EFFECT OF CONCENTRATION ON STRUCTURAL AND OPTICAL PROPERTIES OF CuS THIN FILMS

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Abstract

Thin films of Copper sulphide were deposited on glass substrates using chemical bath deposition technique at room temperature from the aqueous solution containing different concentration of copper sulphate between 0.05M and 0.15M. The effects of the copper concentration of the chemical bath on structural and optical properties of the amorphous thin film were investigated and discussed. The optical absorption and transmission of the thin films were observed between of 330-1100nm taken at room temperature. The optical band gaps of the as-synthesized copper sulphide thin film for various concentrations were measured. The surface morphology has been observed using scanning electron microscopy (SEM) and atomic force microscopy (AFM). The results obtained from AFM demonstrated that the reflectivity was closely related to the surface roughness of the film. High surface roughness has a strong scattering effect on light and lowers the reflectivity. X-ray diffraction (XRD) patterns show that crystallinities of the films are dependent on the copper concentration in the solution.

Keywords: *Copper sulphide, CBD; XRD; AFM; SEM; Thin films*

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1. INTRODUCTION

Nanostructures materials have attracted a great deal of attention in the last few years for their unique characteristics that cannot be obtained from conventional macroscopic materials. Copper sulphide has complex crystal chemistry owing to its stability to form stochiometric compounds. Copper sulphide thin films are very attractive materials for a wide variety of technological applications such as ferroelectric thin films, high-density optical data storage or semiconductors [1], optoelectronic devices [2], energy storage and conversion [3], solar cells, gas sensors [4], etc. due to their structural, optical and electrical properties [5]. The copper sulphide exhibits high transmission in the visible region and absorption throughout the near IR region (800 -1500nm) [6]. It also exhibits fast ion conduction at higher temperatures. Therefore copper sulphide is suitable for the fabrication of solar cells. Recent research on solar cells has been aimed at lowering the fabrication cost to decrease the price of the energy obtained. In this context, suitable materials should be prepared easily, must show stable behavior over a long period of operation and inexpensive. A material is said to be a thin film when it is build up as a thin layer on a substrate by controlled condensation of the individual atomic, molecular or ionic species either directly by a physical process or through a chemical/electrochemical reaction. Various methods are been used for deposition of thin films, like vacuum evaporation, electro deposition, spray pyrolysis, sputtering, sol gel method, molecular beam epitaxy, chemical bath deposition (CBD) etc. Of all these techniques, the CBD method is used to deposit over a large surface area, with out the need of any sophisticated instruments, it is suitable for deposition at low temperature and inexpensive. CBD is a simple reproducible and cost effective technique for the preparation of metal halide and sulphide thin films on various substrates. This technique is based on slow controlled precipitation of the desired compound from its ions in a reaction bath solution. A ligand or complexing agent acting as a catalyst is usually employed to control the reaction in a medium of suitable pH and concentration to obtain desirable crystalline thin films, otherwise spontaneous reaction will occur that affect the thin film growth and also sedimentation of materials will be resulted. The condition for compound to be deposited from a solution bearing its ions is that its ionic product (IP) should be greater than the solubility product (SP). The complexing agent of a metal in solution forms fairly stable complex ions of the metal and provides a controlled release of free ions according to an equilibrium reaction. The negative ions required for the precipitation of the compound are also generated slowly by suitable complex compounds bearing those ions. The deposition technique can be improved by maintaining parameters like suitable complexing agent, pH, concentration and temperature. Hitherto number of thin films such as CdSe [7], In_2S_3 [8], SnS [9], FeS [10], etc are obtained by CBD technique have also been reported.

In the literature most studies have been concentrated on the effect of various factors such as pH [11], solution and substrate temperature [12], annealing temperature [13], deposition time [14, 15], molar ratio in the bath solution [16], the influence of the substrate on the properties of the chalcogenide thin films [17] etc., on the surface morphology, the optical and structural properties. The present work is focused on the preparation of amorphous CuS thin films on the glass substrates by CBD using various copper ion concentrations in the precursor solution and also its influence on structural and optical properties such as absorbance (A), transmittance (T) reflectance (R) thickness (T) and the band gap energy of the films are investigated, which is hitherto not reported. Comparative study is also made to show how the concentration of the copper ions in the reaction bath can alter the nature of the deposited thin film. The surface morphology of the film was studied using SEM and AFM. The structural characterization was also carried out using XRD.

2. EXPERIMENTAL

In this work, commercial glass slides were used as substrates. Substrate cleaning plays an important role in the deposition of thin films, because contaminated surface of the substrates results in the non-uniform film growth due to the nucleation formed by the impurities. Prior to deposition, substrates were cleaned using detergent, nitric acid and double distilled water in an ultra sonicator bath, and finally dried in an oven. Copper sulphate, thiourea, triethanolamine (TEA) and ammonia solution of analytical reagent grade were used as received. The films were prepared at room temperature for different copper sulphate concentrations viz. 0.05M, 0.075M, 0.1M, 0.125M and 0.15M in the chemical bath by keeping all other bath parameters in the precursor solution are as same. Aqueous solution of copper sulphate, thiourea and triethanolamine were prepared separately using double distilled water before the experiment. To the 0.05M $CuSO_4.5H_2O$ solution, exactly 5ml of 1:1 TEA, 10ml of 1M thiourea and 10ml of 30% ammonia solution were added slowly one after the other with constant stirring and final volume is made up to 100ml using double distilled water. The TEA serves as a complexing agent to chelate with copper ions. The deposition of CuS films is based on the slow release of Cu^{2+} and S^{2-} ions in the solution, which are then condensed on to the glass substrates [18]. The thiourea was used as a source for sulphide ions and ammonia solution was added slowly to maintain the p^H of the bath at 11. Previously cleaned glass slides were immersed vertically in the bath for 5 hours at lab temperature without disturbing the solution during the deposition. In the same way the CuS thin films were fabricated for other concentrations of $CuSO_4$ such as 0.075M, 0.1M, 0.125M and 0.15M using other solutions as indicated in Table-1.

Table-1: Bath constituents for preparation of copper sulphide (CuS) thin films

Sl No.	Concentration of $CuSO_4$ (in Molars)	TEA (ml)	1M Thiourea (ml)	30% Ammonia solution (ml)
1	0.05	5	10	10
2	0.075	5	10	10
3	0.1	5	10	10
4	0.125	5	10	10
5	0.15	5	10	10

The reaction mechanism for the deposition of (CuS) thin film can be given as follows:

$$CuSO_4.5H_2O + TEA \rightarrow Cu\,(TEA)^{2+} + (SO_4)^{2-} + 5H_2O$$

$$Cu\,(TEA)^{2+} \rightarrow Cu^{2+} + TEA$$

$$SC\,(NH_2)_2 + OH^- \rightarrow CH_2N_2 + H_2O + HS^-$$

$$HS^- + OH^- \rightarrow H_2O + S^{2-}$$

$$Cu^{2+} + S^{2-} \rightarrow CuS$$

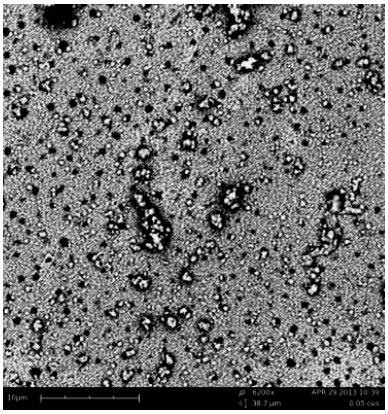
After completion of film deposition, the substrates were taken out and washed using double distilled water and used for analysis.

Scanning Electron Microscopy (SEM) images were obtained with a Phenom SEM. To determine surface morphology and film thickness of the CuS thin films, the sample surfaces were monitored using atomic force microscopy (AFM, PARK system). The AFM was operated in non contact mode to avoid destruction due to using of a standard silicon tip. Optical properties were studied by measuring absorbance of the film using a shimadzu spectrophotometer within the wave length range of 330-1100nm. X-ray diffraction (XRD) patterns were recorded to characterize the structure of the thin films using Bruker D2 phaser x-ray diffractometer with CuK_α radiation of wave length (λ) of 1.5406 Å for 2θ values over 12°-90°.

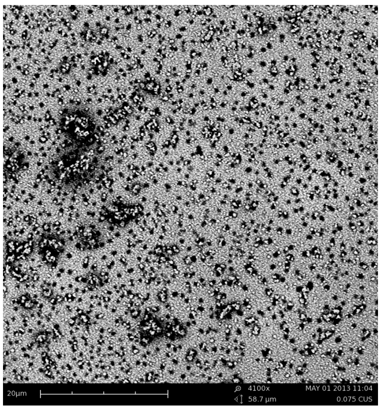
3. RESULTS AND DISCUSSION

3.1 Surface Morphology of the Thin Film

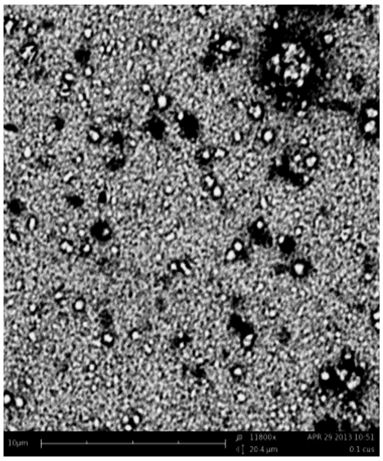
SEM is a promising technique for the morphology of thin films. It gives as important information regarding growth, shape and size of the particles. In the present work, the copper precursor solution prepared for the development of thin film by CBD method, as reported elsewhere [19]. The film may also be obtained by using the acidic bath solution, maintained at pH 1.5 [14]. In this paper, for the first time, we made an attempt by varying the copper concentration to study the effect on the CuS thin film. Figure1(a-e) shows the SEM micrographs for CuS thin film obtained for different concentrations of copper ions in the solution bath. It is observed from the Fig 1c that the grains in the film are relatively good, compact, homogeneous and uniformly covered at 0.1M concentration. Here, an attempt is made for the first time to fix the concentration of copper in the bath solution to get a uniform, crystalline thin film of CuS which is hitherto not reported. The deposition is carried out at various concentrations of copper as mentioned above by maintaining the pH at 11. At lower concentration the grains are very far and as the concentration increases the particles are closely packed. At 0.1 M the film is uniformly covered and stable. Above 0.1 M the film is not homogeneous and uniform, cracks were observed and the film is peeling off, hence unstable. This maximum concentration at which the film obtained is stable and above which it is unstable, was termed as critical concentration.



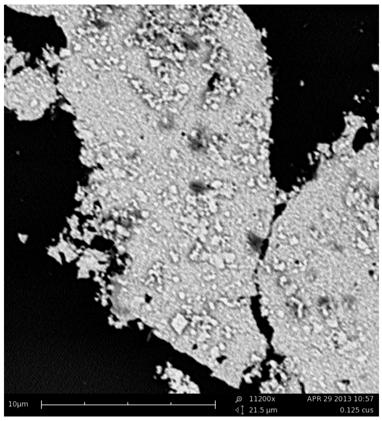
a) 0.05M



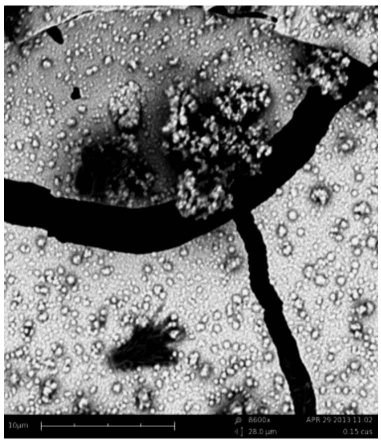
b) 0.075M



c) 0.1M



d) 0.125M



e) 0.15M

Fig-1(a-e): SEM images of CuS thin film on glass substrate at different Cu^{2+} ion concentration

3.2 Surface studies by Atomic Force Microscopy:

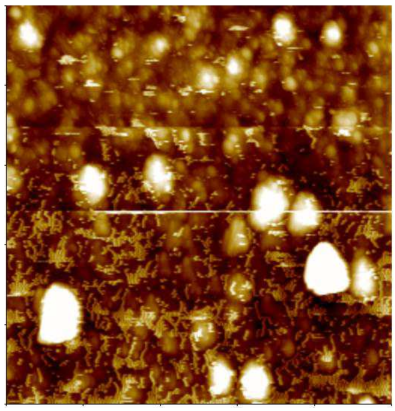
An atomic force microscope (AFM) was used to study the surface nanostructure of the CuS thin film deposited on the glass substrate. This technique is capable of mapping three-dimensional images of the surface of CuS thin films. Figures 2(a-e) shows AFM micrographs of the CuS thin films deposited at various concentrations from 0.05M - 0.15M. From the obtained AFM image the thickness and surface roughness of the film were investigated. At lower concentration <0.1M, the surface coverage was incomplete and particles are not grown completely on the surface of the substrate as shown in Fig. 2a and 2b. This may be due to insufficient amount of sulphide ion and TEA source to form CuS thin film on substrate while depositing. The deposition on a substrate mainly depends on the formation of nucleation sites and subsequent growth of the thin films from the centre. Hence, irregular shaped grains with different sizes are observed on the surface of the film. Further increase in the Cu^{+2} ion concentration to 0.1M shows complete coverage of the film over the substrate compared to the films prepared at lower concentration. The surface is relatively uniform and particle agglomerations are avoided. The grain sizes were almost similar to each other without any cracks and consists of spherical particles which are well adhered to the substrate. Thickness of the film was found to be 250nm. However, the films deposited at 0.125M and 0.15M is highly irregular and agglomerated with high surface roughness.

Fig. 3 shows the variation in the film thickness as well as surface roughness of the as-deposited amorphous CuS thin films as a function of the Copper ion concentration in the bath solution. We find that the film thickness increases nearly linearly from 130 nm to 250 nm with the increase in the concentration of copper ions from 0.05M to 0.1M (cf. Fig 3). Depositions with concentrations above 0.1M results the decrease in thickness, may be due to the formation of outer porous layer may have developed stress which tends to cause delamination, resulting peeling off the film [20]. Further, due to the competition of heterogeneous nucleation on the substrate and homogeneous nucleation in the solution, would alter the growth of the thin film [21]. The surface morphology of the film deposited at 0.1M is quite uniform and well covered on the substrate when compare with than other concentrations.

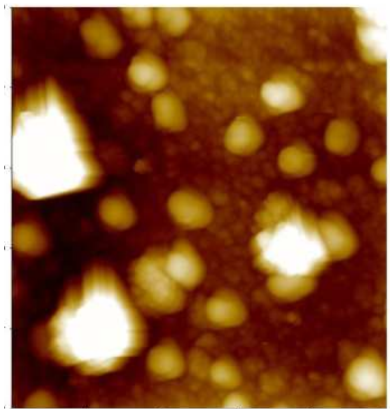
Root mean square (RMS) roughness defined as the standard deviation of the surface height profile from the average height, is the most commonly reported measurement of surface roughness [22]. The surface roughness values 25.88 and 114.31nm were observed for the films prepared using 0.05M and 0.15M respectively, indicating that the surface roughness increases with increasing concentration of copper ions in the bath. According to the data obtained for surface roughness as indicated in Table 2, the films deposited for 0.05M have a smoother surface while the films prepared for 0.15M have a rougher surface. However, for the films deposited using 0.15 M is highly irregular, agglomerated and unstable with surface roughness and thickness is 114.31 nm and 110nm respectively. We have observed that the surface roughness depends on concentration of copper ions in the bath solution and the surface roughness is unavoidable due to three-dimensional growth of the films.

Table-2: Thickness and Surface roughness of amorphous CuS thin films deposited at various copper ion concentration

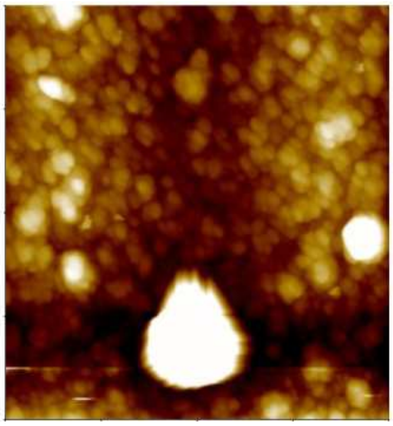
Molar concentration of CuSO4	Thickness in nm	Roughness in nm
0.05	130	25.88
0.075	150	91.75
0.1	250	30.25
0.125	220	46.72
0.15	110	114.31



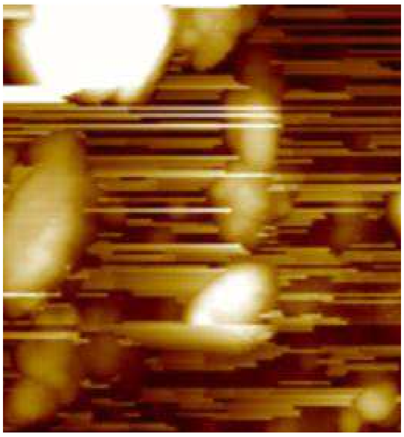
a) 0.05M



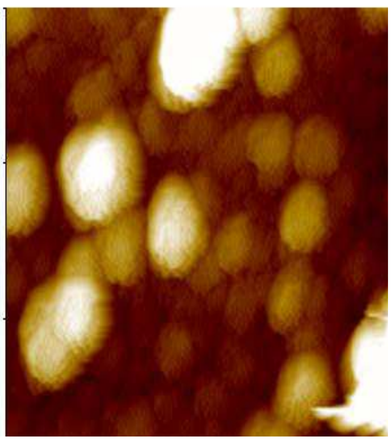
b) 0.075M



c) 0.1M



d) 0.125M



e) 0.15M

Fig-2(a-e): AFM images of CuS thin film on glass substrate at Cu^{2+} different concentration

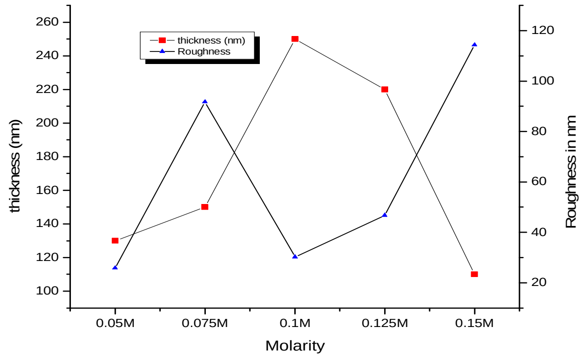


Fig-3: Thickness and roughness spectra of amorphous CuS thin films at Cu^{2+} ion concentrations

3.3 Optical Properties

Optical behavior of amorphous CuS thin film deposited at various concentrations is determined by its absorbance, transmittance, reflectance and optical constant, i.e. the band gap values. The absorption spectrums of the deposited films are as shown in fig. 4. An absorption edge corresponds to an electron excited by a photon of known energy, whereby electron can jump from a lower energy to a higher energy state. The absorption spectrum of CuS thin films were recorded in the wave length region ranging from 330 to 1100nm. The absorption edge is between 450nm to 550nm for all the thin films deposited. It was observed that the absorption edge of the films shifts to a longer wave length side as the concentration increases, which suggests a decrease in the band gap value. The decrease in band gap value from 0.75M to 0.1M is very less. Similar results are also observed in the literature [23, 11]. Due to surface resistance, non uniformity and instability of the thin film, the absorption spectra at 0.15M is not obtained properly.

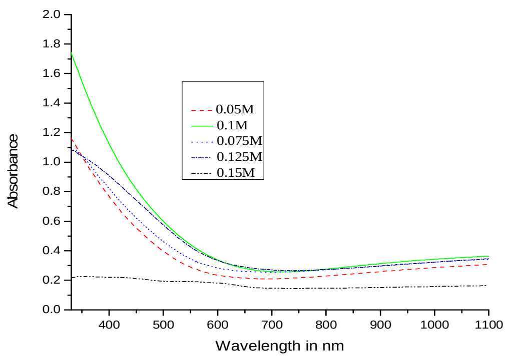


Fig -4: Absorbance spectra of amorphous CuS thin films at different Cu^{2+} concentrations

Figure 5 shows the transmittance spectra as a function of wavelength of the CuS thin films deposited at various concentrations of copper ions in the chemical bath. From the observed data, it is seen that the average transmission (T) in the visible region is about 50-70% at the wavelength around 650nm, which is more than transmittance values reported elsewhere [11]. It is also seen from the fig. 5 that the transmittance decreases in the near infrared (NIR) region, where as reflectance (R) increases (fig.6).The transmission and reflectance spectra obtained at 0.15M are also not clear may be for the same reason as mentioned above.

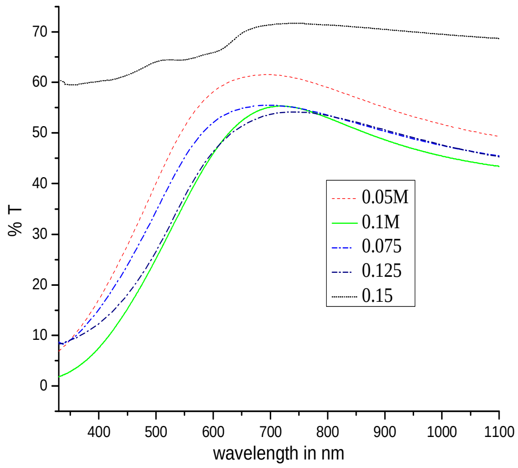


Fig-5: Transmittance spectra of amorphous CuS thin films

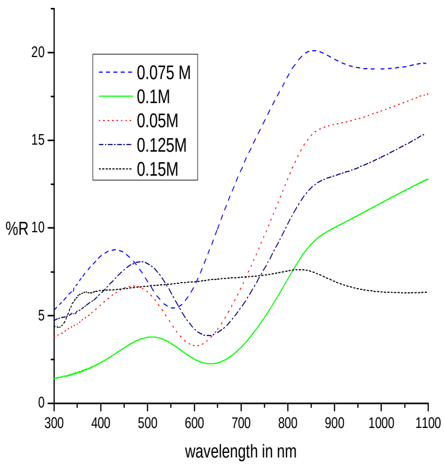


Fig-6: Reflectance spectra of amorphous CuS thin films

The optical band gap (E_g) of the prepared CuS was calculated by using the relation [24, 25]:

$$(\alpha h\nu) = a\,(h\nu - E_g)^n \qquad (2)$$

Where α is the optical absorption coefficient, 'a' is a constant and n depends on transition type. The value of α is obtained from the following relation [26].

$$\alpha = 2.303\ A / t \qquad (3)$$

Where A is the absorbance and t is the thickness of the film. The $(\alpha h\nu)^2$ is plotted as a function of photon energy (hν) is shown in fig.7. It varies almost linearly with photon energy above the band gap energy (Eg). Thus, the equation 2 is used for the determination direct inter band transmission [27]. The linear extrapolation of this curve to the energy axis gives the value of band gap.

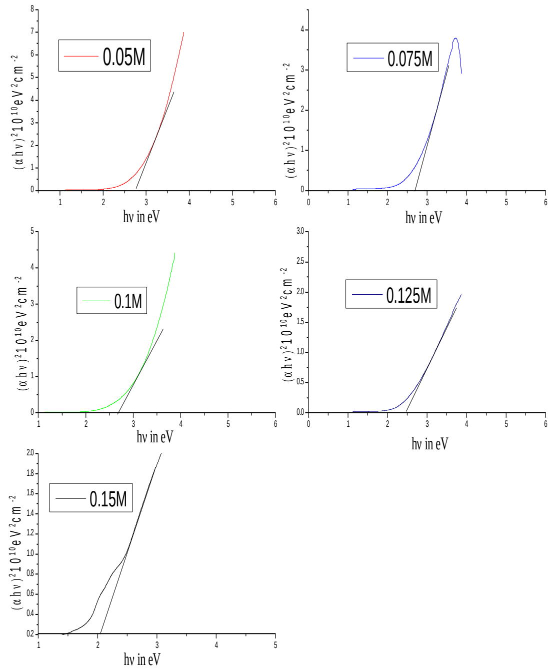


Fig- 7: $(\alpha h\nu)^2$ verses hν plot of amorphus CuS thin films at different Cu^{+2} concentrations

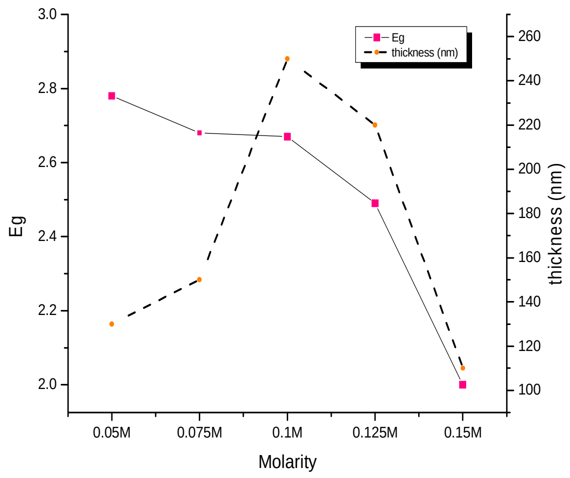


Fig.-8: Band gap and thickness spectra of amorphous CuS thin films

Table-3: band gap CuS thin films at different Cu^{2+} concentrations

Molar Concentration of copper ions	Thickness in nm	E_g(eV)
0.05	130	2.78
0.075	150	2.68
0.1	250	2.67
0.125	220	2.49
0.15	110	2.00

As shown the table-3, the obtained thin film at various concentration exhibits a linear dependence of $(\alpha h\nu)^2$ on $(h\nu)$ in the band gap range 2.0-2.78eV. The fig.8 shows the variation in the band gap of the CuS thin films as a function of the various copper sulphate concentration in the chemical baths. It is observed that indirect band gap varies from 2.0-2.78eV. The optical band gap values obtained for CuS thin films are lower than the values reported elsewhere [11]. The band gap energies of highly crystalline films are similar to crystalline bulk materials, whereas in amorphous films Eg values are higher than those corresponding bulk materials.

3.4 Structural Properties

X-ray diffraction is a powerful non-destructive method for characterization, by which, the crystal structure, grain size and orientation factor can be determined. The structural identifications of amorphous CuS thin films were carried out with Bruker XRD D_2 model. The XRD patterns were recorded from 12°- 90° (2θ). The XRD spectrum of the CuS thin film deposited at various concentrations are as shown in the fig 8. It is observed that, the structural properties of the thin films deposited were not affected by the concentration up to 0.1M of copper ions in the chemical bath. Further, it is clear from the figure that as the concentration increases; the crystalline nature of the film also increases.

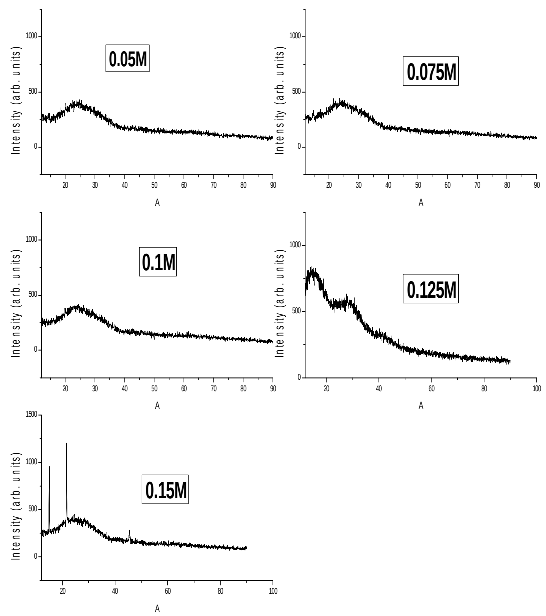


Fig.-9: XRD spectrum of amorphous CuS thin films at various Cu^{2+} concentrations

CONCLUSIONS

A simple and convenient CBD method was employed, and successfully deposited amorphous CuS thin film on commercial glass at various concentrations of copper ions in the chemical bath. The effect of the concentration on the optical properties and surface morphology of the obtained thin films were studied. The surface morphology by SEM reveals that 0.1M is the best concentration to get an uniform thin film of amorphous CuS, at which the film is homogeneous with uniform grain size and closely packed particles over the entire substrate area without any cracks. The obtained XRD pattern shows the amorphous nature of the film. At higher concentrations it shows that the thin films are crystalline in nature and up to 0.1M copper ions concentration, it does not affect much on the film structure. However, the characteristic UV–VIS spectrum data of the deposited film demonstrated that the bath concentration value will affect the optical properties of the as-deposited CuS thin films. Optical transition was found to increase from 50% - 70% in the visible region, as the concentration is increased. Additionally, the optical reflection of the film varied from ~7 to 20% in the visible range respectively. It was found that the indirect band gap varies from to 2 to 2.78 eV due to the deposition conditions and concentration of the copper ions in the bath solution. The AFM measurements have shown that the CuS thin film has high roughness at higher concentration. From all the above analysis it was found that, the film deposited at 0.1M copper concentration showed the best optimum concentration for the preparation of the amorphous thin film of CuS because of uniform surface coverage, higher absorption and minimum reflectance characteristics when compared to the films deposited at other concentrations. These results matched well with the information obtained from XRD, SEM, AFM and optical properties.

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