Applied Surface Science 393 (2017) 369–376

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Full Length Article

Antimony sulfide thin films prepared by laser assisted chemical bath deposition

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ARTICLE INFO

Article history:
Received 31 July 2016
Received in revised form
26 September 2016
Accepted 8 October 2016

Keywords:
Sb_2S_3 thin films
Chemical bath deposition
XRD
XPS
Optoelectronic properties

ABSTRACT

Antimony sulfide (Sb_2S_3) thin films were prepared by laser assisted chemical bath deposition (LACBD) technique. These thin films were deposited on glass substrates from a chemical bath containing antimony chloride, acetone and sodium thiosulfate under various conditions of normal chemical bath deposition (CBD) as well as in-situ irradiation of the chemical bath using a continuous laser of 532 nm wavelength. Structure, composition, morphology, optical and electrical properties of the Sb_2S_3 thin films produced by normal CBD and LACBD were analyzed by X-Ray diffraction (XRD), Raman Spectroscopy, Atomic force microscopy (AFM), X-Ray photoelectron spectroscopy (XPS), UV–vis spectroscopy and Photoconductivity. The results showed that LACBD is an effective synthesis technique to obtain Sb_2S_3 thin films for optoelectronic applications.

1. Introduction

Antimony sulfide (Sb_2S_3) is one of the interesting metal chalcogenides and their thin films are of considerable interest in the semiconductor industry for making infrared detectors, diodes, Hall-effect devices, high-reflecting dielectric film, microwave devices, switching devices, photocatalysts etc. [1–4]. Chemically deposited Sb_2S_3 films were incorporated as absorber layer in different heterojunction photovoltaic structures as a promising material because of high absorption coefficient ($\alpha \sim 10^5\ cm^{-1}$) and the band gap between 1.7–2.5 eV [5,6]. Various physical and chemical techniques are known to prepare Sb_2S_3 thin films. However, thin films deposited by chemical bath deposition (CBD) are widely considered because this technique is relatively simple, low temperature process and suitable for inexpensive large-area deposition [7–9] with respect to high-cost vacuum techniques [10–12]. The quality and stoichiometry of the films differ as their structural and optical properties depend on the preparation methods (chemical bath deposition, thermal evaporation, pulsed laser deposition, atomic layer deposition, spray pyrolysis etc.) and for CBD also on pH of the solution, deposition temperature, deposition time and thermal treatments (annealing temperature and time because the films as deposited by CBD are amorphous) [5,6,8,13–17]. Recent advances on use of Sb_2S_3 in photovoltaics as absorber include nanoporous [18] and nanofibrous networks of TiO_2 [19], Sb_2S_3/metal oxide (Al_2O_3 or ZrO_2) with a high open voltage of 0.712 V [20] and hybrid structures using poly(3-hexylthiophene) (P3HT) as hole transporting material [9].

Recently, we have found that the modification of CdS CBD process by in-situ irradiation of the bath using a continuous laser [21] or a pulsed laser [22], resulting an accelerated film growth and the thin films of improved morphology and electrical conductivity. In the present work, we report the effects of continuous wave laser irradiation of the Sb_2S_3 chemical process (LACBD) during the film deposition. The effect of in-situ irradiation of the chemical bath by 532 nm laser for different power densities as well as different durations of depositions (30, 45 and 60 min) are investigated. The

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http://dx.doi.org/10.1016/j.apsusc.2016.10.051
0169-4332/

structure, morphology, composition, optical and electrical properties of Sb_2S_3 thin films obtained by LACBD technique are analyzed and the results are compared with thin films prepared under normal CBD conditions.

2. Experimental

2.1. Preparation of Sb_2S_3 thin films

The films were deposited on glass substrates (Fisher Scientific) previously washed with chromic solution, then rinsed with distilled water and dried in the flowing air. Sb_2S_3 thin films were prepared from a chemical bath containing $SbCl_3$ (Antimony trichloride, 99%, Fermont), $CH_3(CO)CH_3$ (acetone, 99.5%, Fermont) and $Na_2S_2O_3{\cdot}5H_2O$ (sodium thiosulfate pentahydrate, 99.5%, Fermont). The deposition process was as follows: in a 100 ml beaker, 650 mg of $SbCl_3$, 2.5 ml of $CH_3(CO)CH_3$ and 20 ml of 1 M $Na_2S_2O_3{\cdot}5H_2O$ was added followed by 72.5 ml of water as reported [6]. The substrates were immersed horizontally in the bath and the chemical reaction was carried out at 40 °C in a constant temperature bath system. Laser output from a diode pumped solid state (DPSS) continuous wave laser at 532 nm of wavelength with regulated power (0.1–10 W, CNI Laser, Model MGL-W-532) was expanded to irradiate the solution during the deposition process; a concave lens was used to expand the laser beam, varying the incident laser power densities of 0.8, 1.0 and 1.3 W/cm^2 for three different deposition times (30, 45 and 60 min). Also the thin films were prepared from an identical bath without laser irradiation for 30, 45 and 60 min. Thin films deposited on the substrate side facing the bottom of the beaker were considered for analysis and the other side was cleaned carefully with very dilute hydrochloric acid and dried well at ambient conditions. Since the as prepared thin films of Sb_2S_3 were amorphous in nature, all the films obtained under normal CBD and laser assisted CBD were annealed in vacuum at 350 °C for one hour. These thin films characterized to explore their structure, morphology and optoelectronic properties.

2.2. Characterization

The structural properties of the thin films obtained were analyzed by X-ray diffraction (XRD) using an Empyrean PANalytical diffractometer using CuKα radiation of wavelength 1.5406 Å operated at 45 kV and 40 mA, at grazing incidence mode at an angle of incidence 1°. The scan range (2θ) was from 15 to 70° at a scan speed of 0.005°/s. The thin films were also characterized by Raman spectroscopy (Thermo Scientific DXR Raman microscope) using 532 nm excitation wavelength. Film thickness was measured using a stylus profiler (Alpha Step D-100, KLA-Tencor). X-ray photoelectron spectroscopy (XPS) study was done using Thermo Scientific K-alpha XPS system employing a monochromatized Al Kα X-ray radiation of energy 1486.6 eV. All the XPS spectra were recorded with reference to C 1s peak (284.6 eV). The surface morphology of the films was examined by atomic force microscopy (AFM, Model Solver Pro from NT-MDT) in contact mode. The optical transmittance at normal incidence, T (%), and specular reflectance spectra, R (%), of the films were measured using a spectrophotometer Shimadzu model UV-1800. in the UV–vis-NIR region (200–1100 nm wavelength range). Electrical measurements were carried out using a picoammeter/voltage source (Keithley 6487). For photoconductivity measurements the contacts were made using conductive silver paint (SPI supplies).

3. Results and discussion

3.1. X-ray diffraction

Crystalline structures for the Sb_2S_3 thin films prepared by CBD and LACBD that annealed at 350 °C for one hour in vacuum were analyzed from the XRD patterns. Fig. 1(A, B) shows the diffraction patterns for LACBD Sb_2S_3 thin films deposited for 30, 45 and 60 min under various power densities. XRD patterns corresponding to Sb_2S_3 thin films under normal CBD are also included for a comparison. From Fig. 1A, all the peaks present in the case of 30 min deposited film under CBD as well as under LACBD of 1.3 W/cm^2 are identified as diffractions from the planes corresponding to Sb_2S_3 orthorhombic structure (PDF#42-1393). Most intense peak is along (130) plane. Other peaks are identified as (020), (120), (220), (211), (221), (240), (041), (141), (421), (501), (351), (132) planes those fitted well with the standard JCPDS data that is included in the figure. The same orientation can be seen for 45 min CBD Sb_2S_3 thin film, while an additional peak is aroused corresponding to (230) reflection. For 45 min under LACBD of 1.3 W/cm^2, the preferred orientation changes to (211) plane and (111), (301) and (311) planes reflections appear, with the expense of (020), (120) and (130) peak intensities. Further, (211), (221) and (501) peak intensity increases as evident from the figure. All the peaks are corresponding to the orthorhombic structure. Fig. 1B shows the diffraction patterns for the thin films deposited for 60 min under normal CBD and LACBD of three different power densities (0.8, 1.0 and 1.3 W/cm^2). All the peaks identified are corresponding to the stibnite structure with more prominent peaks and same preferred orientations along (211) for all the LACBD films compared to that of normal CBD. Thus, XRD analysis showed that the annealed thin films obtained under different conditions were polycrystalline [6–8,13]. The crystalline changes can be due to annealing temperature and film thickness.

3.2. Raman spectra

Raman spectral analysis was done using 532 nm laser wavelength as excitation at 3 mW laser power for all the spectral measurements. Fig. 2(A,B) shows the Raman spectra for Sb_2S_3 thin films obtained under normal CBD and LACBD. Fig. 2A shows the Raman spectra for samples prepared under normal CBD for 30 and 45 min as well as under laser assisted CBD. There was an increase in peak intensities for LACBD thin films compared to that under normal CBD. This can be related to the improved crystallinity for these films under LACBD as observed in XRD analysis. Peaks were observed at positions of 128, 155, 189, 236, 280 and 305 cm^{-1} for all the samples with slight variations in intensities for different conditions. Interesting observation is that for 45 min deposition under normal CBD, the most intense peak is at 280 cm^{-1} and the presence of peak at 236 cm^{-1} also well defined which may be due to its preferred orientation along (130) plane as observed in XRD results (Fig. 1A). These bands are in agreement with the Raman analysis reported for Sb_2S_3 [23–25]. In a study on the lattice dynamics of Sb_2S_3, 30 Raman active modes constituting 10 A_g, 5B_{1g}, 10 B_{2g} and 5B_{3g} modes are identified[25], the notations have usual meanings. Such modes constitute vibrations of symmetric and anti-symmetric Sb-S bonds, and symmetric and anti-symmetric S-Sb-S bending vibrations. Comparing with the reported Raman peak data [25,26], peaks at 155, 189 and 280 cm^{-1} can be attributed to Ag modes and the peaks at 128, 236 and 305 cm^{-1} can be correlated to B1 g modes of vibration. Fig. 2B shows the Raman spectra for all samples deposited for 60 min under normal CBD and LACBD. All the characteristic Raman modes are present in all the samples as seen in the figure. These findings of Raman spectral analysis also support the XRD results that the thin films are of stibnite structure.