A comparative study of the physical properties of Sb$_2$S$_3$ thin films treated with N$_2$ AC plasma and thermal annealing in N$_2$

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ABSTRACT

As-deposited antimony sulfide thin films prepared by chemical bath deposition were treated with nitrogen AC plasma and thermal annealing in nitrogen atmosphere. The as-deposited, plasma treated, and thermally annealed antimony sulfide thin films have been characterized by X-ray diffraction (XRD), energy dispersive X-ray spectroscopy, scanning electron microscopy, atomic force microscopy, UV–vis spectroscopy, and electrical measurements. The results have shown that post-deposition treatments modify the crystalline structure, the morphology, and the optoelectronic properties of Sb$_2$S$_3$ thin films. X-ray diffraction studies showed that the crystallinity of the films was improved in both cases. Atomic force microscopy studies showed that the change in the film morphology depends on the post-deposition treatment used. Optical emission spectroscopy (OES) analysis revealed the plasma etching on the surface of the film, this fact was corroborated by the energy dispersive X-ray spectroscopy analysis. The optical band gap of the films ($E_g$) decreased after post-deposition treatments (from 2.36 to 1.75 eV) due to the improvement in the grain sizes. The electrical resistivity of the Sb$_2$S$_3$ thin films decreased from $10^9$ to $10^7$ Ω-cm after plasma treatments.

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1. Introduction

Antimony sulfide (Sb$_2$S$_3$) is a semiconductor compound that belongs to the groups V–VI, and due to its nature it can be used in optoelectronic devices, thus becoming of technological importance [1–3]. Recently, this material has been used in solar energy storage cells [4], and photovoltaic devices [5–9]. In addition, chemically deposited Sb$_2$S$_3$ thin films have been used in the preparation of photovoltaic materials such as CuSbS$_2$ [5] and AgSbSe$_2$ [7,10]. Chemical bath deposition is one of the most important techniques used to grow metal chalcogenide materials in thin film form, due to its simplicity and low cost.

Plasma treatment is an interesting technique that has been used to modify the surface properties of the materials. Sagar and Srivastava [11] have reported that ion irradiation of crystalline CdS films employing dense plasma focus has resulted in amorphization; Zhong and Jiang [12] found that O$_2$ plasma treatment on indium tin oxide (ITO) substrates yielded the best performance of polymer light-emitting electrochemical cells (PLECs); equally Lavareda et al. [13] have reported the a-Si$_x$ thin film transistors (TFTs) enhancement after H$_2$ plasma treatment.

Several methods have been employed to modify the structural, morphological, and optoelectronic properties of the Sb$_2$S$_3$ thin films: laser irradiation, in which the crystallization of the evaporated amorphous films was mainly due to the thermal component in the photo-thermal process of continuous wave laser irradiation [14]; electron beam irradiation, where surface modification was observed in evaporated amorphous Sb$_2$S$_3$ thin films [15]; and thermal treatments which are commonly used to improve the crystallinity of the as-prepared antimony sulfide thin films [16–18]. However, plasma treatment has not been explored yet for Sb$_2$S$_3$ thin films. In this work, we report the results of a comparison of two different post-deposition treatments of antimony sulfide thin films: nitrogen AC plasma treatment and thermal annealing in nitrogen atmosphere.

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2. Experimental details

2.1. Deposition of thin films

Sb$_2$S$_3$ thin films were prepared using the chemical bath deposition technique, following the procedure reported by Nair et al. [17]. The bath was prepared using antimony trichloride (SbCl$_3$) and sodium thiosulfate (Na$_2$S$_2$O$_3$) as follows: In a 100 ml beaker, we have used 721 mg instead of 650 mg of SbCl$_3$ which was dissolved in 2.5 ml of acetone. To this mixture was added 25 ml of sodium thiosulfate 1 M followed by 72.5 ml of deionized cold water (both maintained $\sim$10 °C) and stirred well. Borosilicate microscope glass slides from Corning with dimensions of 7.5 cm × 2.5 cm × 0.1 cm were used as substrates. The substrates were placed vertically in the solution. The deposition was made at $\sim$10 °C for 4 h without stirring. At the end of the deposition the slides, coated on both sides with orange yellow films, were removed from the bath, washed well with distilled water, and dried with a constant flow of air. The coating deposited on the side of the substrate facing the wall of the beaker was retained for nitrogen plasma treatments and thermal annealing in nitrogen atmosphere. The coating on the other side was wiped off with dilute acid. Thickness of the films was measured using an Alpha Step model 100 profilometer from Tencor Instruments. Typical thickness obtained for as-deposited films was 385 nm, while for films after nitrogen plasma treatment and thermal annealing in nitrogen atmosphere were 311 and 260 nm, respectively.

2.2. Post-deposition treatments of antimony sulfide thin films

The experimental apparatus and technique to generate the pulsed plasma was recently reported [19,20]. A brief description is reported here. The discharge chamber used in this work has two stainless steel circular plate electrodes, 1 mm thick and 30 mm in diameter. The electrodes are positioned horizontally at the center of the reaction chamber with 4 mm of separation between them. Samples were placed on the bottom electrode. The N$_2$ gas was injected into the reaction chamber through the front flange. The same gas connection was used for pressure sensor. The discharge in injected into the reaction chamber through the front flange. The beaker was retained for nitrogen plasma treatments and thermal annealing in nitrogen atmosphere. The bath was prepared using antimony trichloride deposition technique, following the procedure reported by Nair et al. [17]. The bath was prepared using antimony trichloride, with a preferential orientation along the (3 1 0) direction. The mean value of the crystallite sizes for the Sb$_2$S$_3$ thin films treated with nitrogen plasma and films thermally annealed in nitrogen atmosphere were 311 and 260 nm, respectively.

2.3. Characterization

XRD diffraction patterns were recorded on a Rigaku D-Max X-ray diffractometer using Cu-K$_\alpha$ radiation ($\lambda$ = 1.5406 Å). The chemical composition of the as-deposited, plasma treated, and thermally annealed antimony sulfide thin films was determined by energy dispersive X-ray spectroscopy (EDS) using an Inca Oxford Instruments system attached to the scanning electron microscope (SEM). The surface morphology was studied by scanning electron microscopy (SEM) JEOL model JSM 5800LV at 15 kV and 10,000×. Atomic force microscopy (AFM) analysis was done using a Nanosurf EasyScan E-line equipment, the topography contrast images were acquired in the contact mode. For the optical emission spectroscopy (OES) analysis, an optic fiber was connected to the entrance aperture of a high-resolution Ocean Optics Inc. Spectrometer Model HR2000CG-UV-NIR, equipped with a $3 \times 10^5$ lines-m$^{-1}$ composite blaze grating and a UV2/OFLV-5 detector (2048-element linear silicon CCD array). The grating response has a spectral response in the range of 200–1100 nm with efficiency >30%. The optical transmittance at normal incidence, and specular reflectance spectra of the samples were measured with a spectrophotometer Shimadzu model UV-1601PC in the UV–vis–NIR region (190–1100 nm wavelength range). For the electrical measurements, current versus time data were recorded on an automated system using a Keithley 619 electrometer and a Keithley 230 programmable voltage source. A pair of coplanar silver print electrodes of 3 mm in length, 3 mm in separation, was applied on the surface of the films.

3. Results and discussion

3.1. X-ray diffraction (XRD) and compositional analyses

Fig. 1 shows the X-ray diffraction (XRD) patterns for as-deposited, plasma treated, and thermally annealed antimony sulfide thin films. No diffraction peaks were observed in the XRD pattern of the as-deposited thin film, indicating that the deposited material is either amorphous or of poor crystallinity. It is a common result for as-prepared antimony sulfide thin films obtained by the chemical bath deposition method [21–24]. The diffraction patterns corresponding to films after nitrogen plasma treatment, and thermal annealing match well the standard for Sb$_2$S$_3$ (JCPDS 42-1393) which has an orthorhombic structure. The XRD pattern of the Sb$_2$S$_3$ thin film after thermal annealing showed peaks higher than those obtained for film treated with nitrogen plasma, with a preferential orientation along the (3 1 0) direction. The mean value of the crystallite sizes for the Sb$_2$S$_3$ thin films treated with nitrogen plasma and films thermally annealed were calculated for the diffraction peak oriented in the direction (3 1 0) using the Scherrer formula $D = (0.9\lambda)/(\beta \cos \theta)$, where $D$ is the diameter of crystallites, $\lambda$ is the wavelength of

![Fig. 1. X-ray diffraction patterns for as-deposited, plasma treated, and thermally annealed antimony sulfide thin films.](image-url)
CuKα line, β is full width at half maximum (FWHM) in radians and θ is Bragg’s angle. The mean crystallite size for the plasma treated film was 13.7 nm, and for the film thermally annealed was 19.1 nm. The nitrogen plasma and thermal treatments improved the crystalline structure of the as-deposited antimony sulfide thin films.

Table 1 shows the chemical composition in atomic percent (at%) for as-deposited, plasma treated, and thermally annealed antimony sulfide thin films. The chemical composition of as-deposited films was: 53.46% for S and 46.54% for Sb, this suggests that the as-deposited films are close to the Sb2S3 stoichiometric composition. The decrease in the antimony content obtained for the film after plasma treatment might be due to the plasma etching of this element on the surface of the film. The little decrease in the sulfur content obtained for film after thermal annealing is probably due to the loss of sulfur during the annealing process.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sb (at%)</th>
<th>S (at%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-prepared</td>
<td>46.54</td>
<td>53.46</td>
</tr>
<tr>
<td>Plasma treated</td>
<td>45.50</td>
<td>54.50</td>
</tr>
<tr>
<td>Thermally treated</td>
<td>46.70</td>
<td>53.30</td>
</tr>
</tbody>
</table>

3.2. Morphological analysis

Fig. 2 shows typical SEM pictures of the morphology of (a) as-deposited, (b) thermally annealed, and (c) plasma treated antimony sulfide thin films. There are no significant changes in the morphology for the as-deposited and plasma treated films. The morphology in the thermally annealed film looks very smooth. In the three cases there are clusters of quasi-spherical shape and varying size. The mean grain sizes of these clusters on the surface of the as-deposited, plasma treated, and thermally annealed films are 249, 313, and 359 nm, respectively.

3.3. Optical emission spectroscopy (OES) analysis

The interaction of the nitrogen plasma and the surface of antimony sulfide thin film allows the generation of new species in the plasma. To identify these species, OES measurements were carried out during the experiments. Fig. 4 shows a typical optical emission spectrum for the plasma. The measurements allowed the analysis of the most luminous area that corresponds to the negative glow near the cathode dark space. The identified species from the Sb2S3 film–nitrogen plasma interaction were: N2 at 235.14 nm (D3^1S_u^-B3^1P_g), 246.16 nm (A3^1S_u^-X1^1S_g^+), 280.46, 295.32, 297.68, 313.60, 315.93, 337.13, 353.67, 370.62, 380.49, 399.84, 405.94, and 434.36 (C3^1Π_u-B3^1Π_g); N2⁺ at 334.96, and 375.61 (B2^1Σ_u^-X2^1Σ_g^+); NS at 246.56 (A2^1D_u^-X2^1Σ_g^+), 258.70 (C2^1Σ^-X2^1Σ), 269.74 (A2^1D_u^-X2^1Σ); S2 at 269.76 (f3^1Σ_u^-a1Σ_u^-), 313.22, 355.56, 358.72, 393.89, 419.17, 419.36, and 456.30 (B2^1Σ_u^-X2^1Σ); and SbS at 380.87, 399.18, 413.68, and 448.73 [25,26]. The majority of the species are vibrationally excited. S2 and SbS species were detected in the plasma, the origin of these species is from the film surface, so plasma treatment changed the chemical composition of the Sb2S3 film as revealed by the EDS analysis.

![Fig. 2. SEM images for (a) as-deposited, (b) thermally annealed, and (c) plasma treated antimony sulfide thin films.](image-url)
3.4. Optical and electrical properties

Fig. 5a–c shows the behavior of the optical transmittance $T(\lambda)$ and specular reflectance $R(\lambda)$ spectra for as-deposited, plasma treated, and thermally annealed antimony sulfide thin films. The as-prepared films are transparent at wavelengths, $\lambda > 526$ nm. A shift in the absorption edge toward larger wavelength is observed for plasma treated and thermally annealed films. The values of the absorption coefficient $\alpha(\lambda)$ for the as-deposited, plasma treated, and thermally annealed films were calculated from the data obtained from the transmission $T$, reflection $R$, and thickness $d$, using the well-known relationship [27]

$$T = \frac{(1 - R)^2}{\exp(a\lambda) - R^2 \exp(-a\lambda)}.$$  

For allowed direct transitions, $\alpha h\nu$ is given by [28]

$$(\alpha h\nu)^2 = A(h\nu - E_g),$$

where $A$ is a constant and $E_g$ is the optical band gap. Thus $E_g$ can be obtained from a plot of $(\alpha h\nu)^2$ versus $h\nu$. The $E_g$ values were calculated from the best fit of the plot $(\alpha h\nu)^2$ versus $h\nu$, and its extrapolation to $(\alpha h\nu)^2 = 0$ (see Fig. 6). The as-deposited antimony sulfide thin film has a band gap of 2.36 eV. The $E_g$ values for plasma treated and thermally annealed Sb$_2$S$_3$ films were 1.83 and 1.75 eV, respectively. A higher band gap for the as-deposited film (2.36 eV versus 1.75 eV for thermally annealed films) is attributed to size quantization as explained by Nair et al. [17] and Salem and Selim [29] for chemically deposited antimony sulfide thin films. The reduction in the band gaps of the films after post-deposition treatments is ascribed to the improvement in the crystallinity, which is evidenced in the XRD patterns given in Fig. 1.

The electrical resistivity ($\rho$) value for the as-deposited thin film was $6.2 \times 10^8$ Ω-cm. The $\rho$ values for plasma treated and thermally annealed Sb$_2$S$_3$ thin films were $4.5 \times 10^8$ and $5.3 \times 10^8$ Ω-cm, respectively. A $\rho$ value of $10^8$ Ω-cm was reported by Cardenas et al. [30] for chemically deposited antimony sulfide thin films after annealing in nitrogen at 300 °C. Although, films after thermal treatment had better crystalline structure compared to as-deposited films, it was not observed a decrease in its electrical resistivity. Films after plasma treatment showed a reduction in the electrical resistivity in two orders of magnitude, this might be due to the etching at the film surface. The etching at the film surface in the plasma treatment improved the electrical transport at the surface. Although, the electrical measurements were done on the surface of the films in the planar configuration. It was unable to measure the conductivity type using the hot point probe technique in these samples because of its high electrical resistivity.
4. Conclusions

Antimony sulfide thin films chemically deposited were treated in nitrogen plasma and thermal annealing in nitrogen atmosphere to compare their structural, optical and electrical properties after the post-deposition treatments. XRD results revealed that the best crystallization of the films was obtained by thermal annealing. The $E_g$ values for plasma treated and thermally annealed antimony sulfide thin films were 1.83 and 1.75 eV, respectively. Films after thermal annealing in nitrogen atmosphere did not show any change in the electrical resistivity value ($10^8 \Omega$-cm). Films after plasma treatment showed a reduction in the electrical resistivity from $10^8$ to $10^6$ Ω-cm. Plasma treatments can be used to improve the electrical properties of as-deposited Sb$_2$S$_3$ thin films.

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