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Effect of copper concentration on the properties of chemically deposited $MoSb_{2-x}Cu_xSe_4$/CdS thin film absorbing layer for photovoltaic applications

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ABSTRACT

In this present work, a novel mixed metal chalcogenide $MoSb_{2-x}Cu_xSe_4$ nanocrystalline thin films deposited for different copper concentrations (x = 0.0 M, 0.1 M, 0.2 M & 0.3 M) on glass substrate using ethylenediaminetetraacetic acid (EDTA) as complexing agent by chemical bath deposition method at room temperature. XRD patterns revealed the incorporation of copper content by the conversion of orthorhombic Sb_2Se_3 into Cu_3SbSe_3 with a shift to higher angles. Average crystallite was found to be 134, 51, 34 and 17 nm for the deposited films. FTIR spectra confirm the presence of functional groups of Ethylenediaminetetraacetic acid (EDTA) and the metal oxide vibrations. FESEM analysis depicted the morphological changes with the addition of Cu content. UV–vis analysis shows higher absorption in the visible region and the band gap values are found to be 4.09–1.63 eV. Hall Effect analysis confirms the p-type nature of the material. The photo-current analysis shows higher photo-conversion efficiency of 1.78% for 0.3 M copper content.

1. Introduction

To meet the growing global energy demands with inorganic thin film solar cells a broad absorber material basis is required. So far efficiencies over 10% have only been successfully realized with a small number of inorganic compound semiconducting absorber materials such as CdTe, $CuInGaSe_2$, $Cu_2ZnSn(S,Se)_4$ and Cus. Several alternative semiconductors are known to have appropriate bulk properties such as absorption coefficient, band gap energy and diffusion length of charge carriers but did not lead to high efficiencies, yet [1]. Recently, chalcogenide and transition metal doped thin films have become attractive materials for fundamental research due to their structural, optical and electrical properties. In particular, p-type multinary chalcopyrite compounds began to attract attention because of their suitable band gap and they have proven to show efficient optical energy conversion compared woth n-type semiconductors. Study and development of an efficient p-type photoelectrode can greatly help in the improvement of solar radiation conversion efficiency by forming *p-n* heterojunction solar cells as they offer more protection against photocorrosion because the p-type semiconductors are cathodically protected under illumination [2]. Suvarta et al., have already reported the p-type solid solution of CuSe, Bi_2Se_3 and $MoSe_2$ semiconducting thin film with band gap energy (1.26 to 1.6 eV) to absorb visible light radiation and produced the photoconversion efficiency of 0.074 for higher copper concentration. Also, Patil et al. [3], Salunkhe et al. [4], Mane et al. [5] and Patil et al. [6], have prepared mixed metal chalcogenide films by Arrested Precipitation Technique (APT). Recently Kharade et al., prepared a novel $MoBi_{2-x}Cu_xSe_2$ thin films by chemical bath deposition method [2]. We have also reported [7] mixed metal chalcogenide $MoSb_{2-x}Cu_xSe_2$ thin films using Triethanolamine (TEA) as complexing agent by simple Chemical Bath Deposition (CBD) method. Hence, it is planned to utilize all these materials to prepare a new, cheap mixed metal chalcogenide for solar cell applications by simple CBD method.

In this investigation, we have deposited $MoSb_{2-x}Cu_xSe_4$/CdS (x = 0.0 M, 0.1 M, 0.2 M & 0.3 M) thin films by CBD method using EDTA as complexing on glass substrates at room temperature. In this paper, we have investigated the effect of copper concentration on opto-structural, morphological, electrical and photoresponse properties of the films.

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2. Experimental procedure

In typical synthesis, an appropriate volume of cationic precursor solution such as 0.2 M $SbCl_3$ (≥98%) – acetone (5 mL), 0.1 M $Cu(NO_3)_2$ (95%) – distilled water (15 mL), 0.1 M Na_2MoO_4 (≥98.5%) – distilled water (15 mL) was prepared. A 0.2 M SeO_2 (98%) solution was prepared by dissolving SeO_2 in 15 mL distilled water and then 1 mL N_2H_4 was added. Subsequently, a brick red colour solution was obtained indicating SeO_2 reduced as Se^{2-} ions in the solution. Then the solution was mixed into the cationic precursor solution followed by the addition of 0.1 M EDTA (10 mL of water) and stirred well for 15 min. The total volume of reaction solution was made to 80 mL by adding distilled water and was stirred well for 15 min to obtain homogeneous solution. During the reaction process, green colour of the solution turned into brownish black. The pre-cleaned glass substrates were immersed in the reaction container at room temperature for deposition. After 48 h of deposition period, the glass substrates were withdrawn from the solution, rinsed with double distilled water and annealed at 200 °C for 1hr for further investigations. Similarly, the copper concentration in each reaction bath was varied by adding the 0.1 M, 0.2 M and 0.3 M $Cu(NO_3)_2$ solution.

The structural properties of thin films were studied using X'pert PRO X-ray Diffractometer using Cu kα (k = 1.5406 Å) radiation. FTIR spectra were recorded using Perkin Elmer, Spectrum Two. The surface morphology was examined using Field Emission Scanning Electron Microscope (FESEM) using BRUKER-QUANTAXEDS and the elemental analysis was carried out by Energy Dispersive Spectroscopy (EDS) analyzer FEI Quanta FEG 200. UV analysis was carried out using the instrument SPECORD210PLUS. Hall measurements were recorded using the Hall Effect Setup (Digital), Model DHE-21. J-V measurements are carried out by the Keithley Source meter 2450, under the illumination of 20 mW/cm^2 power.

3. Results and discussion

3.1. XRD analysis

Fig. 1(a–e) represents the XRD patterns of $MoSb_{2-x}Cu_xSe_4$ thin films prepared using EDTA as complexing agent for various copper concentrations (0.0 M, 0.1 M, 0.2 M and 0.3 M). In Fig. 1(a), two different binary phases of orthorhombic structured Sb_2Se_3 (at 2θ = 27.62° (3 2 0) and 31.75° (4 1 0) (JCPDS ICDD Card No: 89-0821)) and Mo_9Se_{11} (at 2θ = 31.75° (0 4 2) (JCPDS ICDD Card No: 65-4363)) are seen. When introducing Cu (0.1 M) into $MACS_0$ system, the crystalline peak at 2θ = 27.62° shifted towards higher diffraction angle at 29.60° (1 1 2) (JCPDS ICDD Card No: 86-1751) indicating the formation of ternary orthorhombic structured Cu_3SbSe_3. Some binary phases such as cubic structured $CuSe_2$ shown at 2θ = 51.87° (JCPDS ICDD Card No: 71-0047) and rhombohedral structured $Mo_{15}Se_{19}$ (JCPDS ICDD Card No: 85-1690) or orthorhombic structured Sb_2Se_3 (JCPDS ICDD Card NO: 65-1317) are seen at 2θ = 31.24°. The detected XRD peaks are tabulated in Table 1.

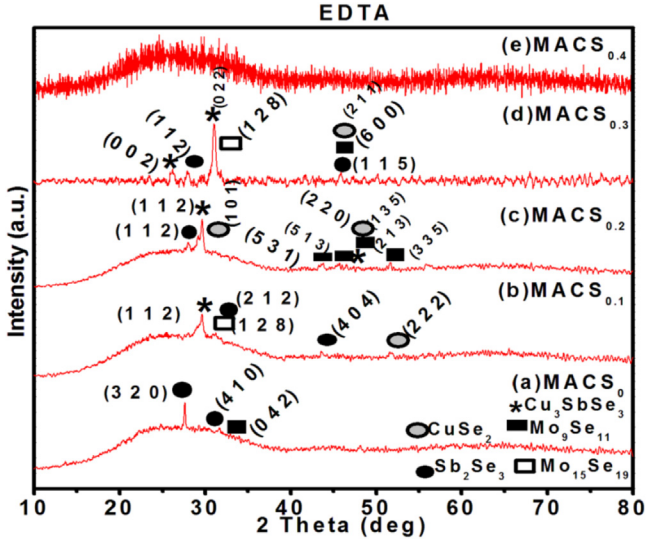

Fig. 1. XRD patterns of $MoSb_{2-x}Cu_xSe_4$ thin films (a) $MACS_0$, (b)$MACS_{0.1}$, (c) $MACS_{0.2}$, (d) $MACS_{0.3}$ and (e) $MACS_{0.4}$.

The peak shift is more pronounced with increase the copper content into $MoSb_{2-x}Cu_xSe_4$ systems and it revealed in Fig. 2. Addition of Cu content decreases the peak intensity and cause the peak shift. Similar trend is noticed in $MoSb_{2-x}Cu_xSe_4$ systems prepared using Triethanolamine complexing agent film [7].

The average crystallite size of the films were calculated using diffractogram and Scherer's formula [8],

$$D = 0.9\lambda/\beta \cos\theta \quad (1)$$

where, λ is the wavelength of X-ray (1.54 Å), β is Full Width at Half Maximum and θ is the diffraction angle. The average crystallite size is found to be 134, 51, 34 and 17 nm for $MACS_0$, $MACS_{0.1}$, $MACS_{0.2}$ and $MACS_{0.3}$ respectively. It is clearly seen that as Cu content increases the crystallite decreases. The dislocation density (δ) and micro strain (ε) of the films were calculated using Eqs. (2) and (3):

$$\delta = n/D^2 \text{ lines/m}^2 \quad (2)$$

where, n is a factor which equals unity giving minimum dislocation density. Dislocations are an imperfection in a crystal associated with misregistry of the lattice in one part of the crystal with respect to another part. The origin of strain (ε) has related the lattice 'misfit' which in turn depends upon the growing conditions of the film [11].

$$\varepsilon = \beta \cos\theta/4 \quad (3)$$

Table 1
XRD values of $MoSb_{2-x}Cu_xSe_4$ thin films for different Cu concentrations.

System	2θ (deg)	Observed Phases	(*hkl*)	d-spacing (Å)	
				Observed	Standard
$MACS_0$	27.62	Sb_2Se_3	(3 2 0)	3.2258	3.2270
	31.75	Mo_9Se_{11}	(0 4 2)	2.8149	2.8156
		Sb_2Se_3	(4 1 0)	2.8149	2.8126
$MACS_{0.1}$	29.60	Cu_3SbSe_3	(1 1 2)	3.0143	3.0134
	31.24	$Mo_{15}Se_{19}$	(1 2 8)	2.8597	2.8638
		Sb_2Se_3	(2 1 2)	2.8597	2.8606
	43.72	Sb_2Se_3	(4 0 4)	2.0680	2.0672
	51.87	$CuSe_2$	(2 2 2)	1.6326	1.7655
$MACS_{0.2}$	28.14	Sb_2Se_3	(1 1 2)	3.1673	3.1683
	29.68	Cu_3SbSe_3	(1 1 2)	3.0064	3.0134
	43.84	Mo_9Se_{11}	(5 3 1)	2.0626	2.0619
	45.65	Mo_9Se_{11}	(5 1 3)	1.9850	1.9840
	46.63	Mo_9Se_{11}	(1 3 5)	1.9455	1.9453
		Cu_3SbSe_3	(2 1 3)	1.9455	1.9458
		$CuSe_2$	(2 2 0)	1.9508	1.9455
	51.71	Mo_9Se_{11}	(3 3 5)	1.7657	1.7675
$MACS_{0.3}$	26.09	Cu_3SbSe_3	(0 0 2)	3.4114	3.4186
	28.14	Sb_2Se_3	(1 1 2)	3.1673	3.1683
	31.01	Cu_3SbSe_3	(0 2 2)	2.8804	2.8739
		$Mo_{15}Se_{19}$	(1 2 8)	2.8804	2.8638
	45.99	Sb_2Se_3	(1 1 5)	1.9711	1.9729
		$CuSe_2$	(2 1 1)	1.9711	1.9770