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STUDY OF PHYSICAL PROPERTIES OF TERNARY $Cu_{11}Cd_{40}S_{49}$ THIN FILM GLASSES

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In this paper we report the study of some physical properties of chemically deposited $Cu_{11}Cd_{40}S_{49}$ thin films on soda lime glass. Compositions of 'as deposited' Cu-Cd-S system were determined by Rutherford Backscattering Spectrometry (RBS). From the optical absorption data the band gap was evaluated and studied as a function of annealing temperature. The data indicate absorption through direct interband allowed transition with red shift of around 0.25 eV and 0.10 eV after annealing at 373K and 473K respectively. Other optical and solid state properties of the annealed thin films were calculated from the absorption data and compared with the as deposited thin film. The detailed result is hereby reported.

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Keywords: Cu-Cd-S system, CBD, air annealing, band gap red shift,

1. Introduction

Thin film chalcogenide glasses are on the list of the most widely known families of amorphous materials and have been studied extensively over the past few decades because of their interesting fundamental properties and wide commercial applications [1- 3]. They behave as semiconductors and exhibit amorphous semiconductor behavior with band gap energy ranging from 1 eV to 3 eV [2]. They are potential chalcogenide glassy semiconductors which are widely used for a variety of applications in optics, optoelectronics, waveguides, optical memories, optical sensors, infrared lasers etc. Metal – metal chalcogenide thin film materials [3- 5] have been intensively studied. Owing to their efficient solar energy conversion ratio, they are potential candidate for photo– electrochemical solar cells fabrication [7- 9]. Also high optical transparency in the near and far infrared region as well as large optical non-linearity are two important and attractive optical properties of chalcogenide glassy semiconductors used in linear and non-linear integrated optical elements [10]. The properties of chalcogenide glassy semiconductors CdS are usually affected by the addition of dopant elements. Several thin film researchers [11- 12] have reported the impurity effects of several elements on the CdS chalcogenide glasses and several physical properties are found to be dependent on certain impurities in them. It has been shown for example that the controlled addition of Zn to CdS improves both the short circuit current and voltage thereby enhancing its conversion rate to yield higher conversion efficiency for $CuGaSe_2$ solar cells [13]. Highly transparent buffer layers have also been found active in $CuGaSe_2$ solar cells [14]. Different preparation parameters such as the sources of metal ions, concentration of metal ions, sources of chalcogenide ions, concentration of chalcogenide ions, the pH of the resultant solution, deposition time, temperature etc and also heat treatments, like annealing in air, open air in hot plate, vacuum or different gaseous environments affect the properties of materials prepared by the CBD method. Therefore this paper describes the properties of Cu-Cd-S film prepared by CBD method and the modifications that occur after open air annealing in hot plate.

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2. Experimental

The deposition of Cu-Cd-S ternary thin film took place at room temperature. The bath contained [1 M $CdCl_2.21/2$+0.08 M $CuSO_4$], 0.01 M EDTA, 25% NH_3 1 M $CS(NH_2)_2$ and deionized water was added to make it up to 50 ml. A pre- cleaned glass slide was immersed into the bath and was allowed to stand for 24 hrs under room temperature (300K). The films were removed from the solution, washed with deionized water and dried. The films were then air annealed at 373K and 473K for 1 hour. The optical transmittance and absorbance were measured with a UV–visible–NIR Jenway 6405 UV-VIS spectrophotometer in the wavelength range 200–1200 nm. Thin film compositions were studied with a 2.2 MeV $^4He^+$ ion beam tandem accelerator with Rutherford backscattering (RBS) cross-section detector. The detection angle of the backscattered particles was at 165^o relative to the incident ion beam and the energy resolution of the system was 12 KeV Full Width at Half Maximum (FWHM).

3. Results and discussion

3.1. Compositional studies

The elemental compositions determined by RBS spectrometry [fig. 1] revealed that the thin films on glass matrix were stoichiometric with the formation of ternary system of the type $Cu_{11}Cd_{40}S_{49}$ in percentage.

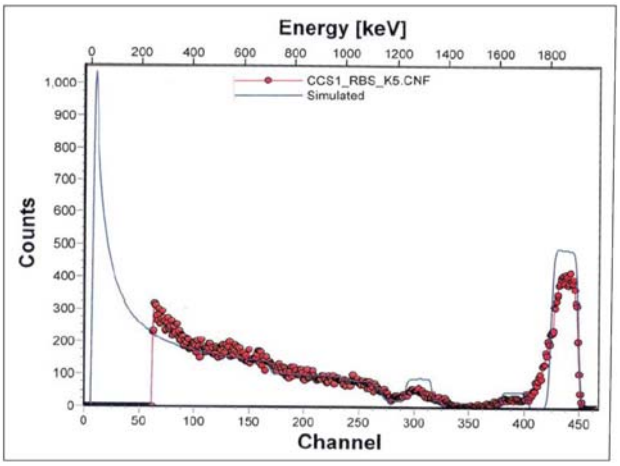

Fig.1. RBS spectrum of $Cu_{11}Cd_{40}S_{49}$ ‘as deposited’ chalcogenide glass.

The solid line is the simulated result while dotted line represents the RBS spectrum of $Cu_{11}Cd_{40}S_{49}$ thin films on soda lime glass. The isotopic compositions of the different ions making up Cu-Cd-S system as determined by Rutherford’s cross section data are presented in Table 1.

Table 1. Isotopic compositions of Cu, Cd, and S in $Cu_{11}Cd_{40}S_{49}$.

	Isotopic Compositions of $Cu_{11}Cd_{40}S_{49}$							
Cu 0.11	^{63}Cu 0.692	^{65}Cu 0.308	-	-	-	-	-	-
Cd 0.40	^{106}Cd 0.013	^{108}Cd 0.009	^{110}Cd 0.125	^{111}Cd 0.128	^{112}Cd 0.241	^{113}Cd 0.122	^{114}Cd 0.287	^{116}Cd 0.075
S 0.49	^{32}S 0.950	^{33}S 0.008	^{34}S 0.042	^{34}S 0.000	^{36}S 0.000	-	-	-

3.2 Optical properties

The optical properties of the $Cu_{11}Cd_{40}S_{49}$ thin films were studied by measuring at normal incidence both transmittance (T) and absorbance (A) spectra in the spectral range 200–1200 nm. This was performed using a Jenway 6405 UV-VIS Spectrophotometer. During scanning, a blank glass slide was placed in one of the beam's direction and another glass slide with film deposit was in the other beam's direction. This ensures that the absorption spectrum displayed by the Jenway 6405 UV-VIS spectrophotometer was only as a result of the film deposited on the glass slide. The variations of absorbance (A) and transmission (%T) with wavelength (λ) are shown in figures 2 and 3 respectively,

Table 2: Optical parameters of annealed and unanealed $Cu_{11}Cd_{40}S_{49}$ films.

Sample No.	Temp. (K)	Absorption coefficient $\alpha(10^4)m^{-1}$	refractive index, n	Extinction coefficient, K	Real dielectric Constant, ε_r	Imaginary Dielectric Constant, ε_i	Thickness t(Å)
A	300	89.4	1.57	50.44	3.12	132.61	5958
B	373	109.0	1.51	58.77	3.02	152.91	6800
C	472	100.0	1.56	55.06	3.13	144.83	6424

The films show an increase in absorbance and a decrease in transmission after annealing the film at 373K and 473K in an electric oven. This is due to corresponding increase in the crystallite sizes of the aggregate grains after air annealing. Also the increase in the surface roughness of the films after annealing could be another possible cause of drastic decrease in transmittance and increase in absorbance of the films [17]. The average values of absorption coefficient (α), refractive (n), extinction coefficient (K), real dielectric constant (ε_r), imaginary dielectric constant (ε_i) of the thin films were observed to vary from the 'as deposited' thin after air annealing (table 2).

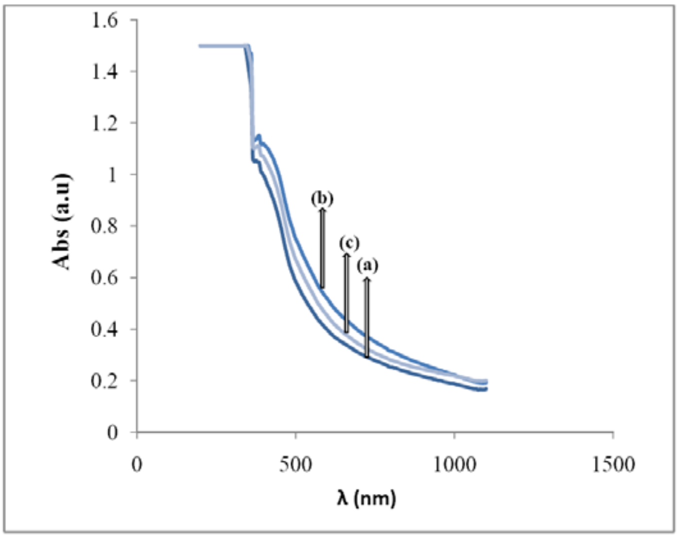

Fig.2: Optical absorption spectra of $Cu_{11}Cd_{40}S_{49}$ chalcogenide glasses (a) unannealed, (b) annealed at 373K and (c) annealed at 473K.

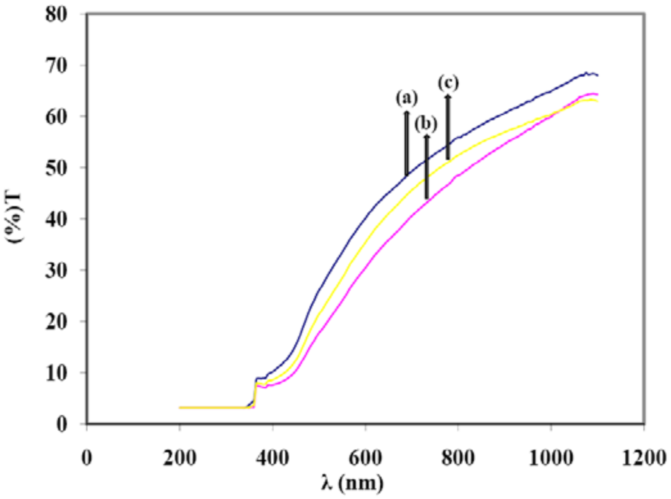

Fig.3. Optical transmission spectra of $Cu_{11}Cd_{40}S_{49}$ chalcogenide glasses (a) unannealed, (b) annealed at 373K and (c) annealed at 473K.

The energy band gap was calculated using the following relation [7-11]:

$$\alpha = A(h\nu - E_g)^p / h\nu \quad (1)$$

where A is a constant and p is a constant equal to 1/2 for direct band gap semiconductors. The estimated band gaps from the plots of $(\alpha h\nu)^2$ versus hν are shown in Fig. 4, for 'as-deposited' and annealed $Cu_{11}Cd_{40}S_{49}$ films. The linear nature of the plot indicates the existence of the direct transition. The band gap was deduced by extrapolating the straight portion to the energy axis at $(\alpha h\nu)^2 = 0$. It was found to be 2.45eV for as deposited and 2.20eV- 2.35eV for annealed $Cu_{11}Cd_{40}S_{49}$ film samples. This shift indicates a decrease of the optical band gap E_g. However wider direct allowed band gap values of 3.70eV- 3.98eV have been reported [13], which were achieved by doping CdS with Cu.

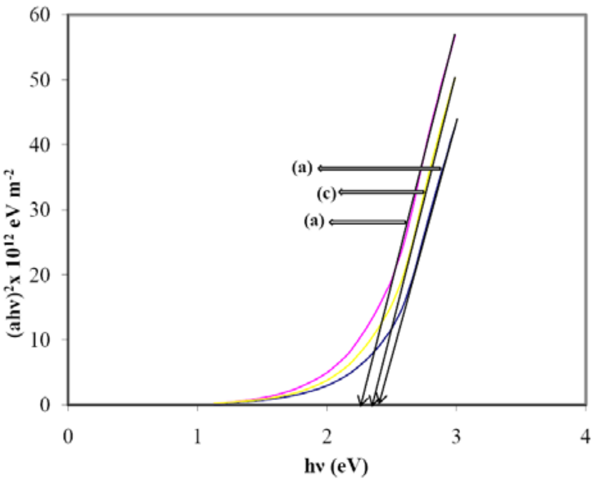

Fig.4: Optical transmission spectra of $Cu_{11}Cd_{40}S_{49}$ chalcogenide glasses (a) unannealed, (b) annealed at 373K and (c) annealed at 473K.

The moderate band gap of 2.45eV reported in this work indicates the film is rich in Cd. The decrease in band gap of the annealed $Cu_{11}Cd_{40}S_{49}$ thin film samples from 2.45eV- 2.35eV and 2.45eV- 2.20eV indicate strong band redshifts of 0.10eV and 0.25eV respectively in the optical absorption spectra. Also ref [16] reported band gap decrease 2.20 eV to 1.70eV and 1.60 eV for Sb_2S_3 after annealing from 453K and 473K. Recently similar red shift in band gap from 2.45eV- 2.30eV was reported for $Cu_{11}Cd_{40}S_{49}$ subjected to laser annealing [12].

Table 3: The optical energy band gap of thin $Cu_{11}Cd_{40}S_{49}$ films.

Sample no	Temperature (K)	Thickness t (Å)	Band gap E_g (eV)	Red shift ΔE_g (eV)
a	Unannealed	5958	2.45	……
b	373	6800	2.20	0.25
c	473	6424	2.35	0.10

Many authors observed band gap variations of chalcogenide glasses (both binary and ternary) after air annealing have been reported [1, 14-16]. It can be readily observed from table 3 that the band gap red shift increases with film thickness. This is of course due to the corresponding increase in the crystallites sizes leading to decrease in the number of defect sites in the films after air annealing [17, 18].

4. Conclusion

$Cu_{11}Cd_{40}S_{49}$ thin films were deposited by chemical bath process at room temperature. The air annealing of the films resulted in the red shifts in energy band gaps of 0.25 eV and 0.10 eV after annealing at temperatures of 373 K and 473 K, respectively. This is due to structural defects caused by abrupt increase in the crystallites after annealing.

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