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Characterization of Electrodeposited Copper Sulphide Thin Films

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Abstract: *Copper Sulphide (CuS) thin films were electrodeposited onto indium doped tin oxide coated conducting glass (ITO) substrates from an aqueous acidic bath containing $CuSO_4$, $Na_2S_2O_3$ and EDTA. The deposition mechanism was investigated using cyclic voltammetry. The appropriate potential region in which the formation of stoichiometric CuS thin films occurs was found to be -500 mV versus SCE and the solution pH was maintained at 3.0 ± 0.1. X-ray diffraction studies revealed that the deposited films are found to be cubic structure with preferential orientation along (111) plane. Optical absorption measurements were used to estimate the band gap value of CuS thin films deposited at different bath temperatures. Surface morphology and film composition was analyzed using an energy dispersive x-ray analysis (EDAX) set up attached with scanning electron microscope (SEM), respectively. The experimental observations are discussed in detail.*

Keywords: Copper sulphide; surface morphology; optical properties.

1. INTRODUCTION

Metal chalcogenides have received much interest, because of their various applications in electrical and optical devices, solar cells, cathode materials in lithium rechargeable batteries and photoelectrochemical cells [1-5]. Copper sulphides are considered as important semiconductors exhibit metallic conductivity and it transform in to a super conductor at 1.6 K [6]. Copper sulphide systems are widely used in solar cells, solar control and solar absorber coatings [7-10]. Thin films of CuS are usually crystallized in cubic structure (PDF-89-2073) with lattice constant (a.=5.387 Å) and in the hexagonal structure (PDF-78-2391) with lattice constants (a=3.796 Å, c= 16.360 Å). Several methods have been used for the preparation of copper sulphide thin films such as chemical vapor deposition (CVD) [11], ultrasonic spray pyrolysis [12], chemical bath deposition (CBD) [13], reactive evaporation [14] and RF sputtering [15]. Among these methods, electrodeposition has emerged as a simple, economical and viable technique to synthesize good quality films for device applications. The attractive features of this method .are: convenience for producing large area devices, low temperature growth, and the possibility to control the film thickness and morphology by readily adjusting the electrical parameters as well as the composition of the electrolytic solution [16-17]. Schimmei and Wendt have reported the preparation and characterization of Cu_2S thin films deposited on Cu substrates by galvanostatic electrodeposition [18]. de Tacconi et al prepared Cu_2S thin films on Cu substrates by potentiostatic electrodeposition technique [19]. Engleken and McCloud [20] have prepared copper sulphide thin films on various substrates such as nickel, tin, titanium, tin oxide and indium doped tin oxide and studied their properties by x-ray diffraction, x-ray microprobe analysis, scanning electron microscopy and optical absorption techniques, respectively. Limited works are available concerning the growth and characterization of CuS thin films by electrochemical route. To the best of our knowledge no report is available for studying the effects of bath temperature and deposition potential on electrodeposited CuS thin films prepared on indium doped tin oxide coated conducting glass (ITO) substrates. Hence, we decided to prepare CuS thin films on ITO substrates at various bath temperatures and deposition potentials and to study their properties.

In the present study, we describe the preparation of CuS thin films on indium doped tin oxide coated conducting glass substrates at various bath temperatures and deposition potentials. The deposited films are characterized by x-ray diffraction, scanning electron microscopy, energy dispersive x-ray analysis and optical absorption techniques, respectively. The effects of bath temperature and deposition potential on their structural, morphological, composi-

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*To whom correspondence should be addressed: Email: maha51@rediffmail.com tional and optical properties of the films are studied and discussed.

2. EXPERIMENTAL DETAILS

All the chemicals used in this work were of analytical grade reagents (99 % purity, E-Merck). Thin films of CuS were deposited onto indium doped tin oxide coated conducting glass substrates from an aqueous acidic bath containing 0.1 M $CuSO_4$, 0.01 M $Na_2S_2O_3$ and 0.05 M EDTA as complexing agent. Prior to deposition, ITO substrates were cleaned with acetone, methanol and then rinsed with double distilled water. All the depositions were carried out cathodically using a scanning potentiostat (EG & G, Model 362, Princeton Applied Research, USA). The depositions were performed in a conventional three electrode system comprising of graphite plate as counter electrode, ITO substrate as working electrode and saturated calomel electrode as reference electrode, respectively. During deposition, the electrolytic bath was stirred slowly using a magnetic stirrer cum heater set up. The reference electrode was introduced into the solution by luggin capillary arrangement whose tip was placed as close as possible to the working electrode. The electrolytic processes were monitored by cyclic voltammetry and governed potentiostatically. In cyclic voltammetric study, the same working electrode was used with constant potential plating. From cyclic voltammetry, the deposition potential was fixed as -500 mV versus SCE. The plating experiments were carried out at various bath temperatures from 45 to 90 ºC with different intervals of time. The pH of the electrolytic bath was maintained at 3.0 ± 0.1. The deposition potential was varied in the range between -300 and -700 mV versus SCE.

The film thickness was measured using stylus profilometer (Mitutoyo SJ-301, USA). The electrochemical behaviour of CuS films were determined using cyclic voltammetry. The deposited films were characterized using x-ray diffraction (X'PERT PRO PANalytical, Netherlands) using CuK_α radiation with λ=0.15418 nm. Surface morphology and film composition were analyzed using an energy dispersive x-ray analysis (EDAX) set up attached with scanning electron microscopy (SEM), respectively (Philips Xl 30). Optical measurements of the deposited films were carried out using UV-Vis-NIR spectrophotometer (HR-2000, M/S Ocean Optics, USA).

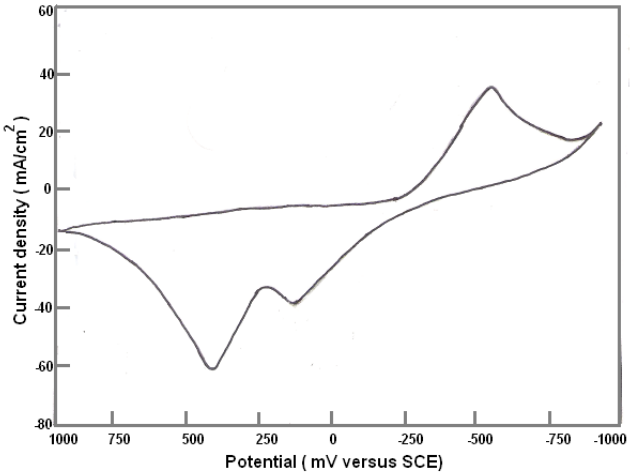

Figure 1. Cyclic voltammogram of ITO substrates containing 0.1 M $CuSO_4$, 0.01 M Na2S2O3 and 0.05 M EDTA. solution pH : 3.0.

3. RESULTS AND DISCUSSION

3.1. Cyclic Voltammetric studies

Cyclic voltammetry is a powerful analytical tool for studying the behaviour of electrochemical depositions. Cyclic voltammetric studies were carried out in a standard three electrode cell using a potentiostat and a data acquisition system. The cyclic voltammetric studies were performed using an aqueous solution mixture consist of 0.1 M $CuSO_4$ and 0.01 M $Na_2S_2O_3$ in presence of 0.05 M EDTA as complexing agent. The scan rate was 20 mV/sec in a three electrode system comprising ITO substrates as a working, a graphite rod as a counter electrode and a SCE as the reference electrode. Typical cyclic voltammogram of CuS thin films coated on ITO substrates is shown in Fig. 1. It is observed from Fig. 1, that the cathodic current increases gradually upto -250 mV versus SCE, beyond -250 mV versus SCE it increases rapidly upto -520 mV versus SCE. The strong peak at -520 mV versus SCE indicates the Cu(II) reduction process suggesting deposition at the electrode can be written as

$$Cu^{2+} + 2e^- \rightarrow Cu$$

$$S + 2e^- \rightarrow S^{2-}$$

$$Cu + S + 2e^- \rightarrow CuS$$

A small wave at -400 mV versus SCE may be associated with the reduction of S^{2-} ion followed by hydrogen evolution in acidic environment. The deposition reaction is reconfirmed by the reverse scan. The two stripping peaks at 225 and 430 mV versus SCE indicate the oxidation of the copper compound.

3.2. Film thickness

The electrodeposition of CuS thin films was controlled by two independent variables such as (i) film thickness and its uniformity (ii) surface morphology. Thickness of the deposited films was estimated using stylus profilometer. The average thickness of deposited layers can be directly controlled by controlling the plating current and the plating time. During deposition, it was observed that at higher bath temperatures (above 75ºC) the film formation is

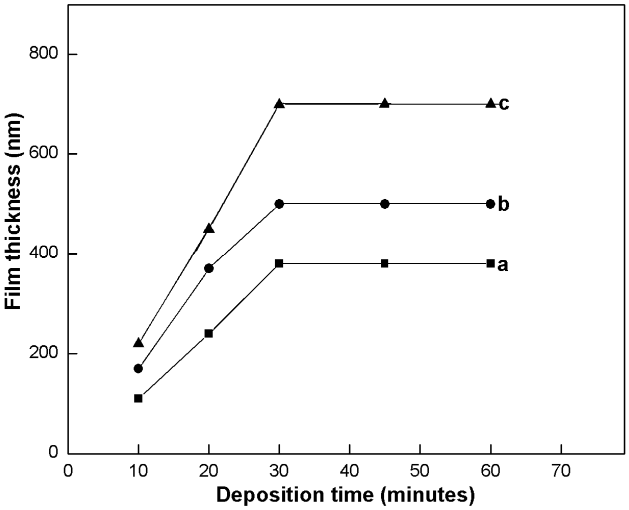

Figure 2. Variation of film thickness with deposition time for CuS thin films electrodeposited at various bath temperatures (a) 45ºC, (b) 60ºC (c) 75ºC.

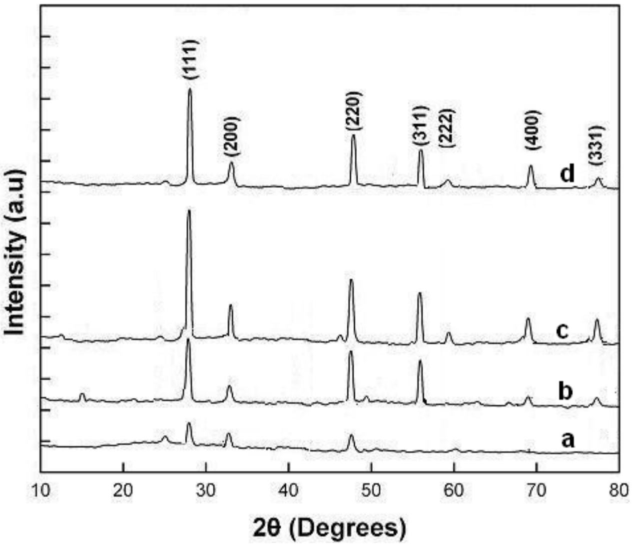

Figure 3. X-ray diffraction patterns of CuS thin films electrodeposited at various bath temperatures (a) 45ºC (b) 60ºC, (c) 75ºC, (d) 90ºC.

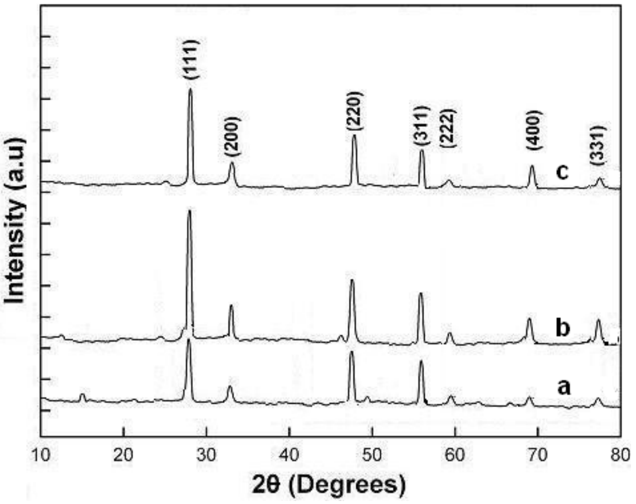

Figure 4. X-ray diffraction patterns of CuS thin films electrodeposited at different deposition potentials (a) -300 , (b) -500 , (c) -700 mV versus SCE.

hindered due to hydrogen evolution. At lower bath temperatures (below 50ºC) an irregular growth with rough surface was obtained. Fig. 2. a, b, c shows the variation of film thickness with deposition time for films deposited at various bath temperatures from 45 to 75ºC. It is observed from Fig. 2 that the film thickness increases linearly with deposition time and tend to attain saturation. The bath temperature is expected to influence the deposition rate by: (i) increase of precursor solubility and (ii) increase of the diffusion coefficient and the decrease of viscosity. Due to the increase in solubility of $Na_2S_2O_3$ with bath temperature, higher thicknesses were obtained for films deposited at higher bath temperature such as 75ºC. It could be observed from Fig. 2 that maximum film thickness of CuS was obtained from a single deposition within 30 minutes for bath temperature of 75ºC. Further, at lower pH (3.0±0.1), free sulphur was deposited and at comparatively higher pH (4.0±0.1), the solution became cloudy due to the precipitation of $Na_2S_2O_3$. Increasing the sulphur ion concentration in the solution by adding $Na_2S_2O_3$ is limited by the solubility of $Na_2S_2O_3$ at a given pH and bath temperature . Since, sulphur is less electropositive than copper, the S could be more likely to deposit as the element from its ions in an electrolytic bath than Cu from its ions. Hence, a very low concentration of S in the electrolytic bath must be maintained compared to Cu ions.

3.3. Structural studies

3.3.1. Effect of bath temperature

X-ray diffraction patterns recorded for the electrodeposited CuS thin films on ITO substrates with bath composition of 0.1 M $CuSO_4$, 0.01 M $Na_2S_2O_3$ and 0.05 M EDTA at various bath temperatures from 45 to 90ºC are as shown in Fig. 3. a, b, c, d. The XRD patterns revealed that the deposited films are found to be polycrystalline in nature with cubic structure with lattice constant (a=5.387 Å). The diffraction peaks of CuS are observed at 2θ values of 28.68, 33.24, 47.72, 56.65, 59.40, 69.81, 77.16 corresponding to the lattices planes(111),(200),(220),(311),(222),(400)and(331), respectively. The different peaks in the diffractograms were indexed and the corresponding values of interplanar spacing "d" were calculated and compared with standard values [21]. The bath temperature affects the nature of the films and higher temperatures are required to obtained good quality films. CuS thin films deposited at bath temperature below 50ºC are found to be poorly crystallized indicated by broad XRD peaks shown in Fig. 3a. However these peaks started to increase while increasing bath temperature above 45ºC indicate the presence of crystalline nature of the films . It is found that higher deposition temperature led to the formation of well crystallized films. It is observed from Fig. 3c higher deposition temperature resulted in good quality films with improved crystallinity as evidenced by intense diffraction peaks indicated in Fig. 3c. CuS thin films deposited at 75ºC is found to be well crystalline in nature. At bath temperature above 75ºC, the current densities are found to be higher. These higher current densities led to the formation of films with rough surface and poor adhesion. The film thickness increases linearly with bath temperature and it is obvious that the bath temperature affects the rate of release of ions. The height of (111) peak in x-ray diffraction pattern for CuS thin films deposited at higher bath temperature(75ºC) has shown sharper peaks and small FWHM data resulted in the enhancement of crystallite size in the deposited films at higher bath temperatures. Similar behaviour exhibited for ZnHgTe thin films have been reported earlier [22].

Effect of deposition potential

X-ray diffraction patterns recorded for the electrodeposited CuS thin films on ITO substrates with bath composition of 0.1 M $CuSO_4$, 0.01 M $Na_2S_2O_3$ and 0.05 M EDTA at three different deposition potentials are as shown in Fig.4. a, b, c. The patterns revealed that the films prepared at different deposition potential exhibit cubic structure with lattice constant (a=5.387 Å) with a preferential orientation along (111) plane. All the peak intensities are found to increase when the deposition potential decrease down to -500 mV versus SCE, thereafter it slightly decreases. The XRD peaks are

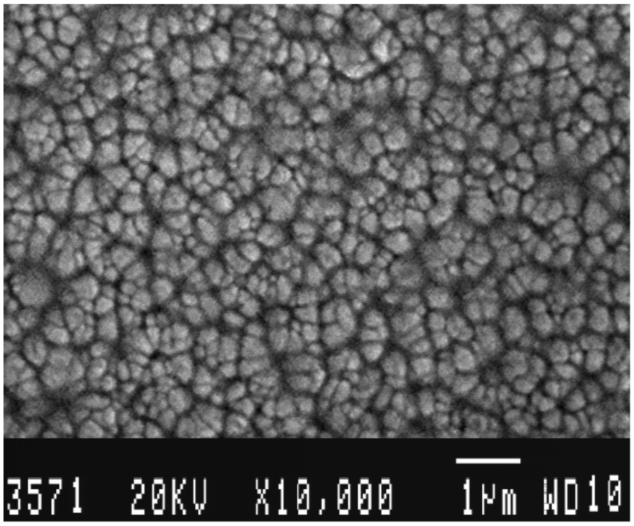

Figure 5. SEM picture of CuS thin films deposited at bath temperature of 75ºC and at a deposition potential of -500 mV versus SCE.

sharpened and more intense at a deposition potential of -500 mV versus SCE indicating the formation of polycrystalline morphology of good quality films. No peaks corresponding to other impurities such as Cu or S can be detected. The best stoichiometry of the films was obtained at a deposition potential closer to -500 mV versus SCE. This study shows that the deposition potential does not change the structural phase of CuS films. However, an increase in crystallinity of the films with deposition potential upto -700 mV versus SCE is indicated. Hence, the deposition potential is fixed as -500 mV versus SCE to deposit CuS films for further studies. Similar behaviour is noted for $FeSe_2$ thin films have been reported earlier [16]. The crystallite size of the deposited films were calculated using FWHM data and Debye-Scherrer formula [17].

$$P = 0.9\ \lambda/\beta\ \mathrm{Cos}\ \theta_B$$

where λ is the wavelength of CuK_α target used (λ=1.5418 Å), β is the Full Width at Half Maximum of the peak in radians, θ_B is the Bragg's diffraction angle at peak position in degrees. The crystallite sizes of the films obtained in this work is found to be in the range between 28 and 49 nm .

3.4. Morphological and Compositional analysis

The scanning electron micrograph of a typical CuS thin film electrodeposited on ITO substrates with 0.1 M $CuSO_4$, 0.01 M $Na_2S_2O_3$ and 0.05 M EDTA at bath temperature and deposition potential of 70ºC and -500 mV versus SCE is shown in Fig. 5. It is observed from Fig. 5 that the films deposited at bath temperature of 75ºC composed of uniform size spherically shaped grains which are closely packed together. The grains are well covered the substrates without any cracks and voids. The sizes of the grains are found to be in the range between 0.18 and 0.72 µm. The average size of the grains is found to be 0.38 µm.

The quantitative analysis of CuS electrodeposits was performed with an aim to determine the relationship between different bath temperatures and film composition. After etching the film surface, a quantitative determination of CuS electrodeposits was made by an energy dispersive analysis of x-rays which revealed the following composition (in atomic %) : Cu (39.22); S (60.78) for a film deposited at 45 ºC, Cu(41.14);S (58.86) for a film deposited at 60ºC , Cu(45.34);S(54.66) for a film deposited at 75ºC and Cu(43.31); S(56.69) for a film deposited at 90ºC. The EDAX results revealed that the content of Cu increases and the content of S decreases while increasing bath temperature from 45 to 75ºC, thereafter the content of Cu slightly decreases. This observation is also evidenced by the improvement of CuS phase in the deposition bath. The stoichiometric films of good quality are obtained at a bath temperature of 75ºC. Typical EDAX spectrum of CuS thin films electrodeposited at bath temperature of 75ºC is shown in Fig. 6. This result is consistent with x-ray diffraction analysis (i.e) the sample phase is CuS.

3.5. Optical properties

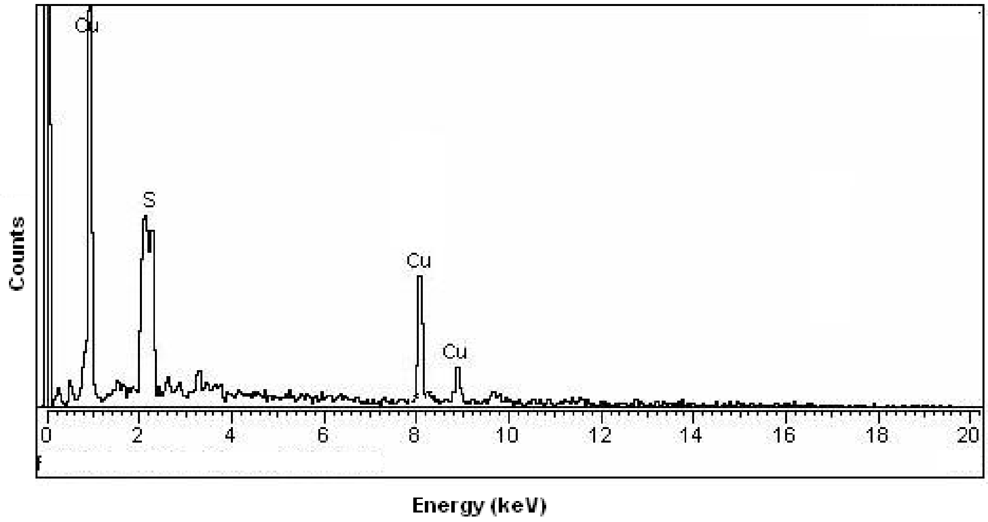

Figure 6. EDAX spectrum of CuS thin film deposited at bath temperature of 75ºC and at deposition potential of -500 mV versus SCE.

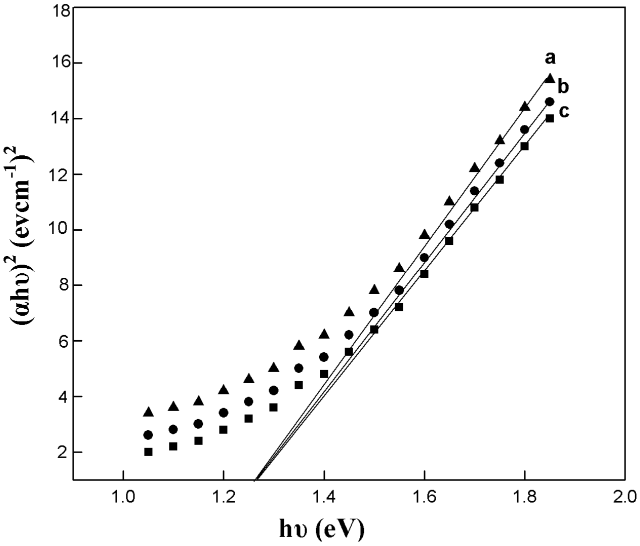

Figure 7. $(\alpha h\upsilon)^2$ versus hυ plot for CuS thin film electrodeposited at various bath temperatures (a) 45ºC, (b) 60ºC (c) 75ºC.

The optical absorption of CuS thin films has been studied without accounting for reflection and transmission losses. The optical band gap E_g is determined from the following relation [16].

$$(\alpha h\nu) = A (h\nu-E_g)^n$$

where A is the constant, hν is the incident photon energy, α is the absorption coefficient and n is an exponent that determines the optical absorption process. For allowed direct transition n=1/2, for direct forbidden transition n =3/2 for indirect indirect allowed transition n=2 and finally for direct forbidden transition n=3. In this case, the value of absorption coefficient is in the order of 10^{-4}cm^{-1} which supports the direct bandgap nature of material. The optical absorption data is used to plot a graph of $(\alpha h\nu)^2$ versus hν (Tauc's plot) where α is the optical absorption coefficient and hν is the photon energy. The plot is linear indicating the presence of direct transition. Extrapolation of the (Fig. 7) plot to the x-axis gives the band gap energy of CuS films deposited 45ºC, 60ºC and 75ºC . The band gap value of CuS films deposited at 75ºC is found to be 1.26 eV. This result is in closed agreement with the value reported earlier [23].

4. CONCLUSIONS

Cathodic deposition of semiconducting CuS thin films onto ITO substrates have been carried out potentiostatically under various bath temperatures and deposition potentials. Cyclic voltammetric studies were carried out to understand the deposition behaviour and fix the deposition potential for the preparation of CuS thin films in the potential range between -1000 mV to 1000 mV versus SCE. X-ray diffraction study shows the formation of polycrystalline CuS films with preferential orientation along (111) plane. EDAX results shows that stoichiometric films of good quality are obtained at a bath temperature of 75 ºC. Optical absorption measurements indicate that the deposited films of CuS have a direct band gap of 1.26 eV which in turn confirms the well-crystalline nature of CuS thin films.

5. ACKNOWLEDGEMENT

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