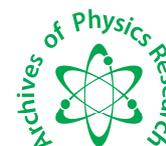




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Synthesis of nanostructured $(\text{Cu}_2\text{S})_x(\text{As}_2\text{S}_3)_{1-x}$ thin films using chemical route at room temperature

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ABSTRACT

Recently, nanostructured thin films have attracted research community from the world as they shows potential applications in semiconductor industry, particularly in fabrication of optoelectronic devices. In the present investigation $(\text{Cu}_2\text{S})_x(\text{As}_2\text{S}_3)_{1-x}$ thin films were deposited onto glass substrates by using chemical bath deposition (CBD) method at room temperature. The XRD studies reveal that the as deposited $(\text{Cu}_2\text{S})_x(\text{As}_2\text{S}_3)_{1-x}$ thin films have mixed phase of hexagonal and monoclinic lattice due to Cu_2S and As_2S_3 respectively. However, the precipitated powder shows mixed phase of orthorhombic and monoclinic structure. The electrical resistivity, activation energy and optical band gap energy of $(\text{Cu}_2\text{S})_x(\text{As}_2\text{S}_3)_{1-x}$ film is found composition dependent.

Keywords: Chemical synthesis, Thin films, Structural, Electrical and Optical properties

INTRODUCTION

The electrical, optical, magnetic and mechanical properties of nanostructured thin films are different than that of bulk material [1]. Hence before fabrication of any device one should know materials physical and chemical properties in detail. The As_2S_3 is a potential glass former highly resistive to the heat and has the properties of semiconductors and is a good photo conductor with dielectric properties [2]. The chemical bath deposition method is one of the cheapest methods to deposit thin films and nano-materials, as it does not depend on expensive equipment's and is a scalable technique that can be employed for large area deposition [3].

Various workers have used chemical methods to deposit As_2S_3 and CuS thin films. Sartale et al. [4] have deposited As_2S_3 thin films by successive ionic layer adsorption and reaction (SILAR) method using As_2O_3 and $\text{Na}_2\text{S}_2\text{O}_3$ as arsenic and sulfide ion source on glass and silicon substrates. Pawar et al. [5] have prepared As_2S_3 films by solution gas interface technique. Yesugade [6] have prepared As_2S_3 thin films by the electrodeposition technique from aqueous acidic baths. The films deposited from an EDTA-complexed bath are thin, uniform and adherent to the substrate. Varkey [7] has reported deposition of Cu_xS using EDTA as a complexing agent in a bath comprising CuCl , NaCl and hydroxylamine hydrochloride solutions. Sagade and Sharma [8] have used solution growth technique to deposit Cu_xS ($x = 1, 1.4, \text{ and } 2$) thin films on glass substrates at room temperature (300 K). The physico-chemical properties of the films are highly influenced by the chemical composition. Nair et al [9] have reported the opto-electronic and solar control properties of chemically deposited Cu_xS thin films. Lindroos et al [10] have prepared copper sulfide thin films by successive ionic layer adsorption and reaction method at room temperature. The films were polycrystalline and showed no preferred orientation. Bezig et al [11] have used vacuum

evaporation technique to prepare Cu_xS thin films. Fatas et al [12] have used CuSO_4 and thiourea in alkaline medium to deposit Cu_xS thin films by chemical method and reported that their optical band-gap and resistivity is of the order of 2.58 eV and $3 \times 10^{-3} \Omega\text{-cm}$ respectively. Ubale et al [13] have prepared nanostructured Cu_xS thin films of thickness 70 to 233 nm by varying the deposition time from 9 to 24 h and reported their electrical, optical and structural properties.

To the best of our knowledge, no report is available on the deposition of ternary $(\text{Cu}_2\text{S})_x(\text{As}_2\text{S}_3)_{1-x}$ thin films. For the present work, we have chosen Chemical Bath Deposition (CBD) method for the preparation of nanostructured $(\text{Cu}_2\text{S})_x(\text{As}_2\text{S}_3)_{1-x}$ thin films at room temperature, which is simple and economic. The structural, electrical and optical properties of composite $(\text{Cu}_2\text{S})_x(\text{As}_2\text{S}_3)_{1-x}$ thin films are reported.

MATERIALS AND METHODS

2. Experimental

The amorphous glass micro slides of size $75 \times 25 \times 2$ mm were used as substrates for present work. As adherence of the film has a direct bearing on the cleanliness of the substrate, the slides were cleaned carefully. Initially the slides were washed with liquid detergent and then boiled in concentrate chromic acid (0.5M) for 2 hour and then kept in it for next 48 hours. The substrates were then washed with double distilled water and finally cleaned in ultrasonic cleaner. Finally, the substrates are dried using AR grade acetone and kept in dust free storage container. For deposition of $(\text{Cu}_2\text{S})_x(\text{As}_2\text{S}_3)_{1-x}$ thin films 0.1 M Cupric acetate, 0.1 M As_2O_3 , 0.1 M EDTA and 0.1 M $\text{Na}_2\text{S}_2\text{O}_3$ are mixed in a 100 ml beaker at room temperature. The deposition scheme used to vary composition parameter x from 0 to 1 to prepare $(\text{Cu}_2\text{S})_x(\text{As}_2\text{S}_3)_{1-x}$ thin films is given in table(1). The deposited Cu_2S ($x=1$) films have dark brown colour and As_2S_3 ($x=0$) films are yellow in colour. However, the film colour of composite changes according to x (fig 1), which confirms formation of $(\text{Cu}_2\text{S})_x(\text{As}_2\text{S}_3)_{1-x}$ film.

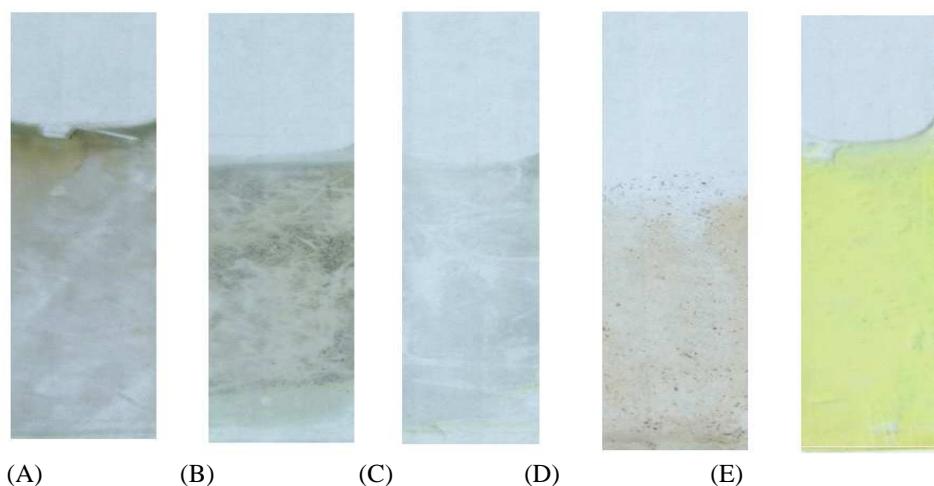


Fig.1. Photograph of $(\text{Cu}_2\text{S})_x(\text{As}_2\text{S}_3)_{1-x}$ films : (A) $x=1$, (B) $x=0.75$, (C) $x=0.5$, (D) $x=0.25$ and (E) $x=0$

Table: 1 Deposition scheme for $(\text{Cu}_2\text{S})_x(\text{As}_2\text{S}_3)_{1-x}$ thin films

S. N.	Bath Composition (ml)				Film composition	Thickness (nm)
	$\text{C}_3\text{H}_6\text{CuO}_4$ 0.1M	As_2O_3 0.1M	EDTA 0.1M	$\text{Na}_2\text{S}_2\text{O}_3$ 0.1 M		
A	40	0	20	40	Cu_2S	505
B	30	10	10	40	$(\text{Cu}_2\text{S})_{0.75}(\text{As}_2\text{S}_3)_{0.25}$	487
C	20	20	10	40	$(\text{Cu}_2\text{S})_{0.5}(\text{As}_2\text{S}_3)_{0.5}$	529
D	10	30	10	40	$(\text{Cu}_2\text{S})_{0.25}(\text{As}_2\text{S}_3)_{0.75}$	481
E	0	40	40	40	As_2S_3	429

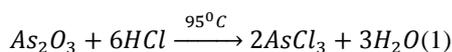
The thickness of As_2S_3 thin film was measured by weight difference method using sensitive microbalance. Crystallographic studies of $(\text{Cu}_2\text{S})_x(\text{As}_2\text{S}_3)_{1-x}$ thin films and powder collected from reaction vessel were characterized by using a PANalytical X'Pert PRO MRD X-ray diffractometer with $\text{CuK}\alpha$ radiation in 2θ range from 20 to 90

degree. The optical properties were studied by taking absorption spectra of the films using a JASCO V-530 UV/Visible Spectrometer in the range of wavelength from 320 to 740 nm at room temperature. The electrical resistance measurements were carried out in the temperature range 303 to 423 K using the two-probe method. A quick drying silver paste was applied to the film for better ohmic contact.

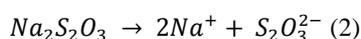
RESULTS AND DISCUSSION

The film formation in the CBD process takes place when ionic product (I.P) exceeds the solubility product (S.P). In the presence of complex EDTA the metal ions Cu^{2+} and As^{3+} forms metal complex with EDTA, which controls the release of metal ions in the solution. The formation of $(\text{Cu}_2\text{S})_x(\text{As}_2\text{S}_3)_{1-x}$ thin films may involve following steps.

The arsenic trioxide is dissolved in distilled water with the help of HCl as,



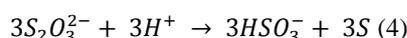
In aqueous solution $\text{Na}_2\text{S}_2\text{O}_3$ dissociates as,



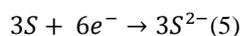
$\text{Na}_2\text{S}_2\text{O}_3$ is a reducing agent by virtue of half-cell reaction,



In acidic medium dissociation of $\text{S}_2\text{O}_3^{2-}$ takes place as,



The electrons released in equation (3) react with S as,



The EDTA complex of Cu^{2+} and As^{3+} with S^{2-} forms $(\text{Cu}_2\text{S})_x(\text{As}_2\text{S}_3)_{1-x}$ as,

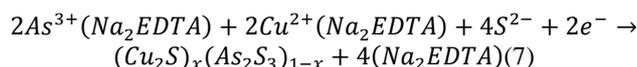


Fig (2) shows the XRD pattern of $(\text{Cu}_2\text{S})_x(\text{As}_2\text{S}_3)_{1-x}$ thin films recorded at room temperature in the range of angle 2θ between 20 to 90 degree. The $(\text{Cu}_2\text{S})_x(\text{As}_2\text{S}_3)_{1-x}$ composite thin films are nanocrystalline in nature with mixed phase of hexagonal and monoclinic lattice due to Cu_2S and As_2S_3 . The observed XRD data is compared with standard JCPDS data (Table 2). The broad hump observed in XRD pattern between 20 to 35 degree is due to amorphous glass substrate. The (221), (621) and (732) orientations are due to monoclinic As_2S_3 lattice. However the (002), (004), (201), (212) and (300) orientations are due to hexagonal Cu_2S lattice. The (732) orientation due to As_2S_3 is repeated in $(\text{Cu}_2\text{S})_{0.25}(\text{As}_2\text{S}_3)_{0.75}$ and $(\text{Cu}_2\text{S})_{0.5}(\text{As}_2\text{S}_3)_{0.5}$ sample. The (004) and (201) orientations due to Cu_2S are repeated in $(\text{Cu}_2\text{S})_{0.75}(\text{As}_2\text{S}_3)_{0.25}$ sample. However the (240) orientation due to As_2S_3 sample is observed only in composite film. Fig. (3) shows the XRD patterns of $(\text{Cu}_2\text{S})_{0.25}(\text{As}_2\text{S}_3)_{0.75}$ precipitated powder collected from reaction bath (Table 3). As compared to the film XRD, the powder collected from the bath shows polycrystalline nature with orthorhombic and monoclinic lattice due to Cu_2S and As_2S_3 lattice. The (320) and (316) orientations due to Cu_2S are repeated in the composite, however, the (911) orientation due to As_2S_3 is repeated in composite. The other prominent orientation (342), (173) and (800) are observed only in composite. The mixing of peaks due to Cu_2S and As_2S_3 observed in film as well as in powder XRD confirms the formation of composite. The average crystallite size of the $(\text{Cu}_2\text{S})_x(\text{As}_2\text{S}_3)$ films were calculated by applying Scherrer's formula,

$$d = \frac{\lambda}{\beta \cos \theta} \quad (8)$$

Where λ is the wavelength used (0.154 nm); β is the angular line width at half maximum intensity in radians; θ is the Bragg's angle. The grain size of Cu_2S and As_2S_3 thin film is 19 and 23 nm and that of powder is 13 and 15 respectively.

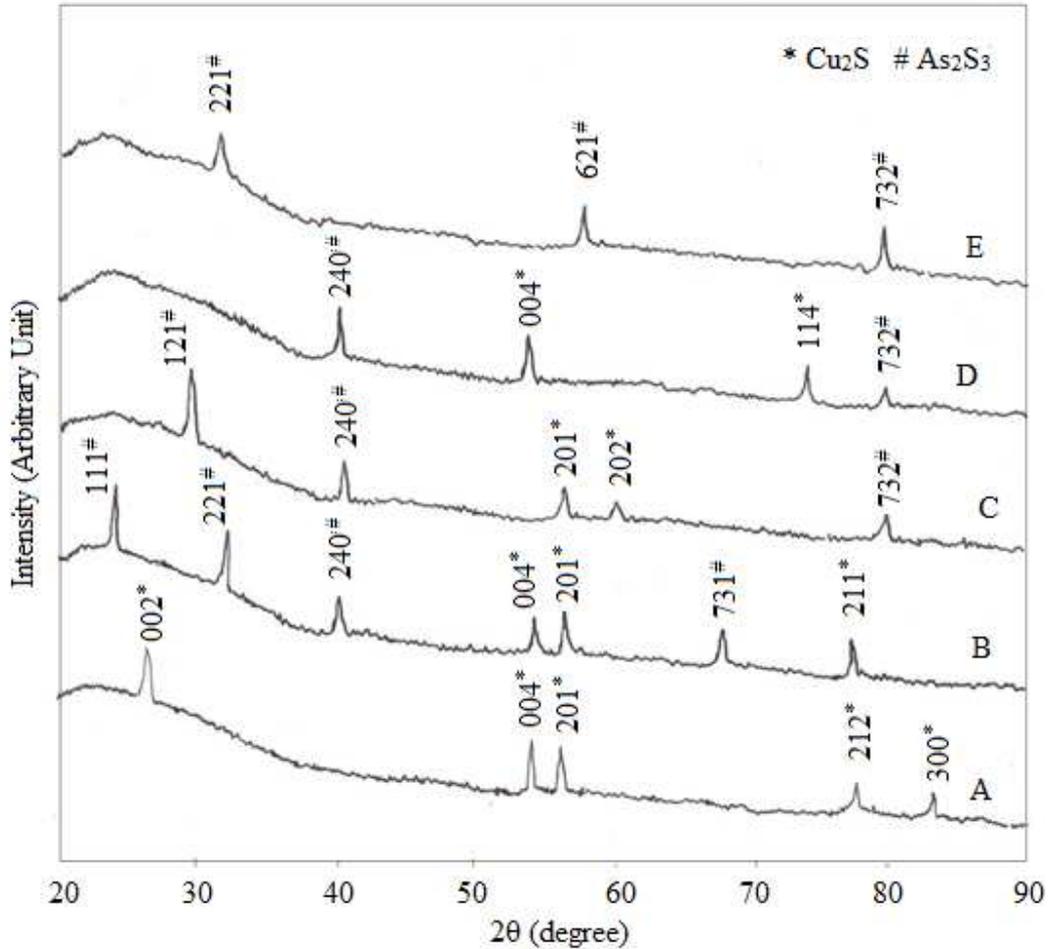


Fig.2. XRD spectra of $(\text{Cu}_2\text{S})_x(\text{As}_2\text{S}_3)_{1-x}$ thin films : (A) $x=1$, (B) $x=0.75$, (C) $x=0.5$, (D) $x=0.25$ and (E) $x=0$

Table: 2 Comparison of observed and standard XRD data of $(\text{Cu}_2\text{S})_x(\text{As}_2\text{S}_3)_{1-x}$ thin films.(JCPDS Cards :24-0057 of Cu_2S and 19-0084 of As_2S_3)

Film	Composition	h k l	Standard data		Observed data		Phase
			2θ (degree)	d (\AA)	2θ (degree)	d (\AA)	
A	Cu_2S	002	26.385	3.375	26.292	3.389	Cu_2S
		004	54.316	1.687	54.677	1.678	
		201	55.364	1.658	54.677	1.678	
		212	79.277	1.207	78.347	1.22	
		300	84.983	1.140	85.65	1.134	
B	$(\text{Cu}_2\text{S})_{0.75}(\text{As}_2\text{S}_3)_{0.25}$	111	23.986	3.71	23.811	3.736	As_2S_3
		221	32.080	2.79	31.757	2.817	As_2S_3
		240	40.639	2.22	40.867	2.20	As_2S_3
		004	54.316	1.687	54.56	1.68	Cu_2S
		201	55.364	1.658	55.73	1.64	Cu_2S
		731	67.203	1.393	67.28	1.39	As_2S_3
		212	79.277	1.207	77.865	1.22	Cu_2S
		121	29.086	3.07	29.175	3.06	As_2S_3
C	$(\text{Cu}_2\text{S})_{0.5}(\text{As}_2\text{S}_3)_{0.5}$	240	40.639	2.22	40.099	2.24	As_2S_3
		201	55.364	1.658	56.46	1.62	Cu_2S
		202	60.643	1.525	60.45	1.53	Cu_2S
		732	79.785	1.20	79.36	1.20	As_2S_3
		240	40.639	2.22	40.7442	2.21	As_2S_3
D	$(\text{Cu}_2\text{S})_{0.25}(\text{As}_2\text{S}_3)_{0.75}$	004	54.364	1.687	54.25	1.69	Cu_2S
		114	73.790	1.28	73.79	1.284	Cu_2S
		732	79.785	1.20	79.386	1.22	As_2S_3
		221	32.080	2.79	31.748	2.81	As_2S_3
E	As_2S_3	621	56.002	1.64	56.15	1.65	As_2S_3
		732	79.785	1.20	79.033	1.21	As_2S_3

The variation of dark electrical resistivity of $(\text{Cu}_2\text{S})_x(\text{As}_2\text{S}_3)_{1-x}$ films deposited was studied in the temperature range 303 to 423 K using dc two-point probe method. The electrical resistivity at 343K temperature was found to be of the order of $9 \times 10^6 \Omega \text{ cm}$ and $7.9 \times 10^4 \Omega \text{ cm}$ for As_2S_3 and Cu_2S film. The high value of resistivity may be attributed to the nanocrystallinity of film, grain boundary discontinuities, presence of surface states and small thickness of the film, etc. Fig.4 shows the variation of log of resistivity ($\log \rho$) with reciprocal of temperature $(1/T) \times 10^3$. It is seen that resistivity decreases with increase in temperature indicating semiconducting nature of $(\text{Cu}_2\text{S})_x(\text{As}_2\text{S}_3)_{1-x}$ films.

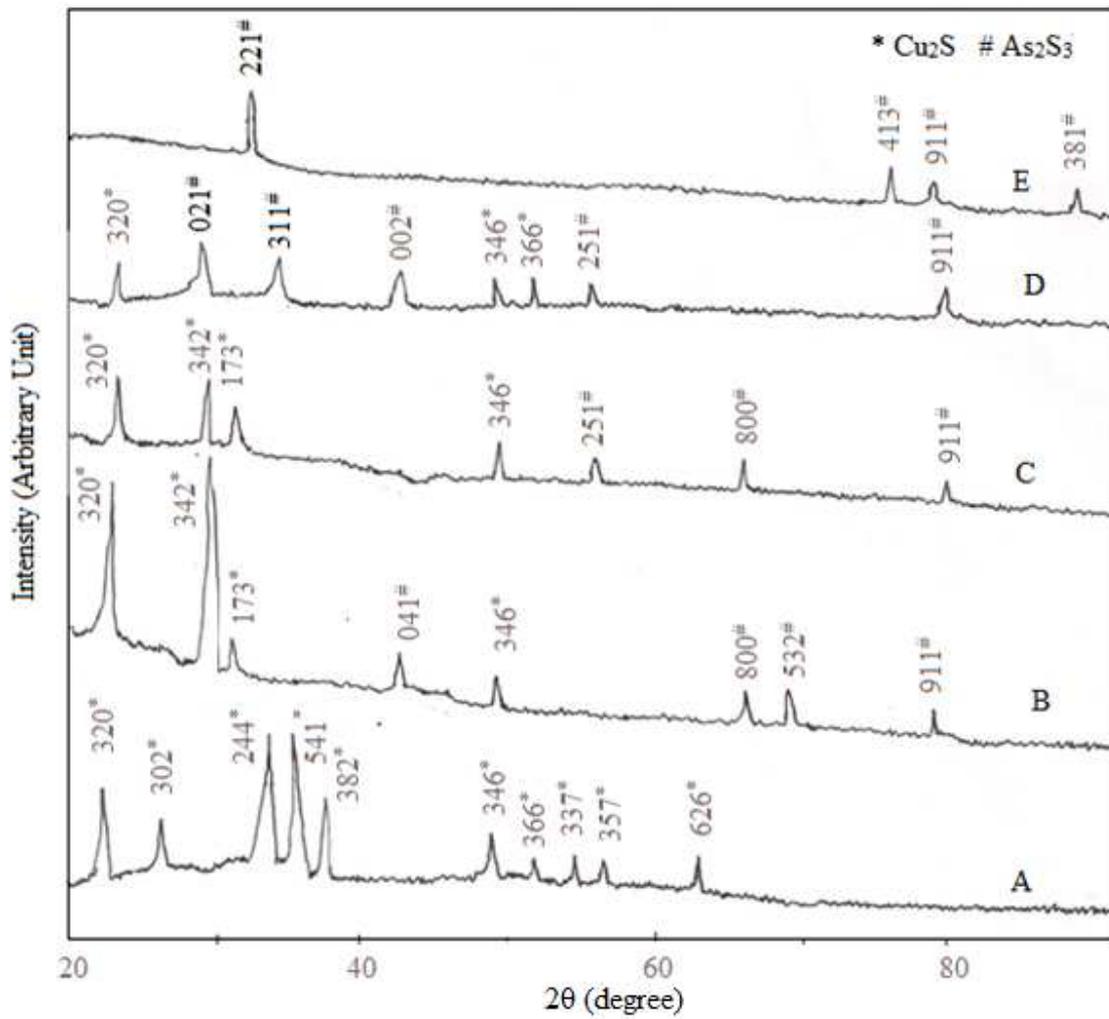


Fig.3. XRD spectra of $(\text{Cu}_2\text{S})_x(\text{As}_2\text{S}_3)_{1-x}$ precipitated powder : (A) $x=1$, (B) $x=0.75$, (C) $x=0.5$, (D) $x=0.25$ and (E) $x=0$

Table: 3 Comparison of observed and standard XRD data of $(\text{Cu}_2\text{S})_x(\text{As}_2\text{S}_3)_{1-x}$ powder. (JCPDS Cards: of 09-328 Cu_2S and 44-1419 As_2S_3)

Powder	Composition	h k l	Standard data		Observed data		Phase
			2 θ (degree)	d (Å^0)	2 θ (degree)	d (Å^0)	
A	Cu_2S	320	23.579	3.77	23.6289	3.763	Cu_2S
		302	26.267	3.39	26.3111	3.387	
		244	33.536	2.67	33.5365	2.672	
		451	35.307	2.54	35.1692	2.551	
		382 346	37.441	2.40	37.1077	2.422	
		366	48.650	1.870	48.3056	1.884	
		337	51.068	1.787	51.6359	1.7701	
		357	54.058	1.695	54.5465	1.682	
		626	55.842	1.645	56.3434	1.632	
					63.154	1.471	
B	$(\text{Cu}_2\text{S})_{0.75}(\text{As}_2\text{S}_3)_{0.25}$	320	23.579	3.77	23.3755	3.8056	Cu_2S
		342	29.257	3.05	29.1219	3.6645	Cu_2S
		173	31.474	2.84	31.4666	2.84310	Cu_2S
		041	43.324	2.0868	43.6896	2.07189	As_2S_3
		800	65.294	1.4279	65.6169	1.42283	As_2S_3
		532	67.340	1.3894	67.6252	1.3853	As_2S_3
		911	79.774	1.201	79.7950	1.2008	As_2S_3
C	$(\text{Cu}_2\text{S})_{0.5}(\text{As}_2\text{S}_3)_{0.5}$	320	23.579	3.77	23.4280	3.7972	Cu_2S
		342	29.527	3.105	29.4493	3.033	Cu_2S
		173	31.474	2.84	31.3144	2.8565	Cu_2S
		346	48.650	1.870	48.3906	1.8810	Cu_2S
		251	55.019	1.6677	55.1416	1.6656	As_2S_3
		800	65.294	1.4279	65.2893	1.4291	As_2S_3
		911	79.774	1.201	78.7179	1.2146	As_2S_3
D	$(\text{Cu}_2\text{S})_{0.25}(\text{As}_2\text{S}_3)_{0.75}$	320	23.579	3.77	23.2720	3.8223	Cu_2S
		021	28.055	3.178	28.1138	3.1740	As_2S_3
		311	33.166	2.699	33.1904	2.699	As_2S_3
		002	42.543	2.1233	42.5372	2.125	As_2S_3
		346	48.650	1.870	48.3454	1.882	Cu_2S
		366	51.068	1.787	51.4011	1.777	Cu_2S
		251	55.019	1.6677	55.1836	1.6644	As_2S_3
		911	79.774	1.2012	79.8973	1.200	As_2S_3
E	As_2S_3	221	32.364	2.764	32.3015	2.77150	As_2S_3
		413	76.099	1.249	75.8621	1.2531	
		911	79.774	1.2012	79.7566	1.20241	
		381	88.674	1.1022	89.0335	1.0986	

The activation energies of $(\text{Cu}_2\text{S})_x(\text{As}_2\text{S}_3)_{1-x}$ were calculated and tabulated in the table(4). The activation energy depends on the composition as well as on the thickness. The pure Cu_2S film has activation energy 0.164 eV and As_2S_3 has 0.081 eV, however, the activation energy of composite is between them.

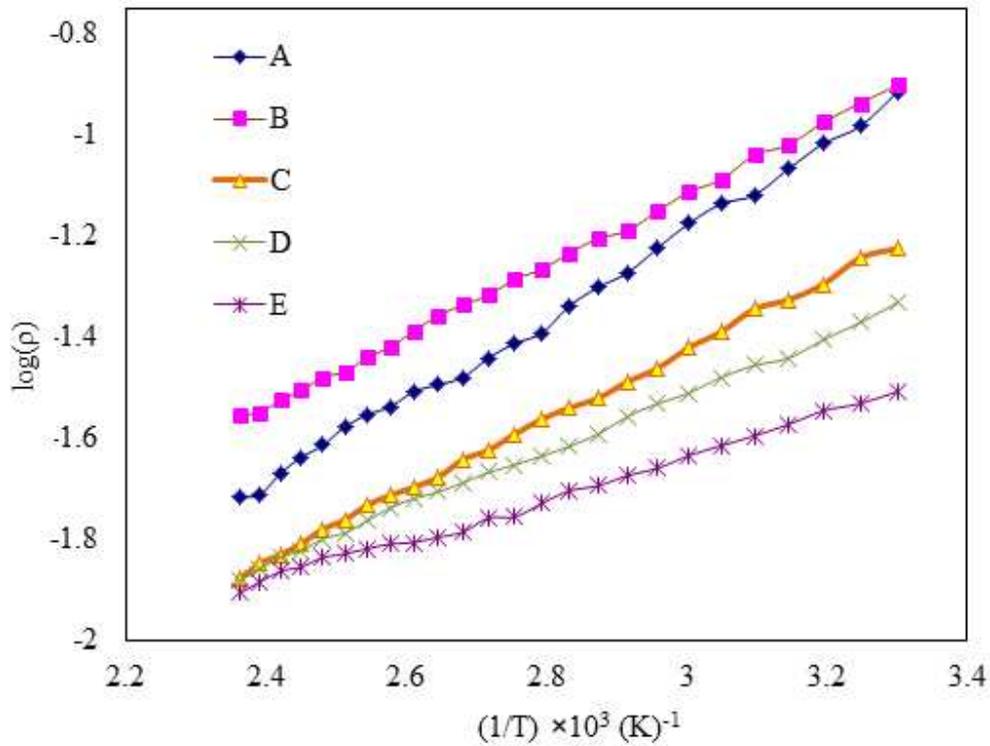


Fig.4. Variation of electrical resistivity of $(\text{Cu}_2\text{S})_x(\text{As}_2\text{S}_3)_{1-x}$ thin film with $(1/T) \times 10^3$ for different compositions: (A) $x=1$, (B) $x=0.75$, (C) $x=0.5$, (D) $x=0.25$ and (E) $x=0$

The absorption coefficient for the as prepared $(\text{Cu}_2\text{S})_x(\text{As}_2\text{S}_3)_{1-x}$ samples has been measured in the wavelength range 320 to 740 nm (Fig.5). All the films show higher absorption on the shorter wavelength side with an absorption edge.

Table: 4 Thickness, activation energy and optical band gap of $(\text{Cu}_2\text{S})_x(\text{As}_2\text{S}_3)_{1-x}$ thin films

Sr. No	Film Composition	Thickness (nm)	Activation Energy (eV)	Band gap Energy (eV)	Contact angle (degree)
1	Cu_2S	5050	0.164	3.05	44
2	$(\text{Cu}_2\text{S})_{0.75}(\text{As}_2\text{S}_3)_{0.25}$	4878	0.140	2.6	55
3	$(\text{Cu}_2\text{S})_{0.5}(\text{As}_2\text{S}_3)_{0.5}$	5299	0.130	2.4	58
4	$(\text{Cu}_2\text{S})_{0.25}(\text{As}_2\text{S}_3)_{0.75}$	4815	0.110	2.9	59
5	As_2S_3	4296	0.081	3.02	34

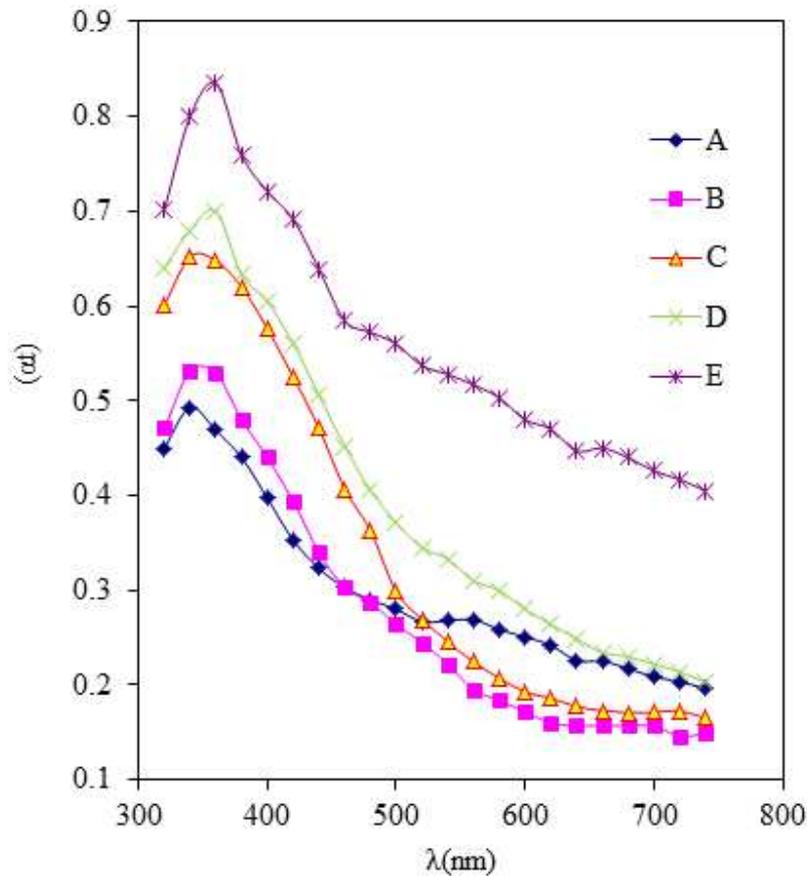


Fig.5.Plots of α versus wavelength λ (nm) of $(Cu_2S)_x(As_2S_3)_{1-x}$ film: (A) $x = 1$, (B) $x = 0.75$, (C) $x = 0.5$, (D) $x = 0.25$ and (E) $x = 0$

The optical band gap energy of the films can be determined from the following equation,

$$\alpha = \frac{A(h\nu - E_g)^n}{h\nu} \tag{10}$$

where $h\nu$ is the photon energy, E_g is the band gap energy, A and n are constants. For allowed direct transitions $n = 1/2$ for allowed indirect transitions $n = 2$. The plots of $(\alpha h\nu)^2$ versus $h\nu$ for $(Cu_2S)_x(As_2S_3)_{1-x}$ films were shown in Fig.6. The optical band gap energy is determined by extrapolating the linear portion of the curve to the energy axis for zero absorption coefficient. The optical band gap energy of Cu_2S and As_2S_3 is found 3 eV and 2.4 eV respectively. However the E_g of composite is between them.

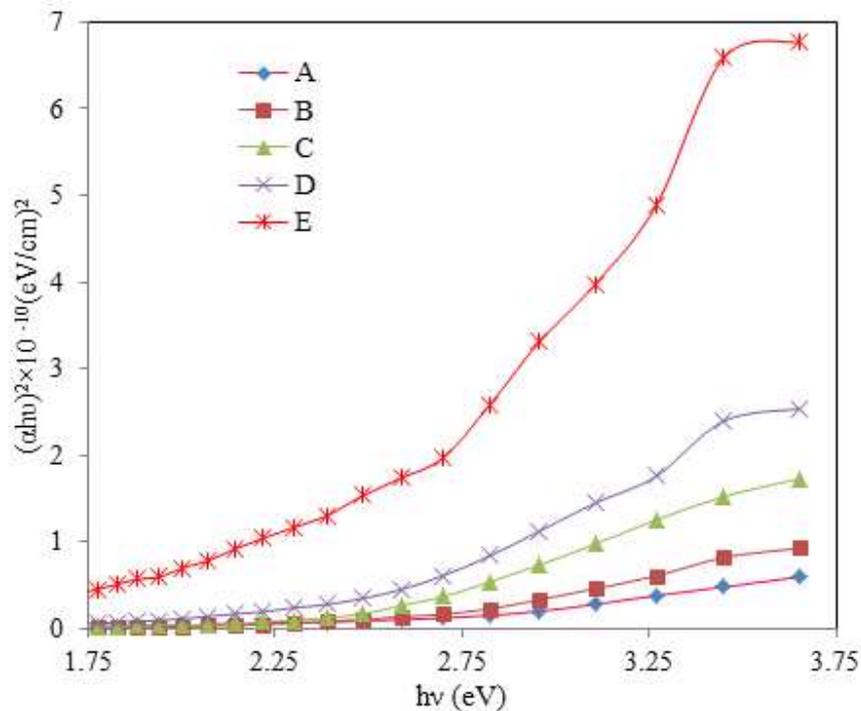


Fig.6.Plots of $(\alpha h\nu)^2$ versus $h\nu$ of $(\text{Cu}_2\text{S})_x(\text{As}_2\text{S}_3)_{1-x}$ film: (A) $x = 1$, (B) $x = 0.75$, (C) $x = 0.5$, (D) $x = 0.25$ and (E) $x = 0$

The contact angle measurement gives information regarding the quality of deposited thin films. The wettability depends on the interaction between a liquid and a solid in contact. If the wettability is high, contact angle will be small and the surface is hydrophilic. On the contrary, if the wettability is low, contact angle will be large and the surface is hydrophobic. The contact angle is an important parameter in surface science and its measurement provides a simple and reliable technique for the interpretation of surface energies. The contact angle depends on the surface morphology of the semiconducting thin films. Fig.7 shows the systematic presentation of measurement of contact angles for $(\text{Cu}_2\text{S})_x(\text{As}_2\text{S}_3)_{1-x}$ films. The Cu_2S and As_2S_3 films have low water contact angle 44° and 34° and the composite has more than 55° indicating hydrophilic nature of $(\text{Cu}_2\text{S})_x(\text{As}_2\text{S}_3)_{1-x}$ film.

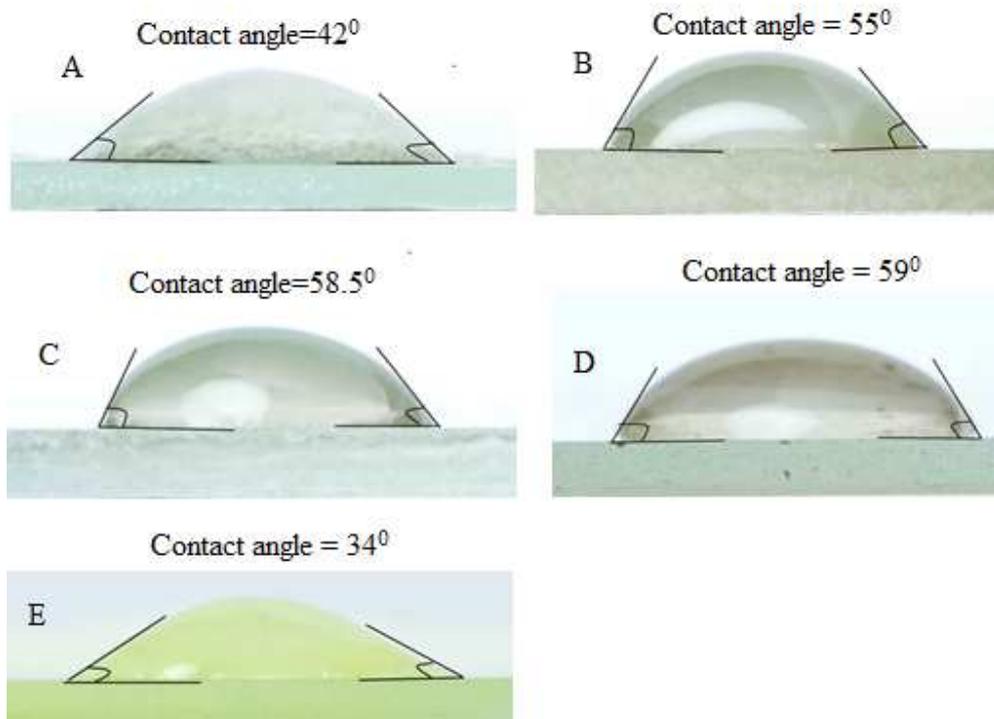


Fig.7. Contact angle of $(\text{Cu}_2\text{S})_x(\text{As}_2\text{S}_3)_{1-x}$ film with water: (A) $x = 1$, (B) $x = 0.75$, (C) $x = 0.5$, (D) $x = 0.25$ and (E) $x = 0$

CONCLUSION

Nanostructured $(\text{Cu}_2\text{S})_x(\text{As}_2\text{S}_3)_{1-x}$ thin films were prepared onto glass substrates using CBD technique in aqueous medium. The X-ray diffraction study reveals that the films are nanocrystalline in nature with mixed hexagonal Cu_2S and monoclinic As_2S_3 structure, whereas in the precipitated powder the hexagonal Cu_2S phase becomes orthorhombic. It is observed that the film thickness decreases with addition of Arsenic. Electrical resistivity measurements indicate semiconducting nature of $(\text{Cu}_2\text{S})_x(\text{As}_2\text{S}_3)_{1-x}$ composite films. It is found that resistivity decreases with increase in temperature. The activation energy decreases with the addition of As_2S_3 . The optical band gap of $(\text{Cu}_2\text{S})_x(\text{As}_2\text{S}_3)_{1-x}$ film lies between 3.05 to 2.4 eV.

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