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Effect of Temperature on Structural and Optical Properties of Spray Pyrolysed $CuSbS_2$ Thin Films for Photovoltaic Applications

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Abstract: The $CuSbS_2$ thin film is one of the most promising materials for absorber layer in thin film solar cells. The aqueous solution of precursors containing cupric chloride, antimony acetate and thiourea was deposited on heated glass substrates at various temperatures between 513K to 593K with the interval of 20K. By using spray pyrolysis deposition method, $CuSbS_2$ thin films were successfully deposited on soda lime glass substrates and the influence of substrate temperature on the structural, morphological and optical properties of $CuSbS_2$ thin films were investigated. The GIXRD pattern showed that all the films were polycrystalline nature having (102), (111), (006) and (116) phases and the crystallinity were improved with increasing substrate temperature. The microstructure of $CuSbS_2$ thin films were studied by Raman spectroscopic measurement at room temperature. Surface morphology of the thin films was studied by employing Atomic Force Microscopy that revealed the average roughness decreased with increasing substrate temperature. Optical band gap of the $CuSbS_2$ films deposited at various temperatures was found to lie between 1.35-1.50 eV which is close to the ideal band gap for the highest conversion efficiency of solar cell.

Keywords: $CuSbS_2$, Optical Properties, Solar Cells, Spray Pyrolysis, Structural Properties, Substrate Temperature , Thin films.

1 Introduction

The ternary chalcogenide $CuSbS_2$ semiconductor with narrow band gap is essential in various optoelectronic devices such as infrared detectors and solar cells. It exhibits suitable band gap energy of 1.5 eV and the absorption coefficient over 10^4 cm^{-1}, which is the optimum value for an absorber material in solar cell applications. This material is also used as an alternative to $CuInS_2$ considering its non-toxicity, relative abundance and nearly equal ionic radii of Indium and Antimony [1],[2],[3],[4]. Copper Antimony Sulfide thin films could be deposited by using several deposition techniques such as thermal evaporation [3],[4], chemical vapor deposition [5], thermal diffusion [6], chemical bath deposition [7], electro-deposition [8] and spray pyrolysis [9],[10],[11]. Chemical Spray pyrolysis is proved to be a versatile and low-cost technique, which is widely used to deposit large-area chalcogenides, selenide, sulfide and oxide semiconductor thin films for photovoltaic applications. After Monalache *et al.,* [10] investigating the influence of the precursor weight ratio on the crystal growth, they reported the grain size, band gap energy increase when increasing the antimony amount. Monalache and Duta [9] investigated the deposition parameters of $CuSbS_2$ thin films and they reported the photovoltaic response was obtained from the sample deposited at 240ºC, band gap 1.13 eV with the cell characteristics V_{oc}=90 mV, I_{sc}=2.39X10^{-2} mA. In order to optimize the substrate temperature to obtain suitable photovoltaic properties of $CuSbS_2$ thin films, we have investigated the influence of substrate temperature on the structural, morphological and optical properties of $CuSbS_2$ thin films deposited in between 513K to 593K. The results of these investigations are presented in this paper.

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2 Experimental Details

2.1 Sample Preparation

The $CuSbS_2$ thin films were deposited by the Spray Pyrolysis technique starting with an aqueous solution containing the precursors such as cupric chloride (0.01 M), antimony acetate (0.003 M), and thiourea (0.006 M). In order to avoid the precipitation and loss of sulfur during pyrolysis, concentration of thiourea was taken three times larger than that is usually required to be present in the aqueous solution to maintain stoichiometry. A small amount of acetic acid was added to increase the solubility of antimony acetate. For the deposition of $CuSbS_2$ thin films, the aqueous solution was sprayed at a rate of 5 ml/min on to heated glass substrates using compressed air as a carrier gas and the distance between the substrate to spray nozzle was placed at 40 cm. The depositions were repeated at various substrate temperatures such as 513K, 533K, 553K, 573K and 593K with an accuracy of ±5K.

2.2 Characterization

The Glancing Incidence X-Ray Diffraction (GIXRD) pattern of $CuSbS_2$ thin films was recorded using Bruker D8 discover glancing incidence X-ray diffractometer with a copper source. The room temperature Raman spectra were performed using Jobin-Yvon Horiba (LABRAM HR-800) Micro-Raman spectrometer. The grain size and the root mean square (rms) roughness of the $CuSbS_2$ thin films were observed using Nano scoped E model Atomic Force Microscope (AFM) with contact mode. The optical analysis of $CuSbS_2$ thin films was carried out by recording the transmission and absorption spectra of the samples using Perkin-Elmer Lambda 35, double beam UV-Visible spectrophotometer.

3 Results and Discussion

3.1 XRD Characterization

The GIXRD pattern of $CuSbS_2$ thin films was deposited at various substrate temperatures are shown in Fig.1. According to JCPDS Card No: 88-0822, the formation of the orthorhombic system are identified in all the deposited films with the representative peaks located at 19.30° and 36.65° corresponding to the (102) and (006) planes. Moreover, two more peaks are appears at 28.40° and 47.05° corresponding to (111) and (116) orientation in higher substrate temperature.

The grain size of the crystallites were calculated using the Debye Scherer's formula,

$$D = (0.94\lambda / \beta \cos\theta)$$

Where, D is the mean diameter of the crystallites, λ is the wavelength of the X-ray source (1.5406 Å), β is the full width of the dominant peak in radians at half its intensity and θ is the Bragg's angle. The calculated size of the crystallites for the deposited thin films is found to lie in the range 15-30 nm. When the substrate temperature increases, the size of the crystallites is increased.

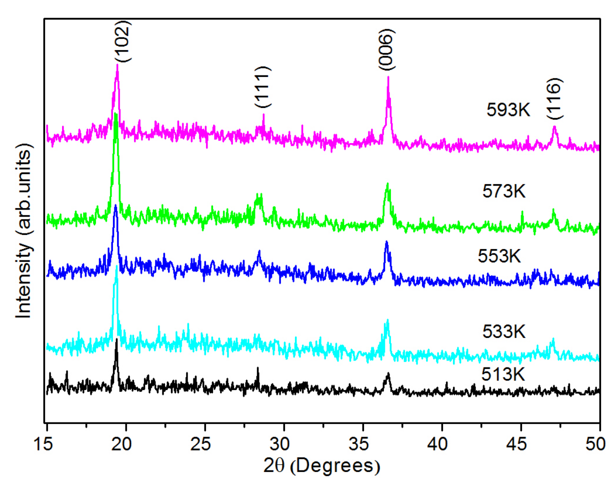

Fig. 1. GIXRD pattern of $CuSbS_2$ thin films sprayed at various substrate temperatures

3.2 Micro-Raman Analysis

In order to support the XRD results, the room temperature Raman measurements were performed in the range 150–1200 cm^{-1} by Micro-Raman spectra using Ar+ laser (488 nm wavelength, 10 mW power) as excitation source. Fig.2. shows the Raman spectra of the $CuSbS_2$ thin films deposited at various substrate temperatures. The Raman spectra was revealed the characteristic of $CuSbS_2$ thin film at 1102 cm^{-1}, then the additional peak located at 471 cm^{-1} corresponds to the $Cu_{2-x}S$ impurity phase, due to the excessive copper element in samples.

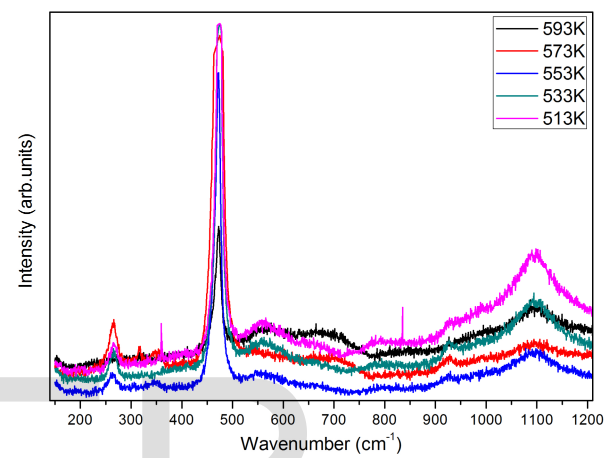

Fig. 2 Micro-Raman spectra of $CuSbS_2$ thin film deposited at various substrate temperatures

3.3 AFM Analysis

Two dimensional and three dimensional micrographs of spray deposited $CuSbS_2$ thin films were recorded using AFM and the resulting micrographs are shown in fig.3. The micrographs clearly show that the surface is uniformly covered with spherical shaped particles. The superstructure of clusters in all micrographs with sizes roughly of 100-300nm were observed. The size of sub-grains in clusters was in the range of several tens of nanometers resembled to the crystallite size calculated from XRD pattern.

The surface of the $CuSbS_2$ thin films is observed to be rough and the vertical height between the highest feature (brightest) and lowest (darkest) is in the range 0.068–0.450 μm indicating that the surface is relatively flat. Based on the AFM analysis, the average roughness of the $CuSbS_2$ films are found to be 16 nm, 25 nm, 38 nm, 62 nm and 89 nm the samples prepared at 593K, 573K, 553K, 533K and 513K respectively. The root-mean-square (rms) roughness of the $CuSbS_2$ films surface was found to be 21 nm, 36 nm, 49 nm, 76 nm and 105 nm. As the substrate temperature increases, the average roughness and rms roughness decreases.

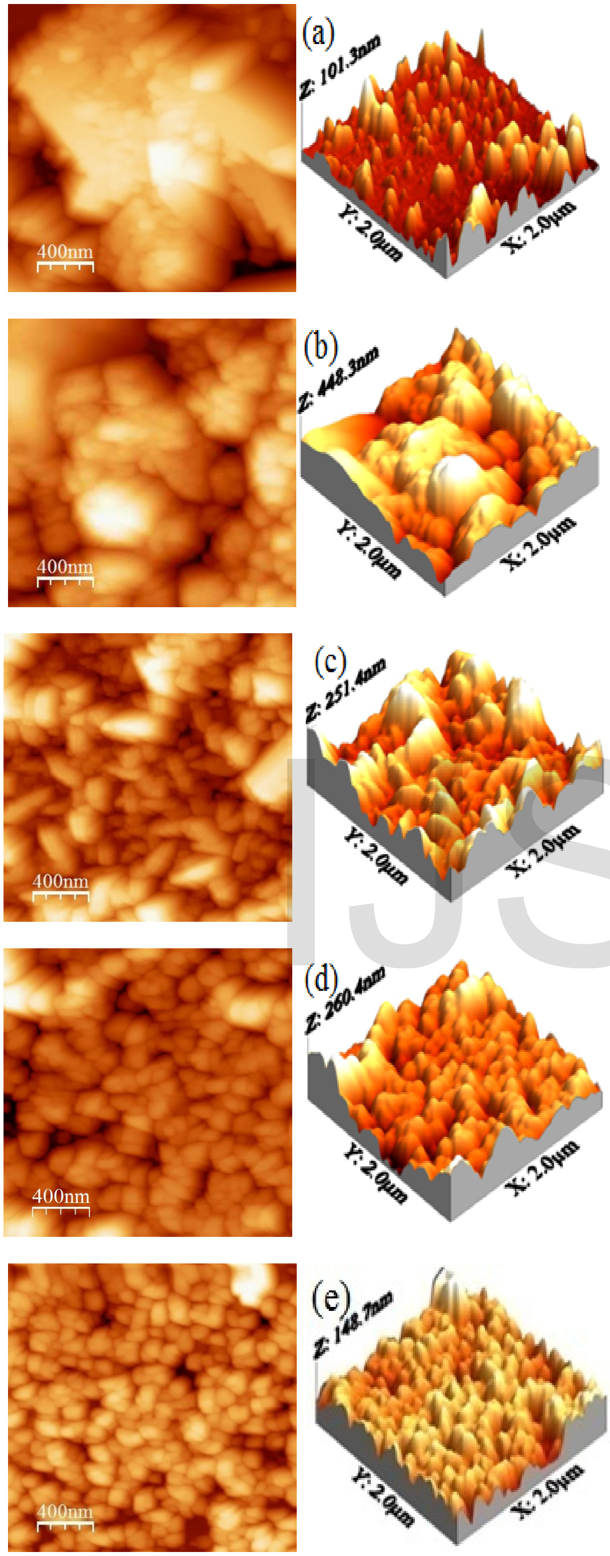

Fig. 3. 2D and 3D AFM micrographs of $CuSbS_2$ thin films sprayed at various substrate temperatures: (a) 513K, (b) 533K, (c) 553K, (d) 573K and (e) 593K.

3.4 Optical Properties

The $CuSbS_2$ thin films were characterized by the optical absorption and transmission spectra in the wavelength range 300-1100 nm using UV-Vis spectrophotometer. The variation of optical density with wavelength is analyzed to find out the nature of transition involved and the optical band gap. The nature of the transition is determined using classical relation,

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

Where, α is the absorption coefficient, A is a constant, h is the Plank's constant, ν is the frequency of the incident beam and E_g is the optical band gap. The value of absorption coefficient in the present case is the order of $10^6 cm^{-1}$, which supports direct band gap nature of the material. A plot of $(\alpha h\nu)^2$ versus $h\nu$ for $CuSbS_2$ thin films deposited at various substrate temperatures are drawn and is shown in fig. 4. Based on the allowed direct inter band transition, the band gap is determined by extrapolating straight line of $(\alpha h\nu)^2$ versus $h\nu$ curve to the intercept on horizontal photon energy axis. The direct optical band gap values are found between 1.35 - 1.50 eV. The band gap of the film is quite close to the optimum band gap required for a solar cell, indicates that $CuSbS_2$ thin films are promising absorber material for solar cells.

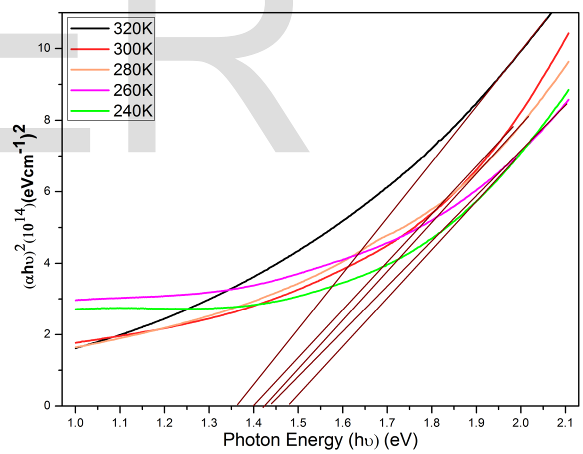

Fig. 4. $(\alpha h\nu)^2$ versus $h\nu$ of $CuSbS_2$ thin films sprayed at various substrate temperatures

4 Conclusions

$CuSbS_2$ thin films were deposited onto heated glass substrates by spray pyrolysis technique. In order to optimize the deposition temperature, the influence of substrate temperature on the growth and properties of spray-deposited $CuSbS_2$ thin film was investigated. The GIXRD pattern of all the $CuSbS_2$ thin films exhibits the formation of orthorhombic system with preferential orientation along (006) direction but when the substrate temperature was increased, crystallinity was improved.

Micro-Raman spectra are revealed the characteristic of $CuSbS_2$ thin films at 1102 cm^{-1}. The average roughness of $CuSbS_2$ thin films was increased owing to decrease in the substrate temperature. The direct optical band gap of $CuSbS_2$ thin films deposited under various substrate temperatures was found to lie between 1.35 - 1.50 eV, as well as an optical absorption coefficient more than $10^6 cm^{-1}$. These characteristics reported in this paper offered perspective for $CuSbS_2$ as suitable absorber material for Photovoltaic applications.

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