Characterization of Nanostructured CuS Thin Films Grown by Successive Ionic Layer Adsorption and Reaction (SILAR) Method

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ABSTRACT

A Successive Ionic Layered Adsorption Reaction technique (SILAR) has been used to deposit CuS thin films on glass substrates at room temperature using cupric sulphate as cationic and sodium sulphide as anionic precursor .

In order to study size-dependent optical, structural and electrical properties, films of different thickness were prepared by varying SILAR deposition cycles from 30 to 110. The XRD studies showed that films are nanocrystalline in nature with hexagonal structure. Band gap energy and electrical activation energy of SILAR grown CuS decreases when film thickness increases. The thermo-emf measurements confirmed that the films prepared are semiconducting in nature with P-type conductivity.

Keywords: Thin film, CuS, SILAR method, Electrical properties.

INTRODUCTION

In recent years, the various size-dependent physical and chemical properties of nanomaterials have been generating a continuous thrust for new technological applications [1]. In this regard, especially many chalcogenides such as CuS, ZnS, CdS, NiS, MnS, CoS, etc. from transition metal group have been extensively studied due to their excellent physical and chemical properties [2-5]. Out of these chalcogenides, Copper sulfide is an important material from the point of view of fundamental research as it is economic and low resistive. CuS has a wide range of well-established and prospective application such as photothermal conversion application [6,7] photovoltaic application [8,9] electroconductive electrode [10,11] microwave shielding coating and solar control coatings [12]. In addition, it is a promising material with potential application in Lithium-ion rechargeable batteries [13], gas sensors [14], photovoltaic applications [15] and catalysts [16].

Because of the effect of the 3*d* electrons, this copper sulphide transition-metal compound has the ability to form various stoichiometries, of which at least five viz Covellite (CuS), Anilite ($Cu_{1.75}S$), Digenite ($Cu_{1.8}S$), Djurleite ($Cu_{1.95}S$) and Chalcocite (Cu_2S) [17,18] are stable at room temperature. It is interesting that these distinct compositions are not responsible for the change in crystalline structure but shows significant variation in the electrical resistivity and optical band gap energy.

As per several chemical and physical techniques have been utilized to prepare different investigated to prepare different phases of CuS. In order to obtain the desirably structured material, various ways have been developed: chemical vapor deposition [19], electrochemical methods [20], solid state reactions [21], ultrasonic spray pyrolysis [22], chemical bath deposition [23], reactive evaporation [24], RF sputtering [25], etc. Even though physical techniques are more

suitable for the growth of uniform and high-quality films, they are expensive and require more efforts and hence chemical method becomes important.

Sagade and Sharma have used solution growth technique to deposit CuS thin films onto glass substrates at room temperature and studied their physicochemical properties [26]. Lindroos, et al. have prepared copper sulfide thin films by successive ionic layer adsorption and reaction method (SILAR) at room temperature [27]. Fatas, et al. have used $CuSO_4$ and thiourea in an alkaline medium to deposit Cu_xS thin films by chemical method [28]. They reported that optical band gap and resistivity of the film is of the order of 2.58 eV and 3×10^{-3} Ωcm, respectively. Gadgil, et al. prepared Cu_2S films onto glass and aluminum substrates using the flash evaporation technique [29]. The film deposited onto aluminum showed the higher value of solar absorptance with a thermal emittance 21 of 0.20. Thermal emittance of the film increased as the temperature increases from 100 to 250°C. Films coated on glass substrates show low values of thermal emittance, thereby indicating the presence of intrinsic selective properties. The films deposited on glass possess excellent conducting properties. In the present work, we have tried to develop a low-cost SILAR technique to grow good quality nanocrystalline CuS thin films at room temperature. The various deposition parameters are optimized as half part of the work. In the second part, various size-dependent properties are studied and reported.

EXPERIMENTAL

In SILAR method, to grow nanocrystalline thin film substrate is immersed repeatedly into separately placed cationic and anionic precursor alternately. To remove loosely bound species, after each precursor immersion, the substrate is rinsed in de-ionized water. The glass micro slides of size $75 \times 25 \times 2$ mm were used as substrates for the present work. Before actual deposition cleaning of the substrate is very important as it affects the growth mechanism. Initially, the slides were washed with liquid detergent, then boiled in concentrate chromic acid for 2 hours, and then kept in it for the next 48 hours. The substrates washed with double distilled water were then cleaned in an ultrasonic cleaner for 10 min. Finally, the substrates were dried using AR grade acetone and kept in dust free storage container. One SILAR deposition cycle involves 4 steps:

1. Immersion of substrate into the cationic precursor, 0.05 M $CuSO_4$ for 10 S where Cu^{2+} ions are adsorbed onto the substrate surface

2. Rinsing of the substrate with double distilled water for 10 S to remove loosely bonded Cu^{2+} ions from the substrate

3. Immersion of substrate into anionic precursor 0.01 M Sodium sulfide, 10 S where S^{2-} ions react with Cu^{2+} to form CuS layer

4. Rinsing of the substrate with double distilled water for 10 S to remove unreacted or excess species from the substrate

This completes one SILAR cycle of CuS deposition. The color of as grown CuS film has changed from faint brown to dark brown as deposition cycles increases from 30 to 110. After 90 cycles film starts to peel off. By taking several trials the deposition parameters were optimized to get good quality adhesive films. The optimized preparative parameters for the synthesis of CuS thin films are tabulated in Table 1.

Deposition Parameters	Cationic Precursor	Anionic Precursor
Precursor	$CuSO_4$	Na_2S
Concentration (M)	0.05	0.01
pH	5	12
Immersion time (S)	10	10
Rinsing Time (S)	10	10
Volume of Precursor (mL)	80	80
Temperature (K)	303	303

**Table 1:** Optimized deposition parameters for CuS thin film.

In the present work, the thickness of the film was measured by gravimetric weight difference method using the relation,

$$t = \frac{m}{\rho * A} \qquad (1)$$

Where 'm' is the mass of the film deposited on the substrate in gm, 'A' is the area of the deposited film in cm^2 and ρ is the density of the CuS in bulk form. The crystal structure of the deposited film was identified by normal and grazing incidence X-ray diffraction analysis with Xpert PRO PAN analytical diffractometer. The film morphology was studied by using Field Emission Scanning Electron Microscope. The optical absorption of CuS thin films was studied in the wavelength range of 350 to 900 nm by using The D.C two-point probe method was employed to understand the variation of electrical resistivity of CuS with temperature. The thermoelectric power measurement was used to determine the type of conductivity.

RESULTS AND DISCUSSION

In SILAR technique glass substrate was immersed alternately into separately placed cationic and anionic precursors. When the glass substrate was immersed in the cationic precursor, Cu^{2+} ions get adsorbed on the substrate due to attractive forces between ions in the solution and that of the surface of the substrate. These forces may be cohesive or van der Waals or chemical attractive [30]. After rinsing in deionized water for 10 S, the glass substrate was then immersed in the Na_2S precursor, where HS^-, S^{2-}, OH^- and Na^+ ions were diffused from the solution in the diffusion layer towards solid solution interface until their concentration in the diffusion that of in bath. The HS^- and S^{2-} enter into the outer Helmholtz layer and reacts with the adsorbed Cu^{2+} to form a monolayer of CuS. This completes one deposition cycle, the overall reaction can be written as,

$$Cu^{2+}_{aq} + SO^{2-}_{4aq} + 2Na^+_{aq} + S^{2-}_{aq} \rightarrow CuS + 2Na^+_{aq} + SO^{2-}_{4aq} \qquad (2)$$
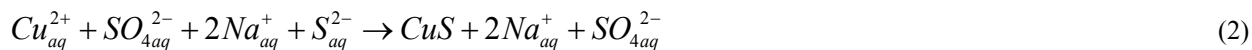
It is observed that for 30 SILAR cycles CuS film has 170 nm thickness, the average growth rate increases up to 8.54 nm/cycle and then again decreases as SILAR cycles were increased from 30 to 110. It may be because the number of nucleation cites on substrate surface increases with cycles and becomes maximum up to 70 cycles. Above that, the excess material from the substrate starts to peel off in the solution giving less thickness. Table 2 shows a variation of CuS film thickness and growth rate with a number of deposition cycles.

No. of SILAR Cycles	Thickness(nm)	Growth rate (Cycles/nm)
30	170	5.66
50	320	6.4
70	598	8.54
90	399	4.43
110	310	2.81

Table 2: Variation of growth rate and thickness.

Figure 1 shows the XRD pattern of as-deposited CuS thin films synthesized by Successive Ionic Layered Adsorption Reaction techniques. The observed diffraction peaks revealed the deposited material belongs to hexagonal CuS phase (Table 3). Also, it is observed that no other diffraction peak due to impurity is identified. This means that pure covellite CuS thin films have been synthesized by using SILAR deposition technique.The average crystallite size of CuS was evaluated using the Scherrer's formula [28].
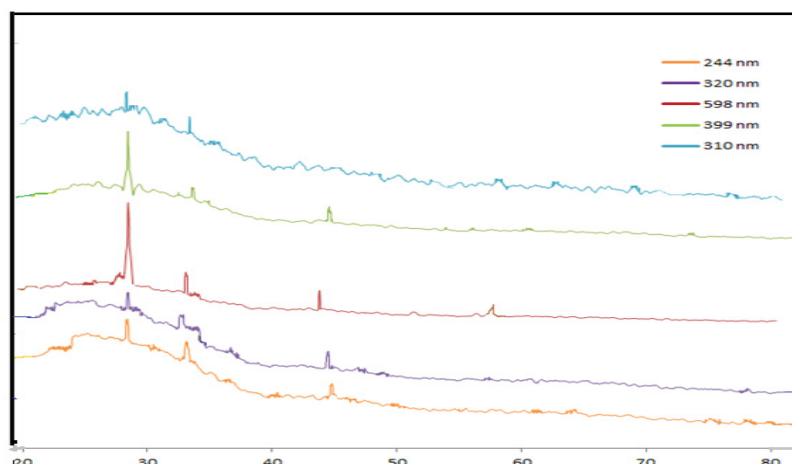
$$D = \frac{K\lambda}{\beta Cos\theta} \qquad (3)$$

Figure 1: XRD Patterns of CuS films.

| Film thickness	Standard 2θ (degree)	Observed 2θ value (degree)	hkl
A (170 nm)	27.768	27.38	101
	32.9	32.123	6
	43.035	43.819	106
B (320 nm)	27.768	27.92	101
	32.9	32.177	6
	43.035	43.035	106
C (598 nm)	27.768	27.123	101
	32.9	32.015	6
	43.035	43.46	106
	59.175	59.927	116
D (399 nm)	27.768	27.109	101
	32.9	32.224	6
	43.035	43.083	106
E (310 nm)	27.768	27.89	101
	32.9	32.211	6

Table 3: Comparison of observed and standard XRD data of CuS thin films, JCPDS Cards: 03-0724 of CuS.

The structural investigation is carried out from X-ray diffractograms taken between 2θ angle from 20 to 80 degree. The crystallite size of CuS increases with film thickness (Table 4).

Thickness (nm)	Crystallite Size (nm)
170	26.94
320	28.1
598	41.3
399	34.5
310	26.9

**Table 4:** Variation of grain size with a film thickness of CuS.

The surface morphological studies of CuS were carried out from FE-SEM images (Figure 2). From SEM analysis, it is observed that the as-deposited CuS thin film is homogeneous and well covers to the glass substrate. Small nanosized grains are uniformly distributed showing smooth surface. This clearly indicates the nanocrystalline nature of the film, however, the improvement in crystallite size with film thickness is observed. The grains are very small and have unequal circular size and shape. Above 598 nm the film surface starts to become quite rough. It may be because above this thickness film starts to peel off into the precursor solution leaving some most adhesive portion of material as it is. As a result above 598 nm thickness, development of patch-like structure is observed.
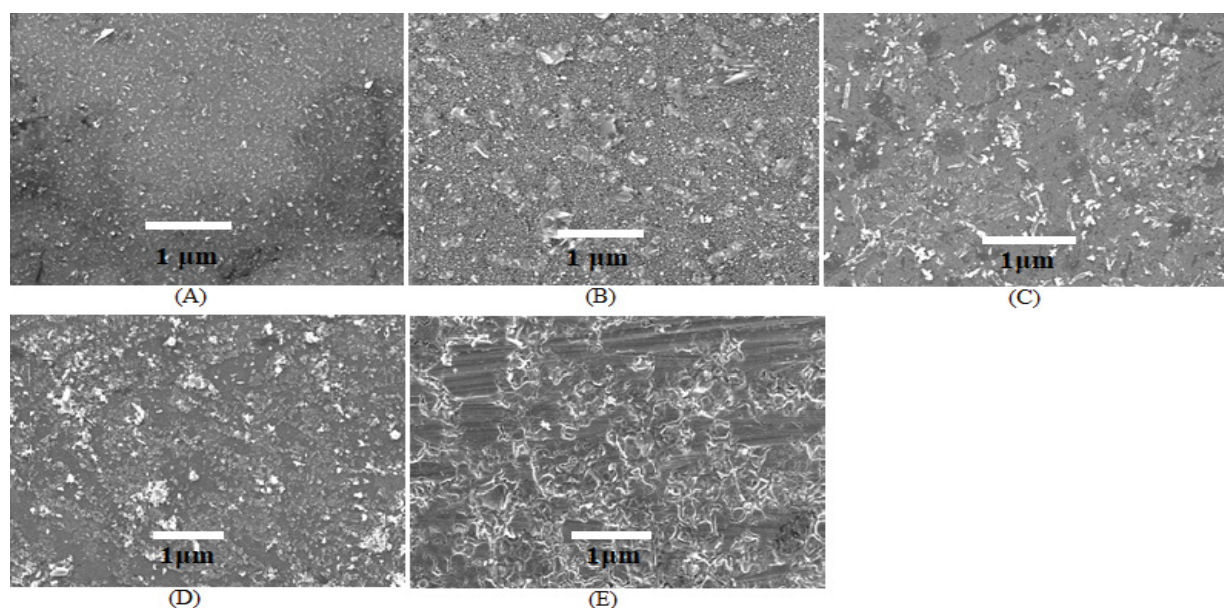
m of thickness (A) 170 nm, (B) 320 nm, (C) 598nm, (D) 399 nm and (E) 310 nm.

The Optical absorption studies were carried out to estimate band gap energy of deposited material. Figure 3 shows the variation of optical density with wavelength for CuS thin films deposited by varying no of SILAR cycles. The absorption spectrum shows high absorbance in the visible region. The nature of the transition (direct or indirect) is determined via the relation,

$$\alpha = \frac{A\left(h\nu - Eg\right)^{n}}{h\nu} \tag{4}$$
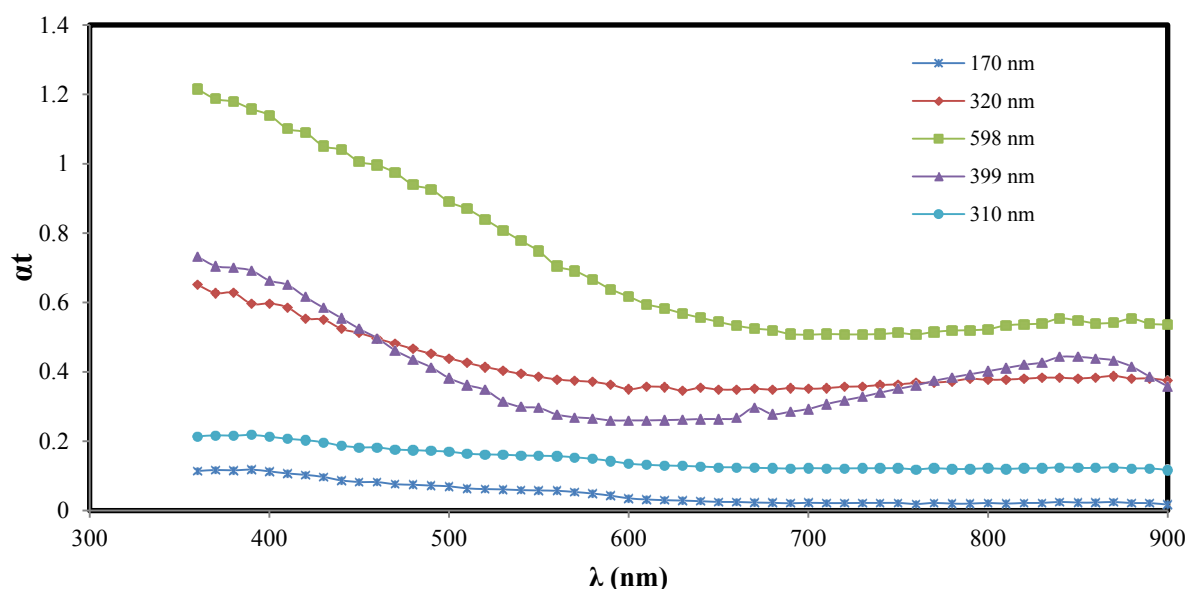
Figure 3: Plots of optical absorption versus wavelength of CuS thin film.

Where $h\nu$ is the photon energy, Eg is the band gap energy, and A and n are constants. For allowed direct transitions $n=1/2$; for allowed indirect transitions $n=2$.

Figure 4 shows the plots of $(\alpha h\nu)^{2}$ versus $h\nu$ for CuS films of various thicknesses. It is observed that the optical band

gap energy of CuS decreases from 2.5 eV to 2 eV as thickness increases from 170 nm to 598 nm and then again increases to 2.4 eV as film thickness decreases as film peel off into the precursor.
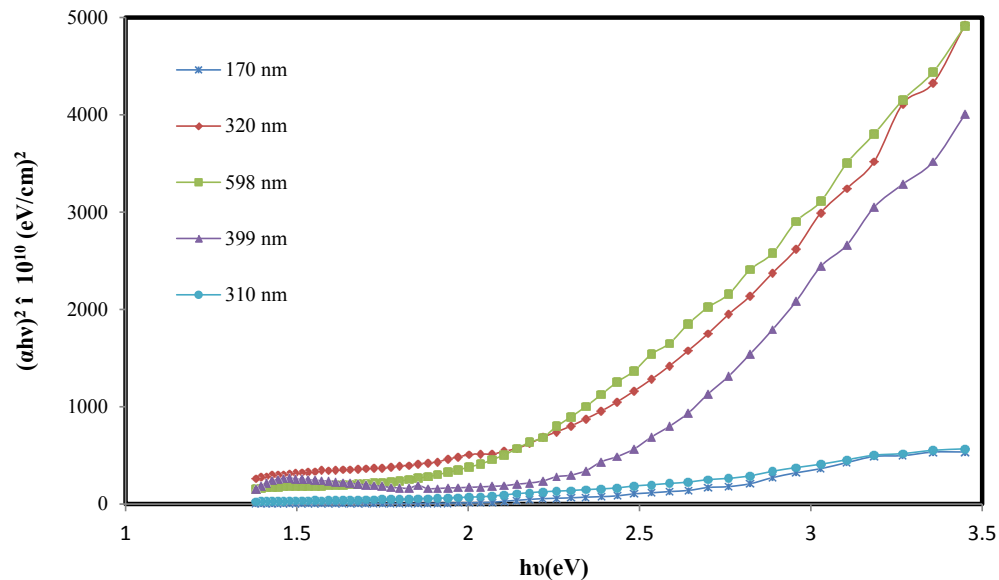
Figure 4: Comparison of Plots of ($\alpha h\upsilon$) 2 Vs *hυ* for CuS thin films.

The electrical resistivity measurements showed that SILAR grown CuS films are semiconducting in nature. Figure 5 shows the variation of log ρ with reciprocal of temperature. It is also observed that the resistivity of CuS decreases with increases in film thickness which may be due to improvement in crystallinity of the films. The thermal activation energy 'Ea' was calculated by using relation,

$$\rho = \rho_o \exp\left(\frac{-Ea}{KT}\right) \tag{5}$$
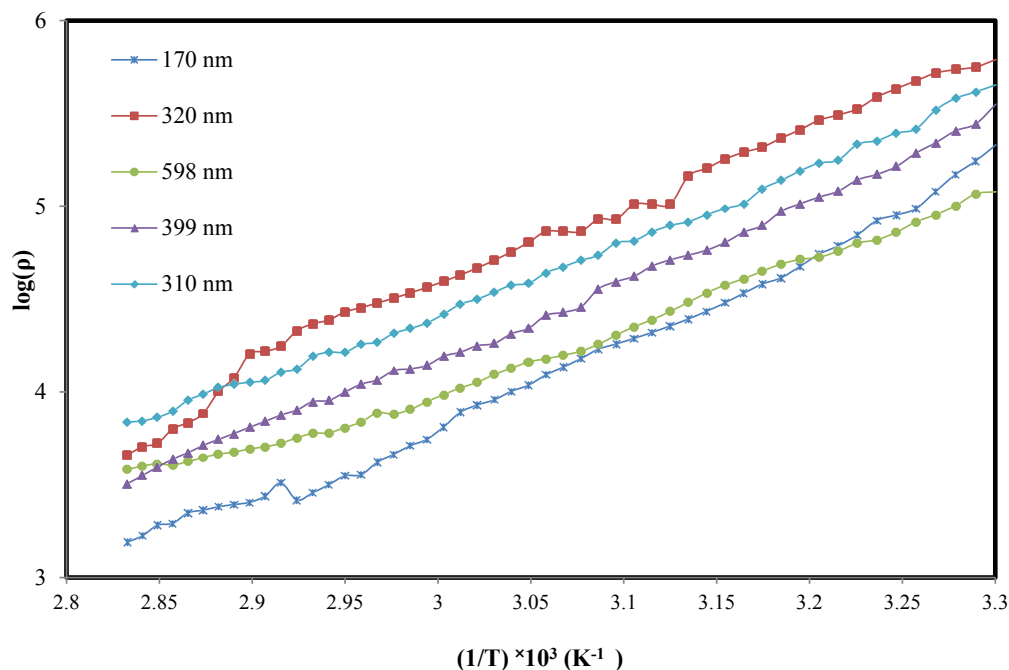
Figure 5: The Variation of log (ρ) with reciprocal of temperature (10^3/T) of CuS thin film.

Where, ρ_o is a parameter depending on the sample characteristics (thickness, structure etc.), Ea denotes the thermal activation energy of electrical conduction, K is Boltzmann's constant and T is absolute temperature. The activation energy is of the order of 0.84 eV for the film deposited at 30 SILAR cycles and it decreases to 0.64 eV as film thickness becomes 598 nm again it increases as the film starts to peel off.

In order to investigate the type of conductivity, the thermoelectric power measurement was used to determine the type of conductivity. The temperature difference between the two ends of the sample causes transport of carriers from the hot to the cold end, thus creating an electric field, which shows thermo-emf across the ends of the sample. The thermo-emf generated is directly proportional to the temperature gradient maintained across the semiconductor ends as well as to the film thickness. The type of conductivity was decided from the sign of the emf generated at the cold and hot end. In the present work, CuS thin films grown by SILAR shows P-type conduction mechanism (Figure 6). The film of thickness 598 nm shows maximum thermal emf as that of other films which may be due to improved crystalline quality of deposited material and its porous morphology.
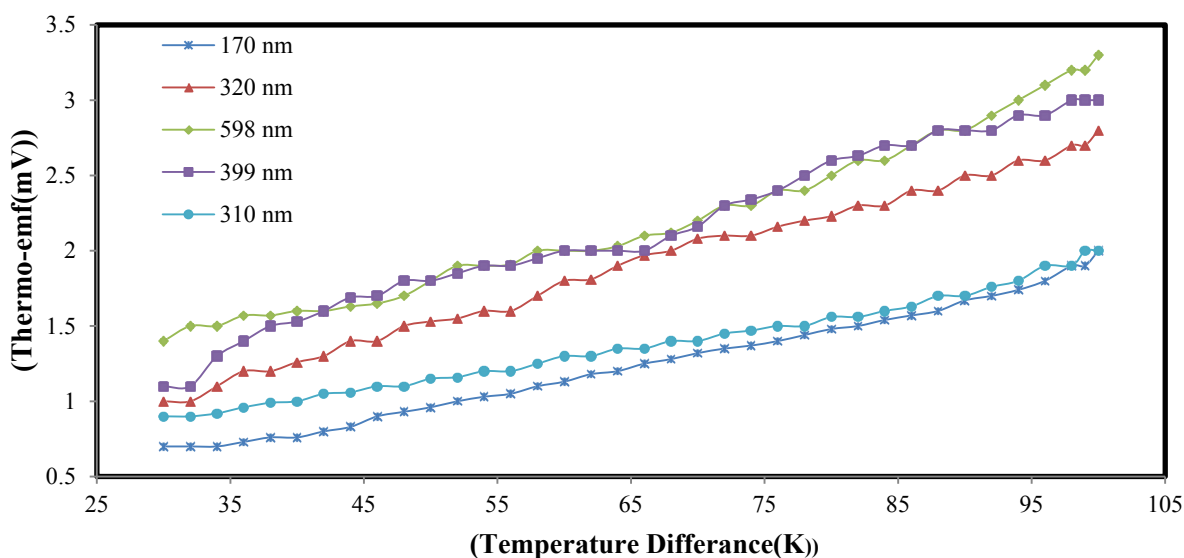
Figure 6: Variation of thermo emf with a temperature difference of CuS thin film.

CONCLUSION

Deposition parameters of simple and economic SILAR method are optimized to grow nanocrystalline hexagonal CuS film. The results of XRD and SEM show that the deposited CuS film consists of nano-sized grains and the grain size increases with increasing film thickness. The optical band gap energy varies from 2 to 2.5 eV depending upon thickness. The thermo-emf measurements confirmed the p-type nature of CuS. The electrical resistivity and therefore activation energy is also found to be thickness dependent.

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