in the plane perpendicular to the c-axis. Therefore, $E_u(\upsilon_{TO})$, $E_u(\upsilon_{LO})$ and $E_u(\upsilon_{2LO})$ are infrared surface activated modes [25]. Abello and al. proposed that the relaxation of the selection rule (k = 0) is progressive when the disorder increases or the crystallite size is reduced to nanoscale [26]. In fact, the significant changes observed in the peaks positions and broadening can be explained by the effect of local structural changes resulting from Sb-doping. The phonon

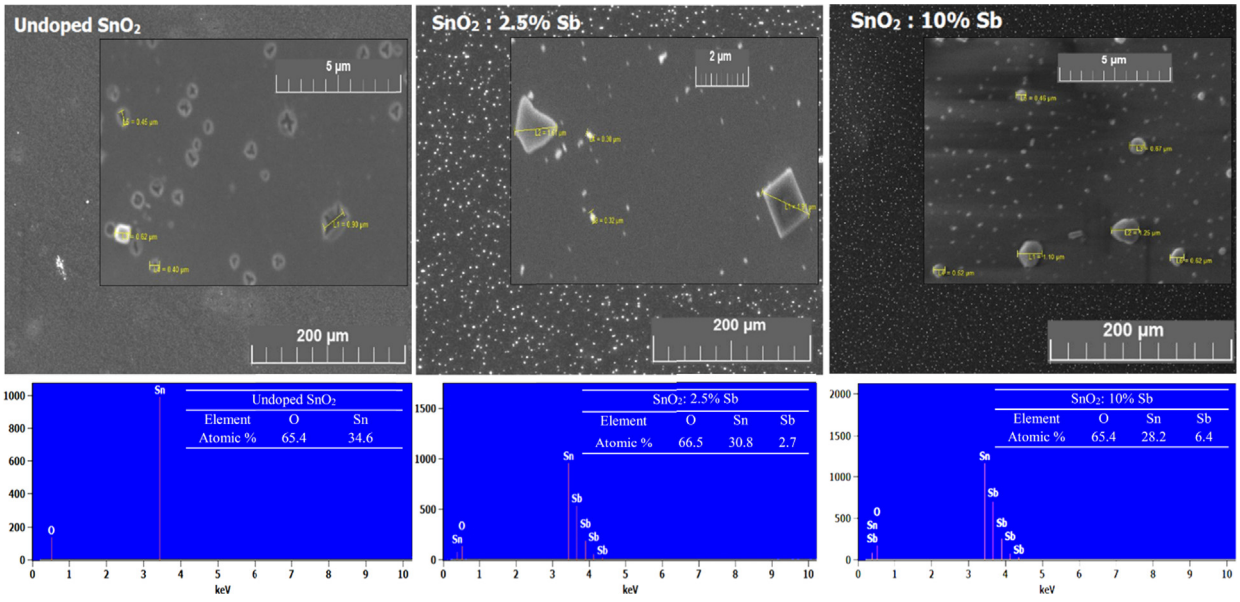

Fig. 1. SEM images and EDS spectra of Sb-doped SnO_2 thin films.