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A comparative study of the physical properties of Sb_2S_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_2S_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_2S_3 thin films decreased from 10^8 to 10^6 Ω-cm after plasma treatments.

1. Introduction

Antimony sulfide (Sb_2S_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_2S_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-SiN_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_2S_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_2S_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_2S_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_2S_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 ($Na_2S_2O_3$) 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 ~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 ~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 power supply was maintained at an output of 300 V and a current of 0.36 A. The base pressure of the reaction chamber was maintained at 3.0×10^{-2} Torr using a mechanical pump (Varian SD-301) and purged with nitrogen at 1.0 Torr for several times in order to remove the background gases. The as-deposited antimony sulfide thin films were treated with nitrogen plasma at 3.0 Torr during 60 min.

For the as-deposited antimony sulfide thin films, a thermal treatment in nitrogen atmosphere at 300 °C and 300 mTorr during 60 min was undertaken, which was performed in an oven with temperature and pressure controls. The as-deposited, plasma treated, and thermally annealed thin films were structurally, compositionally, morphologically, optically and electrically characterized.

2.3. Characterization

XRD diffraction patterns were recorded on a Rigaku D-Max X-ray diffractometer using Cu-K_α radiation (λ = 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 3×10^5 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_2S_3 (JCPDS 42-1393) which has an orthorhombic structure. The XRD pattern of the Sb_2S_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_2S_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, λ is the wavelength of

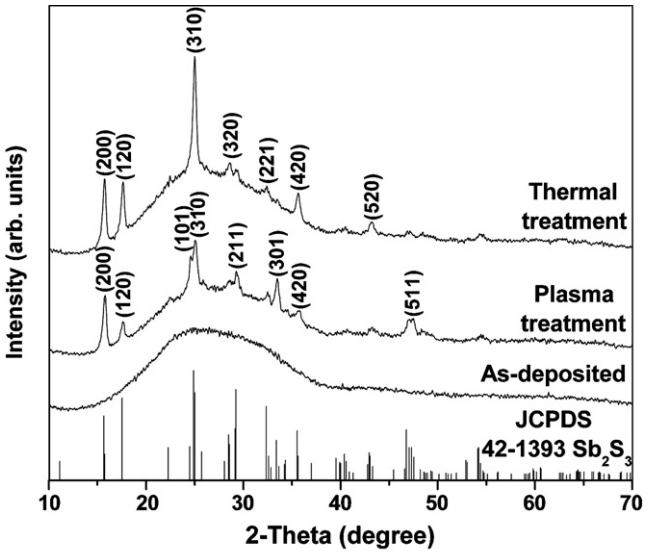

Fig. 1. X-ray diffraction patterns for as-deposited, plasma treated, and thermally annealed antimony sulfide thin films.