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Structural, Morphological, Optical and Electrical Properties of Copper Sulphide Nano crystalline thin films prepared by chemical bath deposition method

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Abstract : Copper sulphide nanocrystalline thin films were prepared on glass substrates by chemical bath deposition method for two different deposition time. Coated thin films were characterized by X-ray diffraction, Scanning Electron Microscope, UV-vis-NIR, Energy Dispersive Analysis of X-rays, photoluminescence spectroscope and Hall measurement studies. The X-ray diffraction studies of the deposited thin films showed that the thin films belong to the hexagonal structure. The crystallite size, dislocation density, strain and lattice spacing of the deposited films were determined. The scanning electron microscope results showed that the grain size varies from few μm to nm in the copper sulphide films prepared for two different coating times. Optical properties of the thin films were studied from UV-vis-NIR spectroscope results. The optical band gap determined from the UV-vis NIR spectral studies showed that the direct band gap is 2.8 eV for 5 hrs and 2.7 eV for 6 hrs deposited film respectively. The indirect band gap is 1.75 eV for coated film for 5hrs and 1.70 eV for the film coated for 6hrs.Photoluminescence studies showed a large blue shift in the band gap energy of the deposited films due to quantum confinement effect exerted by the nanocrystals. Mobility, resistivity, and conductivity were measured at room temperature.
Keywords: Copper sulphide, Thin films, Chemical bath Deposition, X-ray diffraction, Scanning electron microscope, UV-Vis-NIR Spectroscope, Photoluminescence spectroscopy, Hall Effect

Introduction

In the past few decades, semiconducting chalcogenide thin films are being studied widely for their various applications in the fields of science and technology[1]. Copper sulphide (CuS) is one of the important p-type semiconductor materials which has been used for several applications such as Electro conductive coatings[2], solid state solar cell[3], electrodes[4] and catalysis[5]. CuS coated on glass windows (architectural) acts as selective radiation filters[6] in warm climates. Major challenges in the photovoltaic cell applications is to find chalcogenide semiconductor materials with a suitable band gap and high absorption coefficient. Since the discovery of CdS/Cu_2S heterojunction solar cell in 1954 the use of CuS thin films in the solar energy conversion device is well known[7,8] reported that covellite form of CuS shows metallic conductivity as well as super conductivity at 1.6K[9]. Furthermore, ternary and quaternary chalcogenide semiconductor materials such as copper indium

sulphide ($CuInS_2$)[10], copper indium gallium sulphide (CIGS)[11] and copper zinc tin sulphide (CZTS)[12] have been extensively used in photovoltaic solar cell. Synthesised CuS was used to deposite thin films of different morphologies such as flower like[13,] tubular[14,] plate like[15] and spherical[16] structures. CuS thin films have been deposited employing chemical bath[17,] spray pyrolysis[18], vacuum evaporation[9], chemical vapour deposition[20], successive ionic layer absorption and reaction[21] and liquid- liquid interface reaction[22] techniques. Among all these technique chemical bath deposition is a simple, inexpensive, low temperature and large area deposition technique employed to produce several chalcogenides thin films such as ZnS[23], CdSe [24,] and CdTe[25,] ZnSe [26.]

In present work, CuS nanocrystalline thin films were prepared on the glass substrates by chemical bath deposition method for two different coating time. Structural, morphological, optical and electrical properties of the film are reported in this work.

Experimental Method

CuS nanocrystalline thin film was deposited on glass substrate employing chemical bath deposition method. Analytical grade (A.R) chemicals of copper (ll) chloride dihydrate ($CuCl_2.2H_2O$), triethanolamine ($C_6H_{15}NO_3$),ammonia solution (NH_4OH), sodium hydroxide pellets (NaOH) and Thiourea (NH_2CSNH_2) (SISCO Chemical Pvt Ltd. Mumbai) were used. Copper (II) chloride dihydrate and thiourea are source of Cu^{2+} and S^{2-} ions respectively. Triethanolamine and sodium hydroxide is the complexing agent during the deposition process whereas ammonia solution was used for adjusting pH of the solution to achieve the medium. The glass substrates of dimensions (76mm X 26mm X 1.35mm) were used. The glass substrates were washed with mild soap solution and rinsed with distilled water and then the glass slides were immersed in hot chromic acid for 1h. Again the glass slides were washed with de-ionized water and finally ultrasonically cleaned by ethanol then dried in oven for 2hrs at 50º C. 1M of copper sulphide ($CuCl_2.2H_2O$) solution was added with triethanolamine (TEA) ($C_6H_{15}NO_3$) solution in a 100 ml glass beaker and stirred for 10 min. After that 8 ml of aqueous ammonia (NH_4OH), solution was mixed under stirring. Then 1M of sodium hydroxide (NaOH) solution was added in to the solution under continuous stirring. Finally 1M of thiourea (NH_2CSNH_2) solution was mixed and stirred for 5 min.The pH of the solution was 11.2. A cleaned glass substrate was immersed vertically in the solution. The deposition of CuS thin film was carried out at room temperature for two different deposition time of 5hrs and 6hrs.Then the films were removed, rinsed with distilled water and dried. Finally the deposited films preserved in an airtight plastic container and stored in a desiccator for further characteristic studies. The composition of the as-deposited thin films were determined by EDAX (JEOL 5610-LV). The structural properties were studied using X-ray diffraction (bruker D2 phaser AXS using CuKα (1.5418Å) in the 2θ range of 20°- 90°. Surface morphology of the thin films were studied using SEM (JEOL JSM-6380 LV). Optical properties of the films were studied with a double beam UV-VIS-NIR spectrometer (UV-100-Cyber lab). Photoluminescence spectra were recorded by using a Perkin-Elmer LS-55 fluorometer. Electrical properties of the films were studied by Hall effect measurement system (Ecopia HMS-3000 Ver 3.51.3).

Results and discussion

Structural analysis

Fig.1 (a) and (b) shows the XRD patterns of the CuS nanocrystalline thin films deposited for 5 hrs and 6 hrs respectively. The lattice parameters calculated are a = b = 3.768Å, c = 16.27Å, α = β = 90° and γ = 120°. The XRD peaks of CuS thin films corresponding to (101), (102), (105), (106), (006), (110) planes confirm that the films belong to the hexagonal structure (Joint Committee on Powder Diffraction standard data JCPDS reference code 06-0464).When the deposition time is increased the peak intensity gradually increases and full width half maxima (FWHM) decreases thus indicating improvement in the crystallite size of the films. The average crystallite sizes (D) were calculated by Scherrer's formula [27] $D = \frac{0.9\lambda}{\beta \cos\theta}$, where λ is the X-ray wavelength of CuK_α radiation (1.5480Å), β is the Full width half maxima (FWHM) of corresponding XRD peaks and θ is the angle of diffraction. Average crystallite size of the as-deposited films increases from 56.7 nm to 70.1 nm when the coating time increases from 5hrs to 6hrs. The dislocation density (δ), strain (ε) and lattice spacing (d) have been calculated by using the following expression and its values are given in the Table 1. The average strain value calculated using this equation $\varepsilon = \frac{\beta}{4\cos\theta}$ and dislocation density (δ), lattice spacing value calculated using the relations of $\delta = \frac{1}{D^2}$ and $d = \frac{\lambda}{2\sin\theta}$ respectively.

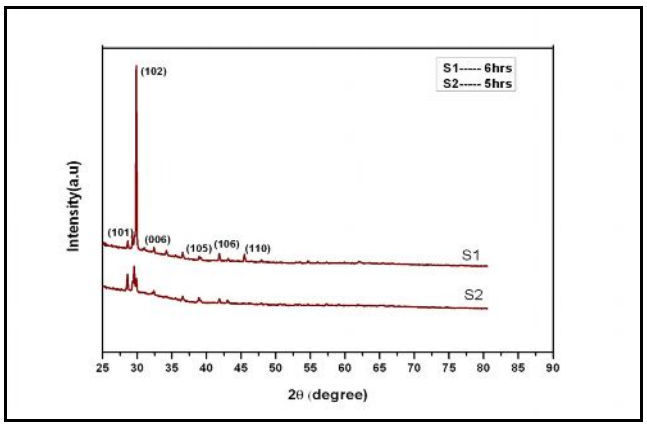


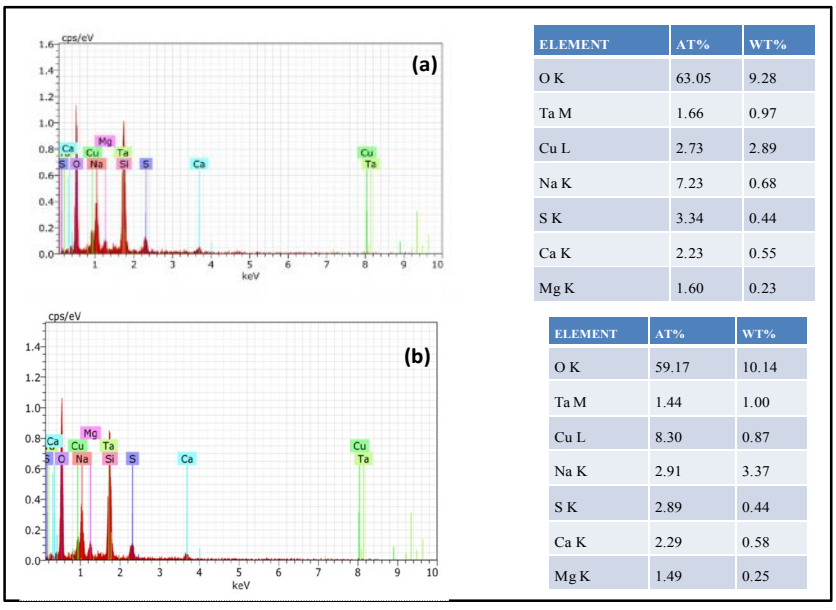
Fig: 1 XRD patterns of CuS nanocrystalline thin films at various time periods

Table 1: To determine the crystalline size (D), strain (ε), dislocation density (δ), lattice spacing (d).

Deposition time	Crystallite size(D) nm	Strain (ε) x 10^{-4}	Dislocation density(δ) x 10^{14}	Lattice spacing(d) Å
5hrs	56.2	6.21	3.24	0.513
6hrs	70.1	5.44	2.75	0.25

Composition analysis

EDAX spectrum of the as- deposited CuS thin film for 5 hrs and 6 hrs period are presented in Fig.2(a) and (b) respectively. Both the spectra confirm the presence of the composition of copper and sulphur in the films.



ELEMENT	AT%	WT%
O K	63.05	9.28
Ta M	1.66	0.97
Cu L	2.73	2.89
Na K	7.23	0.68
S K	3.34	0.44
Ca K	2.23	0.55
Mg K	1.60	0.23

ELEMENT	AT%	WT%
O K	59.17	10.14
Ta M	1.44	1.00
Cu L	8.30	0.87
Na K	2.91	3.37
S K	2.89	0.44
Ca K	2.29	0.58
Mg K	1.49	0.25

Fig: 2 EDAX spectrum of CuS nanocrystalline thin films at two different time periods (a) 5 hrs & (b) 6 hrs. Surface analysis

Fig. 3(a) and (b) show the SEM images of the as-deposited CuS thin films coated for 5 hrs and 6hrs respectively.It can be seen clearly that the films are smooth, uniform and homogeneous without pores. The size of the particles formed on the films are in nanometre range.

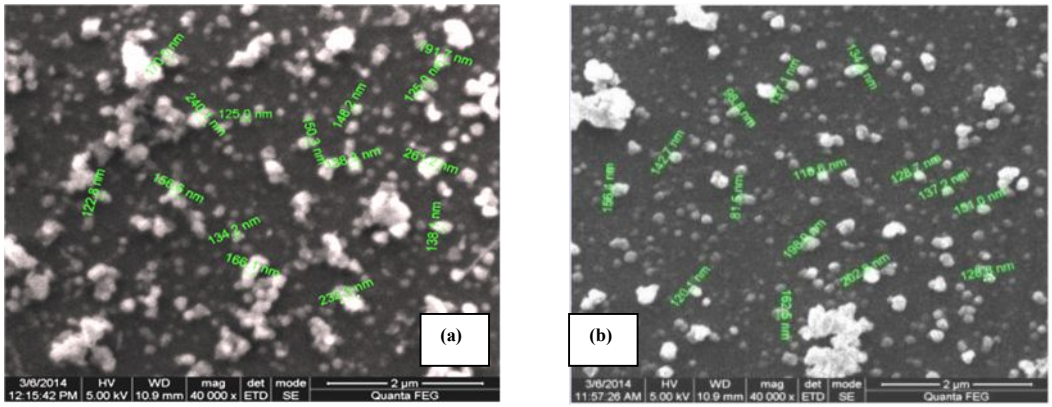


Fig: 3 SEM images of CuS nanocrystalline thin films deposited at different time (a) 5 hrs & (b) 6 hrs.

Optical analysis

Fig.4 shows the optical transmission spectra of CuS films deposited on the glass substrates for deposition time of 5hrs and 6hrs respectively. It can be seen clearly that the deposited films exhibits a higher absorption and lower transmission throughout the uv-region with peaked transmission in the visible region.

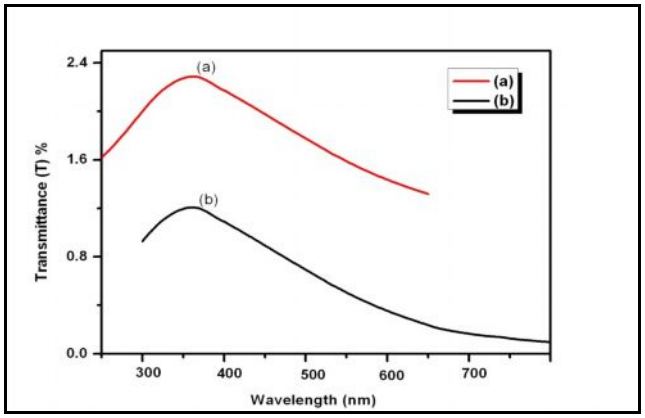


Fig: 4 Transmittance Spectra of the CuS nanocrystalline thin films deposited at various time period (a) 5 hrs & (b) 6 hrs.

Fig.5 shows the UV-vis absorption spectrum for the as-deposited CuS thin films, the strong absorption is in the wavelength range of 252nm to 456nm for 5hrs coated film and 302nm to 450nm for 6hrs coated film.

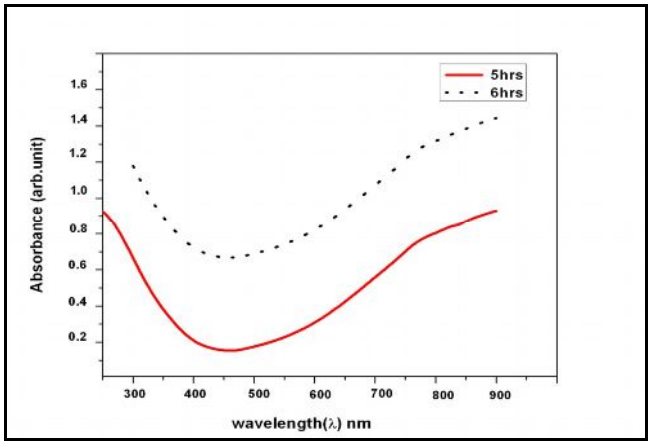


Fig: 5 Absorbance Spectra of the CuS thin films deposited at different time duration

The band gap energy of the deposited CuS thin films was calculated by using Tauc's relation [28].$(\alpha h\nu)^{1/n} = A\,(h\nu - Eg)$ where, α is the absorption coeffient, hν is the incident photon energy, A= constant, E_g is a optical energy band gap and n is the characterizes the transitions. For direct allowed and forbidden transitions, n= 2 and

2/3 respectively and n=1/2 and 1/3 for indirect allowed and forbidden transistions respectively. The analysis of Tauc's relation showed that , n=2 and 1/2 fitted for chemical bath deposition as deposited CuS thin films, confirming direct and indirect allowed transitions. Fig.6 shows the plot of $(\alpha hv)^2$ verus hv for direct band gap of as deposited CuS sulfide thin film for different deposition time.The direct band gap values of prepared CuS thin film is 2.7 eV for 5 hrs coated film and 2.8 eV for 6 hrs coated film. The reported value of direct band gap ranges from 2.1 eV to 2.58 eV for CuS thin film deposited by various methods [17, 21].

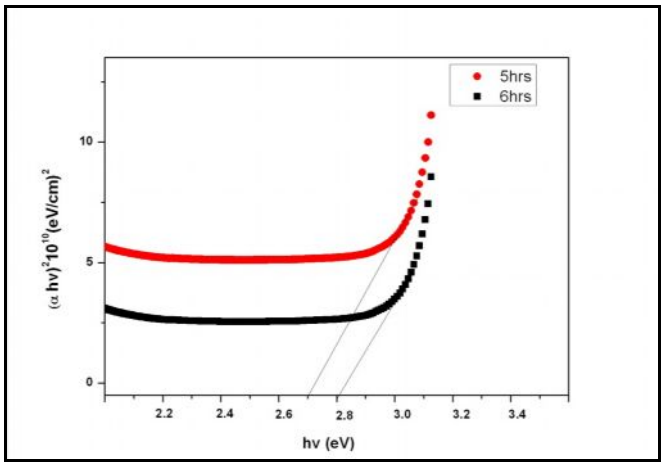


Fig: 6 Plot of $(\alpha hv)^2$ versus hv of CuS nanocrystalline thin films deposited at various time.

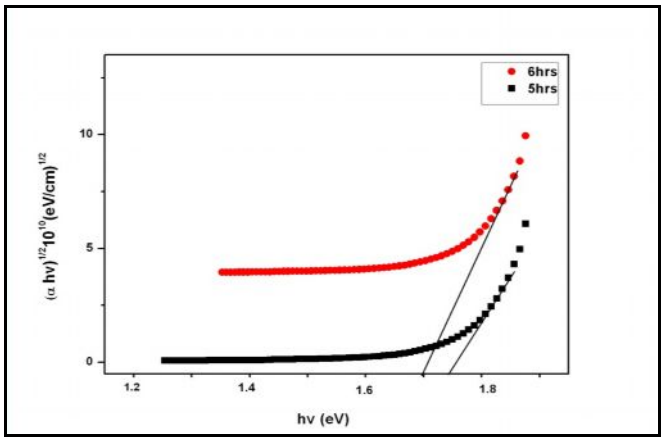


Fig: 7 Plot of $(\alpha hv)^{1/2}$ versus hv of CuS nanocrystalline thin films deposited at various time.

Fig.7 shows the plot of $(\alpha hv)^{1/2}$ verus hv for indirect band gap of as deposited CuS sulfide thin film for different deposition time.The indirect band gap value is 1.75 eV for 5 hrs coated film and 1.70 eV for 6 hrs coated film. The reported value of indirect bandgap value ranges from 1.67 eV to 1.99 eV for CuS thin film deposited by co evaporation method[19]. The obtained direct and indirect bandgap value agree well with the reported values.

Photoluminescence analysis

The room temperature PL spectra of the as-prepared CuS nanocrystalline thin films deposited on the glass substrate for the different time period are shown in Fig.8 respectively. It was established that the nanocrystalline CuS thin film exhibit light emission in the blue –green region[29]. In generally, CuS film containing bulk crystallites exhibit broad emission bands in the NIR-vis region depends upon the film stoichiometry and composition, as obtained from different baths[30]. Here, the strong blue emission peak centered at about 450nm is observed under the excitation wavelength (λ_{exc}). Whenever the dimension, structure and size of the nanoparticle decreases the blue shift is attributed due to the enhancement of the quantum confinement effect.

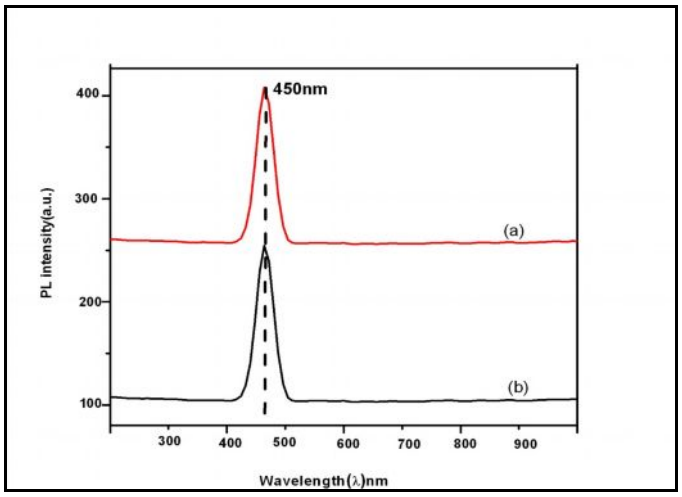


Fig: 8 Photoluminescence Spectra of CuS nanocrystalline thin films at different deposition time (a) 5hrs & 6hrs.

Electrical properties

The carrier concentration, resistivity, hall mobility, conductivity, hall coefficient of deposited CuS nanocrystalline thin films were measured using Hall effect set up (Ecopia HMS ver 3.51.3) and the values are given in Table 2. When the deposition time increases electrical resistivity and Hall coefficient decreases whereas the mobility, electrical conductivity and, carrier concentration increases. The obtained value of Hall coefficient, carrier concentration and mobility of deposited CuS nanocrystalline thin films at different deposition time is close to the reported values [31] are given in a table 2.The positive sign of the hall coefficient indicates that the as-deposited CuS nanocrystalline thin films have p- type conductivity.

Table 2: Electrical properties of CuS nano crystalline thin film at different deposition time

Deposition Time	Resistivity (Ω) (cm)	Mobility(μ) (cm^2/Vs)	Conductivity(1/Ω) (Cm)	Carrier concentration(p) (Cm^{-3})	Hall Coefficient (R_H) (cm^3/coul.)
5 hrs	8.79×10^{-3}	0.221	1.138	3.214×10^{17}	19.43
6hrs	0.13×10^{-3}	0.840	7.431	5.480×10^{17}	11.93
Reported value	----	0.322	-----	5.76×10^{17}	11.058

Conclusion

Copper sulphide (CuS) nanocrystalline thin films were prepared on glass substrate by chemical bath deposition method for deposition time of 5 hrs and 6 hrs. The EDAX Spectrum of as-deposited thin films showed that the presence of Cu and S are confirmed. The X-ray analysis of the CuS thin films showed that the films are single phase covellite CuS possessing hexagonal structure. The crystalline size, strain, dislocation, density, lattice spacing determined from the FWHM of XRD peaks. SEM analysis showed that the synthesized thin films were uniform, homogeneous having no visible pores on the surface. The as- deposited films have the direct band gap value of 2.7 eV for 5 hrs deposition and 2.8 eV for 6 hrs deposition. Whereas indirect band gap value of CuS thin films are 1.75 eV for 5hrs deposition and 1.70 eV for 6 hrs depositions. PL spectrum showed that a strong blue emission peak at low wavelength region appeared at about 450nm for 5h and 6h coating time. Hall measurement analysis showed that as-deposited CuS thin films are p type conductivity.

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