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AC Plasma Induced Modifications in Sb_2S_3 Thin Films

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Abstract. Sb_2S_3 thin films, deposited by the chemical bath deposition method, were treated with N_2 plasma at 3.0 Torr during several minutes. The as-prepared Sb_2S_3 thin films and films treated with N_2 plasma have been characterized using several techniques. X-ray diffraction studies have shown that plasma treatment induced recrystallization on the as-prepared Sb_2S_3 thin films. The band gap values decreased from 2.37 to 1.82 eV after plasma treatment, and the electrical conductivity increased from 10^{-9} to 10^{-7} $(\Omega\ \mathrm{cm})^{-1}$ due to the annealing effect.

1. Introduction

Antimony sulfide (Sb_2S_3) has technological applications as target material of television cameras [1], microwave [2], switching [3], and optoelectronic devices [4]. Recently, considerable attention has been given to the preparation and characterization of Sb_2S_3 thin films for use in photovoltaic devices [5-8]. Chemical bath deposition is a very important method used to grow metal chalcogenide materials in thin film form for solar cell applications, due to the simplicity and non-expensive of the technique.

Plasma treatment is an interesting technological method to modify the structural [9] and surface [10] properties of the materials. This paper deals with N_2 plasma treatment used to modify the structural, optical, and electrical properties of the as-prepared samples of Sb_2S_3 thin films obtained by the chemical bath deposition method.

2. Experimental details

Antimony sulfide thin films were prepared using the chemical bath deposition technique, similarly to that already reported in [11]. The bath was prepared using antimony trichloride, $SbCl_3$ and sodium thiosulfate, $Na_2S_2O_3$, and deionized cold (~10ºC) water. Microscope glass slides were used as substrates. The substrates were placed vertically in the solution. The deposition was made at ~10 ºC for 4 hours without stirring. Thickness of the films was measured with an Alpha Step model 100

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profilometer from Tencor Instruments, the mean value of the film thickness was 240 nm. The as-prepared samples of Sb_2S_3 were treated with N_2 plasma at 3.0 Torr during 15, 30, and 70 minutes.

The experimental apparatus and technique to generate the pulsed plasma was recently reported [12]. The discharge power supply was maintained at an output of 300 Volts and a current of 0.36 A. The glow discharges were monitored by plasma emission spectroscopy using an Ocean Optics Inc. Spectrometer Model HR2000CG-UV-NIR. X-ray diffraction (XRD) patterns were recorded on a Rigaku D-Max X-ray diffractometer using Cu-K_α radiation (λ = 1.5406 Å). The optical transmittance and specular reflectance spectra of the samples were measured with a spectrophotometer Shimadzu model UV-1601PC. For the electrical measurements, current vs. time data were recorded on an automated system using a Keithley 619 electrometer and a Keithley 230 programmable voltage source.

3. Results and discussion

3.1 Structural analysis

The XRD patterns for as-prepared Sb_2S_3 thin films as well as films treated with N_2 plasma are shown in figure 1. It can be seen that no diffraction peaks can be identified on the pattern of the as-prepared film. It is possible that the material is growing with nanometric grains. The diffraction patterns corresponding to films treated with N_2 plasmas during 15, 30, and 70 minutes match well the standard for Sb_2S_3 (JCPDS 42-1393) which has an orthorhombic structure. Films treated with N_2 plasma showed a preferential orientation along the (310) direction. The mean value of the crystallite size for Sb_2S_3 films treated with N_2 plasma was calculated for the (310) diffraction peak, using the Scherrer formula $D = (0.9\lambda)/(\beta \cos\theta)$, where D is the diameter of crystallites, λ is the wavelength of Cu-K_α line, β is full width at half maximum (FWHM) in radians and θ is Bragg's angle. It was found that the value increased from 15.3 nm to 17.8 nm with the increasing in time to the N_2 plasma treatment. This may be due to the recrystallization of the films during the plasma process.

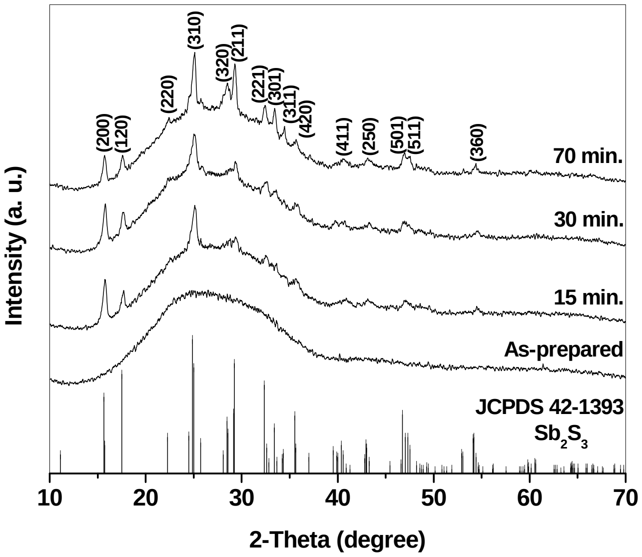

Figure 1. XRD patterns for as-prepared Sb_2S_3 thin films as well as films treated with N_2 plasma.

3.2 Optical emission spectroscopy analysis

Optical emission spectroscopy (OES) measurements were obtained for N_2 glow discharge plasma (figure 2). This fact allowed the analysis of the most luminous area that corresponds to the negative glow near the cathode dark space (it has been subtracted the intensities of the bands coming from the N_2 plasma). The identified species removed from the thin films into the plasma were S_2, NS, Sb and SbS. The majority of the species are vibrationally excited at a fundamental level. There is a flux of material into the plasma that can be deposited somewhere in the chamber and some back on the surface from which it came (in a modified form). By using OES and observing both S_2, NS, SbS and Sb neutrals, it is possible to assume that there is a possible mechanism by which Sb_2S_3 thin film ionization occurs in plasma treatment: electron impact ionization.

$$Sb_2S_3 + e \Rightarrow S_2 + Sb_2S + e \tag{1}$$
$$Sb_2S_3 + N \Rightarrow NS + Sb_2S_2 + e \tag{2}$$
$$Sb_2S_3 + e \Rightarrow Sb + SbS_3 + e \tag{3}$$
$$Sb_2S_3 + e \Rightarrow SbS + SbS_2 + e \tag{4}$$

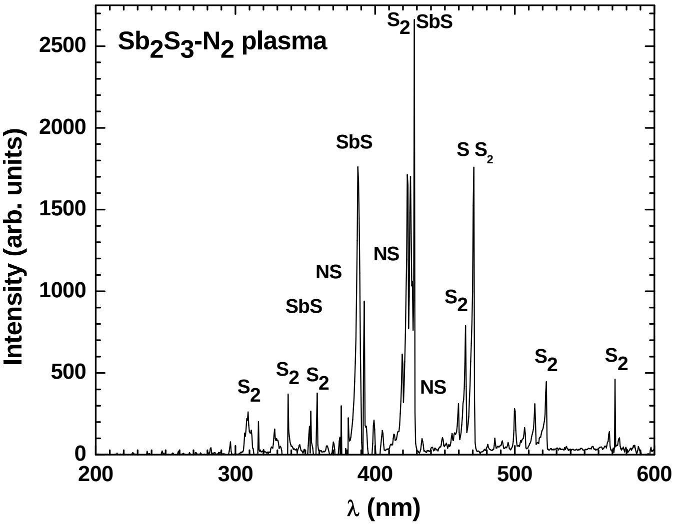

Figure 2. Typical OES spectrum for Sb_2S_3 thin film-N_2 plasma interaction.

3.3 Optical and electrical measurements

The behaviour of the transmittance, T(λ), for as-prepared Sb_2S_3 thin films as well as films treated with N_2 plasma at 3.0 Torr during 15, 30, and 70 minutes are presented in figure 3a. Samples after plasma treatments show a decrease in the optical transmission due to the structural changes. Band gap, E_g, of the samples was determined using the $(\alpha h\nu)^2$ versus $h\nu$ graph by extrapolating the linear portion of the graph to the $h\nu$ axis (figure 3b). The as-prepared Sb_2S_3 thin film had a band gap of 2.33 eV. As the exposition time to the N_2 plasma increased, the band gap decreased. The E_g values for films treated with N_2 plasma during 15, 30, and 70 minutes were: 1.85 eV, 1.80 eV, and 1.73 eV, respectively. This decrease might be due to the increasing in the particle size as observed in the XRD studies.

The electrical conductivity value for the as-prepared thin films was 1.0×10^{-9} $(\Omega\ \mathrm{cm})^{-1}$. The values were ~ 2×10^{-9}, 3×10^{-8}, and 1×10^{-7} $(\Omega\ \mathrm{cm})^{-1}$ for samples treated with N_2 plasma during 15, 30, and 70 minutes, respectively. These results are in agreement with those reported in references [11,13] for Sb_2S_3 thin films deposited by chemical bath deposition and thermal annealed in N_2.

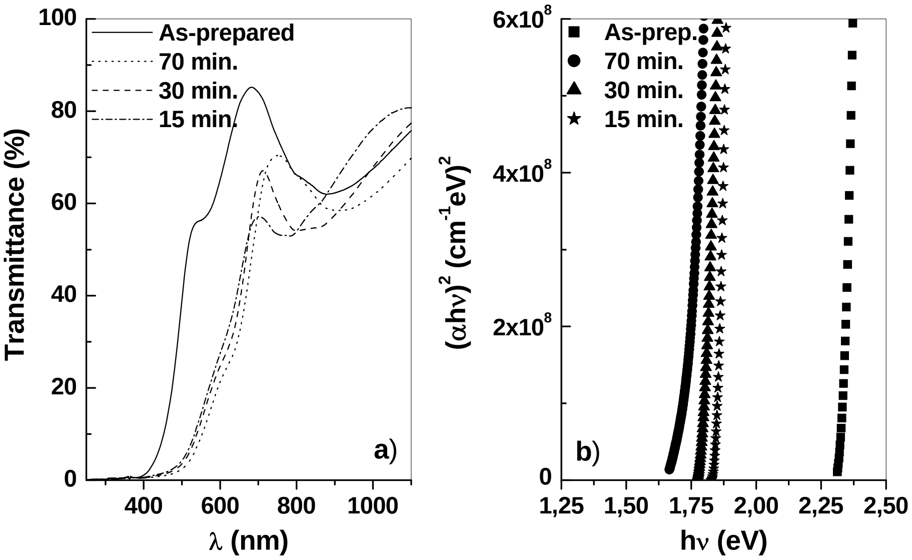

Figure 3. T(λ) and $(\alpha h\nu)^2$ vs $h\nu$ plots for as-prepared Sb_2S_3 film and films treated with N_2 plasma.

4. Conclusions

N_2 Plasma treatments induced recrystallization was observed in Sb_2S_3 thin films due to annealing effect of plasma process. Films treated in N_2 plasma showed optical and electrical properties similar to that obtained through a conventional thermal treatment.

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