JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS, Vol. 11, No. 7, July 2009, p. 940 - 944

Effect of thermal annealing on the band gap and optical properties of chemical bath deposited PbS-CuS thin films

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Thin films of PbS-CuS have been grown on glass substrate by chemical bath deposition technique at room temperature. The films were annealed between 423K and 623K. The structure of the films was studied by x-ray diffraction measurement. UV-VIS spectrophotometric measurement showes a direct allowed band gap lying in the range 2.2 – 2.5eV for the annealed films and 1.7eV for the as-deposited film. The band gap increases with increasing annealing temperature.

(Received June 4, 2009; accepted July 20, 2009)

Keyword: Band-gap, Optical properties, Thermal annealing

1. Introduction

PbS is a direct narrow band gap semiconductor very suitable for infrared detection applications. At room temperature, its energy band gap is approximately 0.37 – 0.4 eV. The band gap can be blue shifted from the near infrared (IR) to the visible region by forming nanocrystallites [3]. Copper sulphides are potentially useful in a range of application including solar control coatings, solar energy conversion, electronic and low-temperature gas sensor [4-6]. In the bulk form Cu_xS exists in five stable phases where x falls in the range between 1 and 2. Copper content variation impacts on both electrical conductivity and optical band gap properties and hence makes these compounds potentially useful in a range of applications [7].

Thin films of copper chalcogenides of multinary compositions containing indium (In) or indium and gallium ($In_{1-x}Ga_x$) are being pursued vigorously as candidate materials for solar cell application due to their band gaps in the appropriate region for high efficiencies of conversion [8-10]. There is also an ongoing effort to look into the prospects of other absorber materials involving copper. Thermal treatment of these thin films is usually required to get metal-metal chalcogenides, as evidenced in the formation of $CuBiS_3$ [11], $CuSbS_2$ [12]. Ternary compounds of copper have been found to be more stable in heterojunction solar cells than copper sulfide [10].

In view of the advantages laid down by ternary alloy thin films, we report on the effect of thermal annealing on the band gap and optical properties of PbS-CuS thin films deposited on glass substrate using chemical bath deposition (CBD) technique.

2. Materials and method

2.1 Deposition of the PbS thin films

PbS thin films were deposited on clean glass substrate using the CBD method. The reagents used were lead acetate $((CH_3COO)_2Pb.3H_2O$, thiourea (NH_2CSNH_2) and sodium hydroxide (NaOH). To obtain the deposition of thin films, 10ml of 0.2M of lead acetate was mixed with 5ml of 1M NaOH in a 50ml glass beaker with constant stirring. This was followed with the addition of 10ml of 1M of thiourea.

The deposition of PbS thin film is achieved by controlled precipitation of PbS in the reaction bath. As the solubility product of PbS is very small, the precipitation is controlled by controlling the concentration of free Pb^{2+} ions in the chemical bath. This is done by using a suitable complexing agent, which releases a small concentration of ions according to the complex-ion-dissociation equilibrium. In this case, NaOH was used as the complexing agent. The chemical reaction for the deposition of PbS by CBD is given by.

$$SC(NH_2)_2 + OH^- = CH_2N_2 + H_2O + HS^-$$
$$HS^- + OH^- = H_2O + S^{2-}$$
$$Pb^{2+} + S^- = PbS$$

When the ionic product of Pb^{2+} and S^{2-} exceeds the solubility product of PbS, the precipitation of PbS can occur on the surface of the substrate. The coated substrates were removed from the bath and rinsed thoroughly with distilled water and dried.

2.2 Deposition of CuS thin film

The deposition of CuS thin film on glass-PbS substrate was achieved by dipping the substrate in a bath composed of 10ml of 0.2m cupper acetate ($(CH_2COO)_2Cu.H_2O$), 4 drops of NH_3, 10ml of 1M sodium citrate (Na_2SiO_2), 10ml of 0.6M thiourea (H_2NCSNH_3), 20ml of distilled H_2O, in that order. After the expiration of 4 hours, the glass-PbS-CuS system was removed from the bath, rinsed thoroughly with distilled water and dried. Five samples were produced, four of which were annealed in the oven for one hour at 150, 250, 300 and 350^{o}C respectively

2.3 Characterization

The structures of the films were studied with optical microscope (at magnification of 200x) and Philips PW 1500 XRD. The absorption coefficient and the band gap of the films were determined by using the absorbance and transmittance measurement from Unico-UV-2102PC spectrophotometer at normal incident of light in the wavelength range of 200-1000nm.

3. Results and discussion

3.1. X-ray diffraction study

Typical XRD diffractograms of CBD PbS-CuS are presented in Fig.1. The films produce XRD patterns matching that of the minerals Galena (card # 05-0592) and Covellit (card # 06-0465), which confirm the formation of PbS-CuS core-shell.

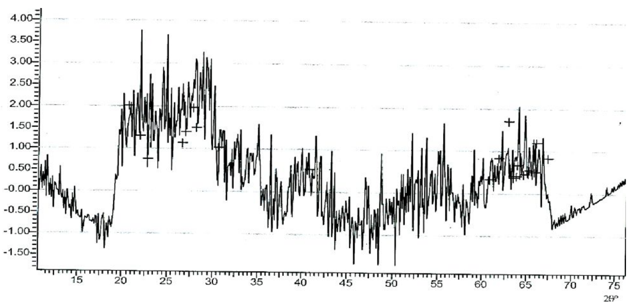

Fig. 1. XRD pattern of PbS-CuS thin film.

The pattern for the film displayed diffraction peaks at 2θ values of approximately 25^0, 27^0, 30^0 and 67^0. The existence of identifiable peaks in the diffractograms suggests that the films are not amorphous but crystalline in nature.

3.2 Photomicrographicol study

The surface microstructure of the films were obtained by taking the photomicrographs of the films coated on the transparent glass slides with wide KPL-W10x/18 Zeiss Standard 14 photomicroscope with M_{35} 4760+2-9901 camera at a magnification of X200. The photomicrographs of the films are displayed in plates 1-2. A close observation of the optical micrographs of PbS-CuS thin films show a decrease in grain size as annealing temperature increases. This proves the increase in crystallinity of the film.

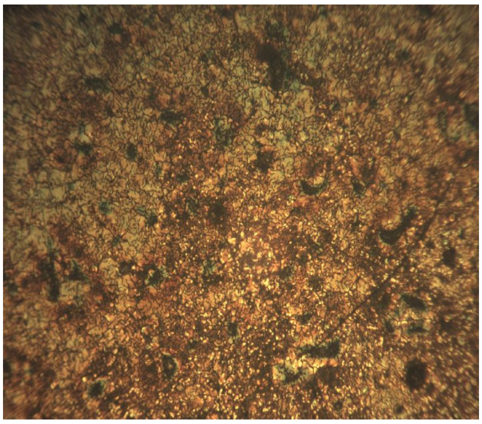

Plate1: PbS-CuS thin film (As-grown)

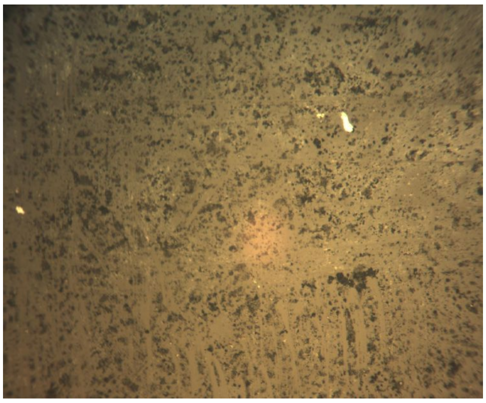

Plate2: PbS-CuS thin film (annealed at 300^{o}C)

3.3. Composition study

The elemental composition and chemical states of the films under study were analyzed by Energy dispersive X-ray fluorescence (EDXRF). The EDXRF of PbS-CuS thin films annealed at 150^{o}C and 300^{o}C are shown in Table 1.

Table 1a: PbS-CuS thin film (annealed at 150^{o}C)

Analysed elements:

El		counts	compd.	conc
K	Ka	962±97	K	5914.177±2151.31ppm
Ca	Ka	24411±1	Ca	4.518±1.580 %w
Ti	Ka	322±32	Ti	112.556±42.372 ppm
Cr	Ka	127±40	Cr	19.103±8.987 ppm
Mn	Ka	611±51	Mn	77.469±29.368 ppm
Fe	Ka	10568±11	Fe	1294.146±453.181ppm
Cd	Ka	1286±69	Cd	254.251±90.958 ppm
Zn	Ka	965±69	Zn	251.499±91.006 ppm
Sr	Ka	305±61	Sr	207.653±98.307 ppm
Cu	La	1436±89	Cu	7684.486±617.31 ppm
Pb	La	1525±59	Pb	8.159±0.569 %w

Table 1b: PbS-CuS thin film (annealed at 300°C).

Analysed elements:

El		counts	compd.	conc
K	Ka	1021±103	K	6276.897±2329.41ppm
Ca	Ka	25728±159	Ca	4.762±1.665 %w
Ti	Ka	400±35	Ti	139.821±51.086 ppm
Cr	Ka	114±42	Cr	<22.265
Mn	Ka	465±52	Mn	58.958±21.971 ppm
Fe	Ka	10335±116	Fe	265.613±442.69 ppm
Ni	Ka	884±64	Ni	138.341±50.390 ppm
Cd	Ka	1184±70	Cd	234.085±82.981 ppm
Zn	Ka	504±65	Zn	131.353±48.933 ppm
Sr	Ka	315±57	Sr	214.461±86.687 ppm
Cu	La	1420±95	Cu	598.865±844.57 ppm
Pb	La	623±62	Pb	8.684±0.517 %w

The concentration of Pb and Cu can be seen in table 1a and 1b. The presence of sulphur can not be detected by the instrument used for this analysis. Other elements present in the table may originate from the glass slide used for the deposition of the films.

4. Optical studies

Absorbance and transmittance spectra data of the deposited thin films are displayed in figs. 2 and 3 respectively. The absorbance and transmittance depend on the annealing temperature and the wavelength. Figure 2 shows that absorbance of the films generally decreased with increasing annealing temperature and wavelength, with the as-deposited having the highest absorbance at all wavelength.

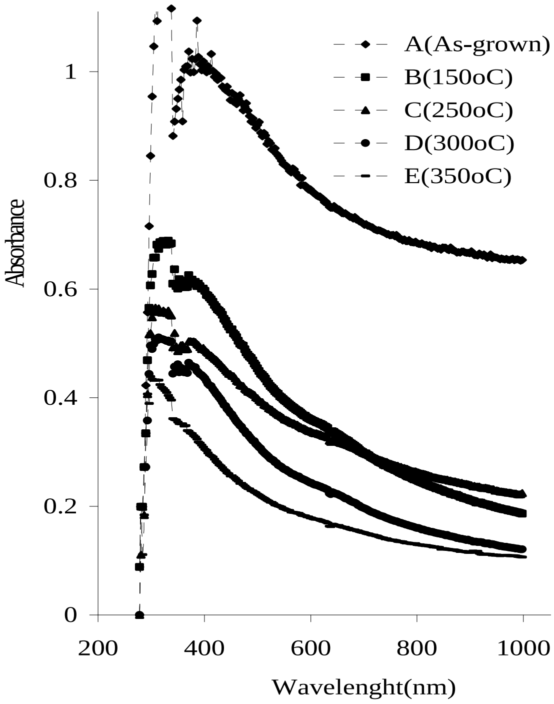

Fig. 2. Absorbance vs. wavelength for PbS-CuS thin film

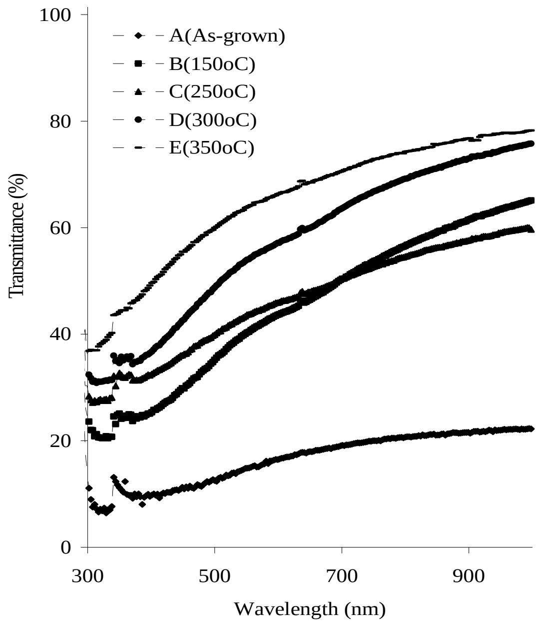

Fig. 3. Transmittance vs. wavelength for PbS-CuS thin film.

The transmittance of the annealed films displayed in fig. 3 shows an increase from 25% for film annealed at 150^0C to 70% for the film annealed at 350^0C in the visible region and in the NIR a high transmittance in the range of 50 – 78%. These values are in close agreement with the work by other authors [5]. However, the as-deposited film exhibits very low transmittance in both VIS and NIR regions.

Fig. 4 shows that the films annealed at different temperature in the oven have reflectance that increased slowly with wavelength in the UV and part of VIS region but decreased with wavelength in the remaining VIS and NIR regions. The reflectance of the unannealed film increased gradually but constantly at a wavelength greater than 500 nm.

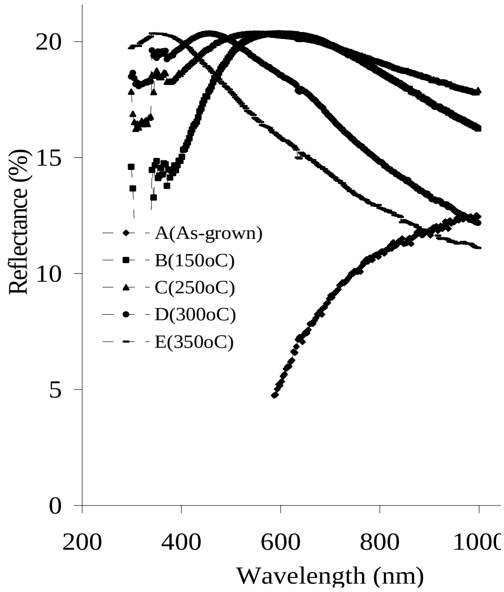

Fig.4. Reflectance vs. wavelength for PbS-CuS thin films

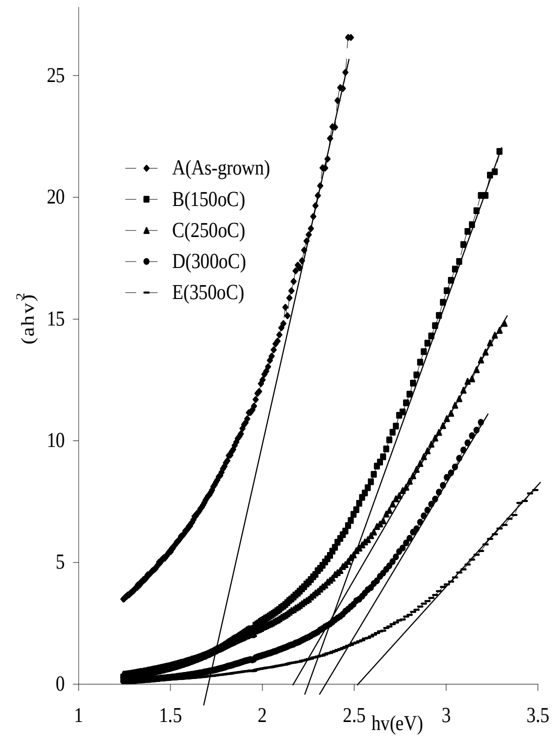

Fig. 5. Plot of $(\alpha h\nu)^2$ vs. $h\nu$ for PbS-CuS thin films

The optical properties exhibited by the films show that some of the films could be applied as spectrally selective window coatings, which could be solar control or low thermal emittance [12]. The former is transparent only in the visible region of the solar spectrum (300 – 700nm) while the infrared part (above 800nm) is reflected so that the interior of the building is kept cool. They are therefore suitable in warm countries and saves energy spent on conventional air conditioners. The later is suitable in cold climate. These coatings are transparent to visible and NIR radiation (300 – 3000nm) to minimize heat loss and have low thermal emittance above 3000nm.

The spectral transmittance and reflectance displayed in Figs. 3 and 4 show that some of the films deposited in this work and annealed at different temperature are suitable as spectrally selective window coating in cold climate to facilitate transmission of VIS and IR while suppressing the UV region of solar radiation. In addition, the properties of high transmittance in the IR region exhibited by these films make them idle for use in poultry roofs and windows to allow enough infrared radiation to warm the very young chicks during day times. This has the potential to minimize the cost of energy consumption associated with the use of electric bulbs, heater, stove etc and the hazards associated with them, while at the same time protecting the chicks from UV radiation.

The optical band gap E_g was calculated using Tauc's plot ($(\alpha h\nu)^2$ vs. $h\nu$) [1] as shown in Fig. 5. The photon energy at the point where $(\alpha h\nu)^2$ is zero represents E_g, which is determined by extrapolation. The values obtained for annealed PbS-CuS thin films lie in the range of 2.2 – 2.5eV and 1.7eV for as-grown film. The results show an increase in band gap energy as the annealing temperature is increased, with the film annealed at 250^{0C} deviating from the trend slightly. However, the large different between the values of the band gap energy of the annealed films and the as-grown film suggests that high temperature annealing has remarkable influence in the energy gap of the films deposited in this work. On the other hand, reports from literature show that the band gap energy of CuS and PbS thin films rather than increase with annealing temperature exhibit a downward trend with high temperature annealing [1, 13]. In our case, the trend observed suggests that a better quantum confinement take place at higher annealing temperature. In other words, particle size decreases as annealing temperature is increased, resulting in higher band gap energy.

5. Conclusions

PbS-CuS thin films have been successfully deposited onto glass slide using chemical bath deposition technique. The optical studies showed that the as-grown film has the highest absorbance in both the VIS and NIR regions of the solar spectrum. The spectral transmittance and reflectance exhibited by the films show that some of the films could be used as spectrally selective window coating in cold climate to facilitate transmission of VIS and IR while suppressing the UV portion of solar radiation. In addition, the properties of high transmittance in the IR region exhibited by the films make them idle for use in poultry roofs and windows to allow enough infrared radiation to warm the very young chicks during day times. This has the potential to minimize the cost of energy consumption associated with the use of electric bulbs, heater, stove etc and the hazards associated with them, while at the same time protecting the chicks from UV radiation.

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