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Effect of substrate temperature on copper antimony sulphide thin films from thermal evaporation

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ABSTRACT

Copper antimony Sulfide (CAS) thin films were deposited on glass substrate using thermal evaporation technique at different substrate temperatures. Using $CuCl_2.2H_2O$, $SbCl_3$ and thiourea as parental materials, the evaporant source material was synthesized by solvothermal method. Moreover, phase identification using X-Ray diffraction was made after the removal of by-products. The $CuSbS_2$ bulk material was pelletized using hydraulic press and used as a target material for developing CAS films on glass substrate with different substrate temperatures such as, Room Temperature (without substrate temperature), 100 °C, 200 °C, 300 °C and 400 °C. The source material and the deposited CAS films were subjected to X-ray diffraction analysis, Raman spectroscopy, Transmission Electron Microscopy, Scanning Electron Microscopy, Atomic Force Microscopy, X-Ray Photo Electron Spectroscopy, Energy Dispersive X-ray Spectral analysis and UV–Vis Spectroscopy. Hall Effect measurement was carried out to investigate, whether the CAS films exhibits p-type conductivity. The deposited films were found to have the band gap in the range of 2.18 eV and 1.62 eV.

1. Introduction

Many researchers have focused their attention in fabricating low cost device using metal chalcogenides for few decades in the field of optoelectronics, mainly in energy conversion and energy storage based innovations; which gained more attention in preventing the future energy requirements due to the reduction in the fossil fuels. Currently, II–VI, IV–VI, I–III–VI_2, I–II–III–VI_2 group compound semiconductors are considered for producing energy from the renewable energy source [1,2]. Recently one of the I–V–VI_2 group compound semiconductors Copper Antimony Sulfide as a new combination is claimed to be useful for device fabrication in photovoltaic application with p-type conductivity having band gap between 0.9 and 1.9 eV, and further which has high absorption coefficient of ($>10^5$) [3–5]. Copper antimony Sulfide has four stable phases in the atmospheric temperature such as $CuSbS_2$ (Chalcostibite), Cu_3SbS_4 (Femitinite), Cu_3SbS_3 (Skinnerite) and $Cu_{12}Sb_4S_{13}$ (Tetrahedrite). The above mentioned phases exhibit p-type semiconducting nature [3,6], compared to the existing absorber materials like CdTe, Copper Indium Sulfide/Selenide (CIS), Copper Indium Gallium Sulfide/Selenide (CIGS) and have advantages like low toxicity than Cd, Se, Ga. CAS contains constituents are of earth abundant and economically adoptable materials used for device fabrication in low-cost and eco-friendly manner [1,7]. Copper antimony sulfide thin films were achieved by different deposition methods as Spray Pyrolysis [7], Chemical Vapour Deposition (CVD), Sputtering, Thermal Evaporation [8–11], Chemical Bath Deposition [12,13] and Electro Chemical Deposition [14–16]. Also, different morphological CAS like nano sheets, nano pyramidal [17], nano brick [18,19], coral like [20], plates like [21], nano fibbers [7], nano flakes and meso-belts [21] were reported earlier in the literature.

In the present work, $CuSbS_2$ bulk material was synthesised from solvothermal route and used as a source material for thermal evaporation. Thin films were successfully deposited on glass substrates at different substrate temperature up to 400 °C using vacuum thermal evaporation technique. The deposited films were investigated for their properties as absorber material for thin film photovoltaics [8].

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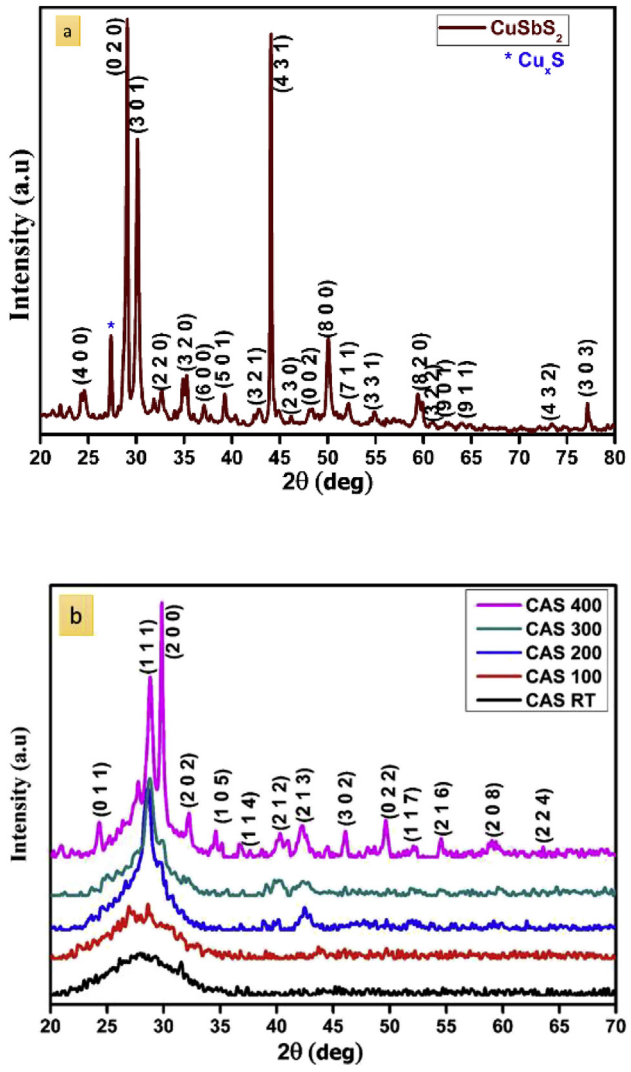

Fig. 1. XRD patterns of as prepared (a) CAS bulk material and deposited (b) CAS thin films.

2. Experimental procedure

2.1. Synthesis of $CuSbS_2$ (CAS) bulk material

The $CuSbS_2$ bulk material was prepared via solvothermal approach. 0.1 M of $CuCl_2.2H_2O$, and 0.1 M of $SbCl_3$ as cationic and 0.2 M Thiourea as anionic of each 40 ml were used as source materials. Oleic acid was used as a complexing agent and 0.01 M of Di sodium salt of ETDA was used as a chelating agent. It forms complexes with the metal ions and once it gets saturated in capturing, it periodically releases the metal ions. The mixture was well stirred and transferred into a stainless steel autoclave (250 ml) with a Teflon liner and the autoclave was tightly sealed to prevent from leakageand formation of oxides. The autoclave was maintained at 200 °C for 24 h in hot oven and then allowed to cool down to room temperature naturally. Later on, as synthesized material was washed several times with double distilled water, to remove unreacted materials and centrifuged for 20 min in 3000 rpm. The collected materials were again washed three times with ethanol for removing by products and centrifuged for 10 min at 3500 rpm. Finally, collected material was washed with acetone. The end product was dried in room temperature and stored in the vacuum desiccator for further process.

2.2. Deposition of $CuSbS_2$ Thin films

The obtained final product was dark garish in colour with glittering surfaces. After the phase identification of the material by the powder X-ray diffraction, the source material was pelletized by hydraulic press with applying 3 ton (N/m^2) pressure. Small pieces of $CuSbS_2$ (0.5 g) material was loaded in the resistive heating crucible (Molybdenum) and the pressure of the chamber during thin film deposition was about 10^{-5} torr. Ultrasonically cleaned and degreased substrate was mounted on thermocoupled substrate heater along with the evaporation source. The thin film deposition was done at various substrate temperature of RT, 100 °C, 200 °C, 300 °C and 400 °C using Hind High vac12A4-D Vacuum Coater.

2.3. Characterization techniques

X-ray diffraction patterns (XRD) of thin films were recorded using BRUKER D2 Phaser Diffractometer by employing CuKα radiation (1.54056 Å). The Raman spectroscopic analysis was carried out at room temperature using Renishaw Laser Raman spectrometer with resolution of 1 cm^{-1} in the wave number range of 200–600 cm^{-1} and an excitation wavelength using Ar ion laser with a wavelength of 488 nm. High resolution transmission electron microscope (HRTEM) images and selective area electron diffraction were made using FEI Tecnai TM G2 F20 (S-TWIN). The surface grain distribution and compositional features were carried out using Carl-Zeiss EVO 18 Special Edition scanning electron microscope equipped with energy dispersive X-ray spectroscopy (EDX) setup. The 2D and 3D topographic images and surface roughness of thin films were taken by A100 SGS APE Research atomic force microscope (non-contact mode), X-ray photoelectron spectroscopic (XPS) analysis was performed by ESCA-3400 Electron Spectrometer. Optical absorption spectra of the films were recorded using a Perkins–Elmer Lambda 35

Table 1
Calculated lattice values, crystallite size, d spacing values, dislocation density, strain of as prepared CAS bulk material.

Sample	Lattice values (Å)	2Theta (deg)	(hkl)	Calculated d spacing values (Å)	Average crystallite size (nm)	Dislocation density (δ) 10^{16} lines/m^2	Strain (ε) × 10^{-3}
CAS powder	JCPDS	24.585	(400)	3.61	9.9	1.02	−9.1
	a = 6.019	29.193	(020)	3.05			
	b = 3.796	30.152	(301)	2.96			
	c = 14.501	34.855	(320)	2.57			
	Calculated	44.074	(016)	2.05			
	a = 6.02	50.060	(800)	1.82			
	b = 3.80	59.170	(820)	1.56			
	c = 14.51	77.129	(303)	1.23			