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Effect of deposition temperature on structural, optical and electrical properties of copper bismuth sulphide ($CuBiS_2$) thin films deposited by chemical bath deposition

V. BALASUBRAMANIAN*, P. NARESH KUMAR, D. SENGOTTAIYAN

Department of Physics, SNS College of Technology, Sathy main road, Vazhiaampalayam Privu, Coimbatore-35, Tamil Nadu, India

The effect of deposition temperature on the structural, optical and electrical properties of copper bismuth sulphide ($CuBiS_2$) thin films deposited by chemical bath deposition onto glass substrates at different deposition temperatures (40 °C, 50 °C, 60 °C and 70 °C) for 5 hours deposition time period was investigated. The obtained films were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDAX) and optical absorption spectra. All deposited films were polycrystalline and had an orthorhombic structure. Their grain size had changed with deposition temperature and their compositions were nearly stoichiometric. The optical band gap value was decreased from 2.44 eV to 2.33 eV with increasing the film thickness. Electrical parameters such as mobility and type of electrical conduction were determined from the Hall effect measurements. They showed that the obtained films have n-type conductivity and mobility values of the copper bismuth sulphide ($CuBiS_2$) films have changed with deposition temperature.

Keywords: *copper bismuth sulphide ($CuBiS_2$); polycrystalline structure; X-ray technique; optical band gap; Hall coefficient*

1. Introduction

In recent times, nanostructured materials have been a focus of scientific research due to their potential applications in solar cells and other electronic devices. The optical and electrical properties of the materials change by changing the grain size. These unique properties are required for the development of modern electronic devices. The members of V-VI compounds semiconductors are considered important materials for the potential application in photosensitivity, photoconductivity and thermoelectric power [1–3]. Among the V-VI compound semiconductors, copper bismuth sulphide ($CuBiS_2$) draws much attention for its superior properties, such as high absorption coefficient, band gap energy of 1.8 eV and good chemical stability.

*E-mail: balavelusamy81@gmail.com

A variety of deposition techniques has been used to grow nanocrystalline thin films with desirable structural, optical and electrical properties [4–12]. Since the last decade, the priority has been given to develop a low cost deposition technique [13]. For this purpose, CBD has attracted much attention because it is simple and cheap technique [14]. Sonawane et al. [15] deposited $CuBiS_2$ thin films from chemical bath deposition method using sodium thiosulphate as a sulphide ion source. The films were polycrystalline with an optical band gap of 1.8 eV. Pawar et al. [16] prepared $CuBiS_2$ thin films using spray pyrolysis technique with thiourea as sulphur ion source and reported their structural and optical properties.

In this paper, we have reported the preparation of $CuBiS_2$ thin films by chemical bath deposition technique using sodium thiosulphate as a sulphide ion source and EDTA as a complexing agent. The prepared films were annealed in air atmosphere for

2 h at 250 °C to study the structural, optical and electrical properties.

2. Experimental

2.1. Fabrication of copper bismuth sulphide ($CuBiS_2$) thin films

In order to obtain copper bismuth sulphide ($CuBiS_2$) films, 9 mL of 1 M copper nitrate ($Cu(NO_3)_2$), 9 mL of 1 M bismuth nitrate ($Bi(NO_3)_3$), 9 mL of ethylenediaminetetraacetic acid (EDTA) and 18 mL of sodium thiosulphate ($Na_2S_2O_3$) were used in deposition bath. pH value of the final solution was 2.5. Each of the $CuBiS_2$ thin films was obtained at different bath temperature of 40 °C, 50 °C, 60 °C and 70 °C on glass substrate for 5 hours. The obtained films were dark brown.

2.2. Characterization of copper bismuth sulphide ($CuBiS_2$) thin films

X-ray diffraction (XRD) patterns of thin film were measured using an X-ray diffractometer (Phillips PW3710) with Ni filtered CuKa radiation ($\lambda = 0.154$ nm) at 40 kV and 25 mA. The crystal size (D) was calculated using Scherer's formula. The film thickness (d) was measured by gravimetric technique. Surface morphology of the film was studied using JEOL-JSM 6380 operating at 20 kV. The optical absorption studies were carried out using UV-Vis-NIR spectrophotometer (JASCO V-570) in the wavelength range of 190 nm to 2500 nm at room temperature using unpolarized light from deuterium and tungsten lamps which were used at near normal incidence. The optical absorption coefficient (α) was estimated from the T and R spectra and film thickness (d). The semiconductor energy band gap was determined by measuring the absorption coefficient as a function of photon energy [17]. Hall parameters were determined by using HMS-300 Hall measurement system.

3. Results and discussion

The measurements of thickness (d) of copper bismuth sulphide ($CuBiS_2$) samples gave the following values: 126 nm, 144 nm, 162 nm and 149 nm for films annealed in air at 250 °C for 2 h.

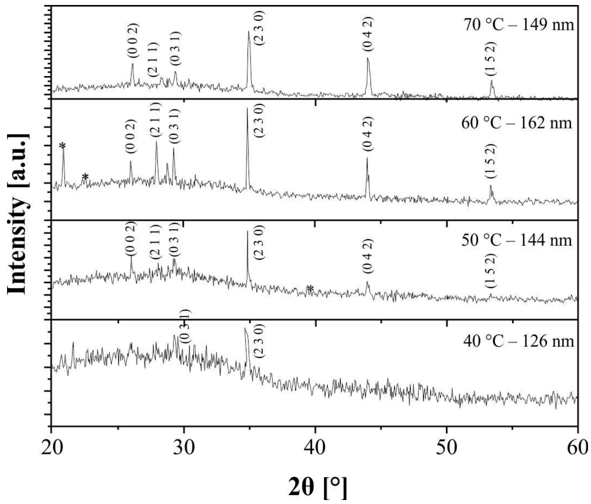

Fig. 1. X-ray diffraction patterns of $CuBiS_2$ thin films deposited at different deposition temperatures.

3.1. Structural analysis

X-ray diffraction studies were performed on copper bismuth sulphide ($CuBiS_2$) films prepared at various deposition temperatures (40 °C, 50 °C, 60 °C and 70 °C) for 5 hours. The deposited $CuBiS_2$ films show polycrystalline nature with orthorhombic structure [18].

Well-defined characteristic diffraction peaks ((0 0 2), (2 1 1), (0 3 1), (2 3 0), (0 4 2) and (1 5 2)) corresponding to $CuBiS_2$ are observed in Fig. 1. The diffraction peaks can be indexed as orthorhombic $CuBiS_2$ (JCPDS Card No. 71-2115). The intensity of the peak (2 3 0) increases significantly faster than that of other peaks ((0 0 2), (2 1 1), (0 3 1), (0 4 2) and (1 5 2)) indicating the preferred structural orientation in the (2 3 0) plane. The preferred orientation factor f (2 3 0) is greater compared to other orientations in all the four films, so it can be concluded that the $CuBiS_2$ thin films have the preferential orientation along (2 3 0) plane. The grain size, microstrain and dislocation density of $CuBiS_2$ films were calculated and the calculated values are presented in Fig. 2 and Fig. 3. It can be seen that the grain size increases from 79.9 nm to 97.65 nm with increasing deposition temperature from 40 °C to 60 °C, whereas the band gap decreases. The microstrain and dislocation density decrease with an increase in deposition temperature. The full width at half maximum (FWHM) is found to decrease remarkably with an increase in the film thickness. Such decrease reflects the decrease in the concentration of lattice imperfections due to decrease in the internal microstrain within the films and increase in grain size [19]. The film thickness increases initially with the increase in temperature and attains a maximum value at 60 °C, and decreases thereafter at a faster rate. It is observed that increasing grain size as a function of the deposition temperature is a consequence of larger mobility of the atoms at high deposition temperature. Since dislocation density and strain are the manifestation of dislocation network in films, the decreasing dislocation density indicates the formation of high quality films at the temperature of 60 °C [18]. This is possibly because of the fact that when the substrate is kept at the temperature of 60 °C, the dislocation gets more thermal energy and has higher mobility. Temperature effect on $CuBiS_2$ films indicates that the thickness goes on increasing with bath temperature and reaches maximum at 60 °C and it decreases with further increase in temperature beyond 60 °C. This may be due to re-evaporation of some Cu and Bi atoms and etching process involved at temperature higher than optimum [18].

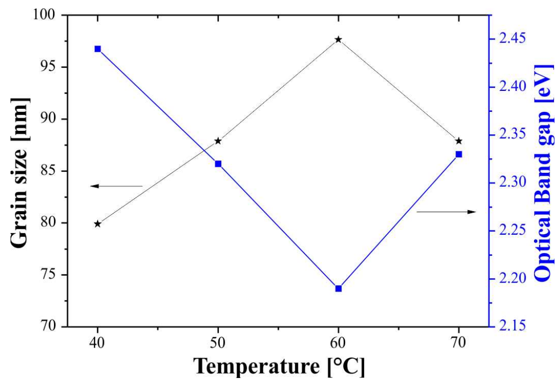

Fig. 2. Plots of grain size and optical band gap vs. temperature.

3.2. Scanning electron microscopy (SEM) analysis

The surface morphologies of $CuBiS_2$ thin films deposited at different deposition temperatures

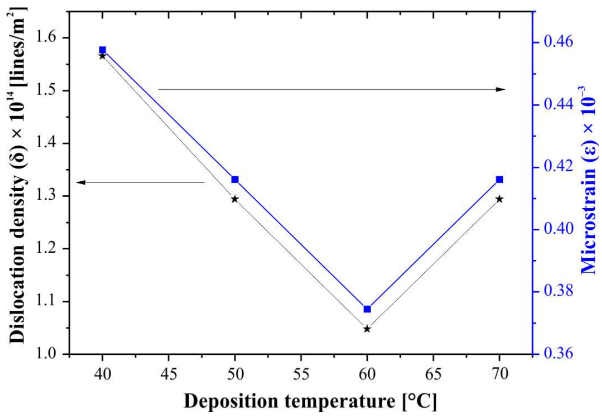

Fig. 3. Plots of dislocation density and microstrain vs. temperature.

(40 °C, 50 °C, 60 °C and 70 °C) are shown in Fig. 4. The grains are of spherical shape and the empty space between the molecules shows the loosely packed nature of the $CuBiS_2$ molecules at 40 °C. For the film deposited at a temperature of about 50 °C, the grains are found to be closely packed and intergrain spacing is reduced, which results in the films of better crystallinity and smooth and homogeneous surface. Fig. 4c clearly shows the secondary growth on the surface. As a result of this growth, a reduction of dislocation density and improvement of crystallite size can be observed. It is noteworthy that due to the increase in film deposition temperature, the obvious improvements of the crystallite size in the films are evident. Fig. 4 shows that the films are uniform and continuous.

3.3. Energy dispersive X-ray (EDAX) analysis

EDAX technique was used to determine the composition of $CuBiS_2$ thin film deposited at different temperatures for 5 hour deposition time period. EDAX patterns of $CuBiS_2$ films confirm the presence of Cu, Bi and S elements in the solid film.

The weight and atomic percentage of Cu, Bi and S elements are depicted in Table 1. It is observed that the composition is homogeneous and stoichiometric [20]. This confirms the formation of almost pure $CuBiS_2$.

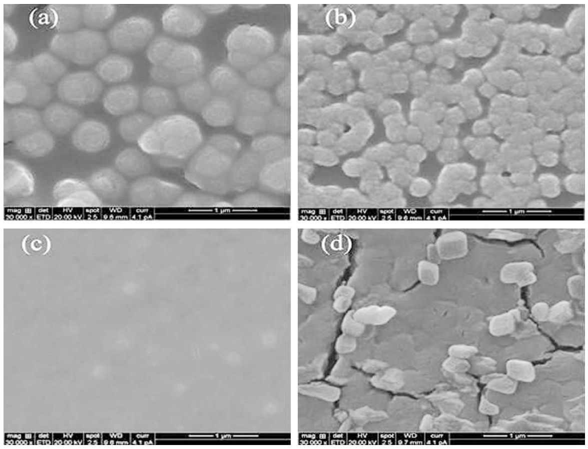

Fig. 4. The SEM pictures of $CuBiS_2$ thin films deposited at (a) 40 °C (b) 50 °C (c) 60 °C (d) 70 °C for 5 h deposition time.

Table 1. Weight and atomic percentage of Bi and S in $CuBiS_2$ thin films prepared at different deposition temperatures.

Deposition temperature [°C]	Element	wt.%	at.%
40	Cu	43.67	40.87
	Bi	28.87	8.21
	S	27.46	50.92
50	Cu	42.67	38.37
	Bi	26.87	7.35
	S	30.46	54.28
60	Cu	47.78	44.36
	Bi	25.96	7.33
	S	26.26	48.31
70	Cu	46.7	44.21
	Bi	27.83	8.01
	S	25.47	47.78

3.4. Analysis of optical properties

Optical absorption in $CuBiS_2$ films deposited at different temperatures has been studied. The inset of Fig. 5 shows that the absorbance increases with deposition temperatures up to an optimum (60 °C) and then decreases with further increase in temperature (above 60 °C). It can be concluded that the material is highly absorbant in nature. In general, a decrease in film thickness improves the transmission. This improvement can be attributed to perfection and stoichiometry of the films [19]. On the basis of this result, it can be concluded that thin layers absorb much of the radiation and that they are adequate to be used as an absorber layer in thin film solar cells [13].

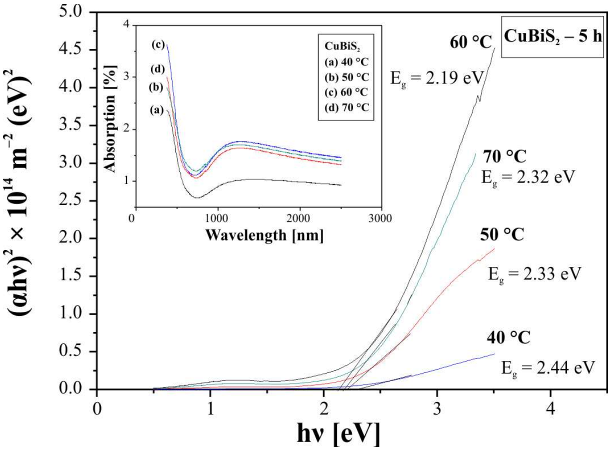

Fig. 5. Plots of $(\alpha h\nu)^2$ vs. $h\nu$ for $CuBiS_2$ thin films deposited at different temperatures; the inset shows the variation of absorption coefficient (α) as a function of wavelength (λ).

The optical band gap decreases with increasing deposition temperature only up to 60 °C (Fig. 6). Further increase in deposition temperature to 70 °C and above, resulting in a sudden increase in band gap (E_g) value, is due to the adatom mobility which also results in the enhancement of crystallite size and crystallinity of the films [21]. The decrease in band gap and increase in film crystallinity as a function of film thickness suggest that quantum confinement effect exists in the $CuBiS_2$ films.

The decrease of film band gap is due to many reasons: (i) it may be caused by the presence of internal electrical fields associated with defects present in the films; (ii) it may be due to the action of atmospheric oxygen on the film surface, which produces an acceptor level in the forbidden band; (iii) the decrease of band gap with an increase of deposition temperature is likely to be attributed to an increase of particle size, a decrease in strain and dislocation density in the films. The values of the optical band gap at different deposition temperatures are tabulated in Table 2.

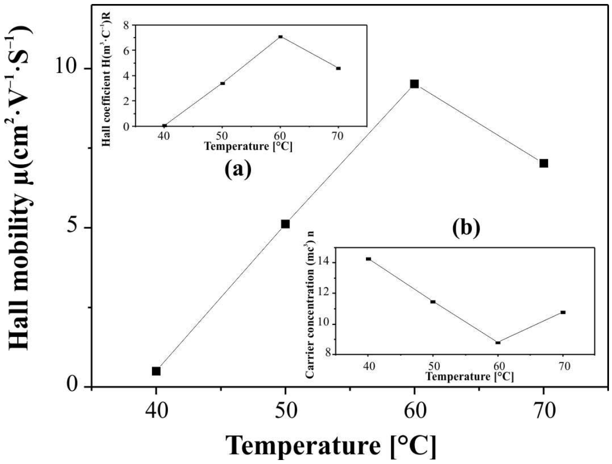

Fig. 6. Temperature dependence of Hall mobility of $CuBiS_2$ thin films; inset (a) shows temperature dependence of Hall coefficient of $CuBiS_2$ thin films; inset (b) shows temperature dependence of carrier concentration of $CuBiS_2$ thin films.

Table 2. The band gap energy of $CuBiS_2$ thin films deposited at different temperatures.

Deposition temperature [°C]	Band gap energy [eV]
40	2.44
50	2.32
60	2.19
70	2.33

3.5. Electrical characterization

Various electrical parameters of the $CuBiS_2$ thin films determined from the Hall effect studies are given in Table 3. Hall coefficients calculated for all the samples have been found to be negative, implying that the majority of the carriers are electrons. Hall coefficient values indicate that $CuBiS_2$ is an n-type semiconductor [18, 22]. Fig. 6 shows the temperature dependence of Hall mobility (inset (a): temperature dependence of Hall coefficient; inset (b): temperature dependence of carrier concentration) of $CuBiS_2$ thin films prepared at different temperatures (40 °C, 50 °C, 60 °C and 70 °C). It is obvious that the Hall coefficient increases with deposition temperature up to the optimum (at 60 °C). It is observed that the increase in carrier concentration is due to the decrease in deposition temperature (up to 60 °C), which ultimately results in a decrease in Hall mobility in the films. This may be explained on the basis of the increase in grain size and decrease in defects number as indicated in the structures of these film samples [23]. Besides, the trend of increasing mobility with decreasing carrier concentration may also be ascribed to grain boundary scattering of charge carriers in polycrystalline films [24].

4. Conclusions

$CuBiS_2$ thin films were deposited by chemical bath deposition technique using EDTA complexing agent. A set of samples was prepared at various deposition temperatures. The XRD analysis result indicate that the obtained films are composed of a pure orthorhombic structure with (2 3 0) orientation. EDAX analysis shows that the average atomic percentage of Cu:Bi:S (copper bismuth sulphide films) exhibits nearly stoichiometric composition without inclusion of any other impurities in each case. The optimum deposition temperature at which maximum thickness of the grown Cu:Bi:S film has been obtained is 60 °C. SEM surface morphology shows that all the films have highly reflecting surface with metallic appearance. The growth of the films on the substrates has been homogeneous and uniform. From the absorbance spectra, the material is found to be highly absorbant in nature. The band gap value decreases with an increase in deposition temperature which also results in the enhancement of crystalline size and crystallinity of the films, but at higher deposition temperatures the band gap (E_g) value increases due to decreased adatom mobility and etching process occurring at a temperature higher than optimum. The negative nature of the Hall coefficients indicates that the majority of the charge carriers in chemical bath deposited $CuBiS_2$ thin films are electrons. The above results demonstrate that $CuBiS_2$ is a material suitable for photovoltaic applications.

Table 3. Temperature dependence of Hall coefficient, Hall mobility and carrier concentrations of $CuBiS_2$ thin films.

Temperature [°C]	Hall coefficient R_H [$cm^3 \cdot C^{-1}$]	Hall mobility μ [$cm^2 \cdot V^{-1} \cdot s^{-1}$] × 10^1	Carrier concentration n [cm^3] × 10^{18}
40	–1.6708	0.952	–3.7407
50	–4.177	2.38	–1.494
60	–7.097	9.522	–0.8796
70	–2.8388	3.8088	–2.2016

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