The Effect of Complexing Reagent on Structural, Electrical and Optical Properties of CuS Thin Film

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Semiconducting CuS thin films were successfully prepared by Successive Ionic Layered Adsorption Reaction technique at room temperature with and without using complexing reagent viz. hydrazine hydrate ($H_6N_2O(N_2H_2)$), tri ethanol amine ($C_6H_{15}NO_3$) and ammonia (NH_3). The structural studies revealed that; the crystallinity of the film can be tailored by using complexing agent. The dc electrical resistivity measured in the temperature range 370 - 473 K confirmed its semiconducting nature of CuS and it varies depending on complexing reagent. The optical absorption measurements were studied in the wavelength range 350 - 950 nm. The thermo-emf measurements confirmed that the films prepared are semiconducting in nature with p-type conductivity.

Introduction

Recently nanotechnology has become an exciting interdisciplinary challenging research community. It is observed that by changing the particle size of a material one can tailor its properties The applications of such nanostructured materials in optoelectronic devices have been widely investigated in the last two decades, and its impact on both fundamental science and potential industrial application has been attracting tremendous interest, investment and effort in research and development around the world. In this regard, this rapid development in synthesis of nanostructured materials understanding of their dramatic physical and chemical properties has led them to enter the world market in a big way in every field. In development of semiconductor industry specially based on optoelctronic and photovoltaic devices, various metal chalcogenides and selenides play key role [1-9]. Out of these various chalcogenide and selenides, in the present work we have focused on CuS thin films as they process various types of applications such as gas sensors [10], supercapacitor [11], solar cells [12], solar filter [13]. Galdikas and Setkus et al. [14,15] reported application of CuS for detection of ethanol and acetone. Nien and chen [16] have deposited amorphous Cu_2S films on Si and glass substrates using a chemical bath deposition method. He et al. [17] have compared Cu_2S and CuS thin films and reported that CuS has higher carrier concentration (hole) of around 1022 cm^{-3} as a result it shows lower resistivity of about 10^{-4} Ω cm. Nagcu et al. [18] have reported that CuS films are conductive and photosensitive even at thicknesses < 0.05 urn. George and Joseph [19] studied the effect of temperature on structure of CuS deposited by reactive evaporation method and showed that amorphous CuS becomes crystalline deposited above 345 K. However CuS films prepared from chemical bath using tartaric acid as a

complexing reagent at room temperature is polycrystalline in nature, with hexagonal structure [20] Offiah et al. [21] have synthesized CuS thin films by solution bath technique and studied optical properties showed that the films annealed at 300 and 400°C exhibits very high transmittance and low reflectance as compared to as-deposited sample. Nair et al. [22] have prepared Cu_xS thin films from chemical bath constituted from copper (II) nitrate or chloride, NH_3 (aq), NaOH, triethanolamine and thiourea for application as solar control coatings and for architectural glazing. Anuar et al. [23] have deposited Cu_2S films by cathodic electro-deposition in the presence of ethylenediaminetetraacetate (EDTA) in aqueous solution on Ti substrates and reported that. In this paper, we present the synthesis of nanocrystalline CuS thin film and investigation of effect of complexing agent on growth process.

Table 1.1. Optimized deposition parameters for CuS thin film.

Deposition Parameters	Cationic Precursor	Anionic Precursor
Precursor	$CuSO_4$	Na_2S
Concentration (M)	0.05	0.01
Immersion time (S)	10	10
Rinsing Time (S)	10	10
Volume of Precursor(mL)	80	80
Temperature(K)	303	303
Deposition Cycles	60	60

Experimental

SILAR is a simple, inexpensive, low temperature versatile bottom up chemical method evolved recently to grow nanocrystalline thin films [24]. Most important is that, the instrumentation is required relatively simple and inexpensive as compared to physical methods. The cleaned

glass substrate is immersed for separately placed cationic and anionic precursors alternately to grow CuS films. Before actual deposition due care is taken to clean the glass substrate as it directly affects the adhesion of depositing material to the substrate [**25**]. The optimized preparative parameters for the synthesis of CuS thin films are tabulated in **Table 1.1**. For deposition of CuS thin film**,** 0.05 M cupric sulphate, $CuSO_4$ (SDFCL AR grade) were used as a cationic precursor and Na_2S (SDFCL AR grade) as anionic precursor. Various complexing reagents all are of SDFCL AR grade used to deposit CuS thin films are hydrazine hydrate ($H_6N_2O(N_2H_2)$), tri ethanol amine ($C_6H_{15}NO_3$) and ammonia (NH_3). The deposition scheme used to study effect of complexing reagent on physical properties of CuS is given in **Table 1.2**.

Table 1.2. Composition of Cationic Precursor.

Film No.	Complex Variation	pH	Thickness (nm)
(A) CuS without complex	80 mL, 0.05 M $CuSO_4$	6	430
(B) CuS with Hydrazine hydrate	79 mL 0.05 M $CuSO_4$ +1 mL, 1M $H_6N_2O(N_2H_2)$	7	261
(C) CuS with TEA	79 mL 0.05 M $CuSO_4$+ 1 mL, 1 M $C_6H_{15}NO_3$	8	274
(D) CuS with NH_3	79 mL 0.05 M $CuSO_4$ +1 mL, 1 M Nh_3	10	481

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

$$t = {}^m/_{\rho * A} \qquad (1)$$

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.

Results and discussion

For the deposition of CuS thin films, a well cleaned glass substrate is immersed in cationic precursor solution of $CuSO_4$ where Cu^{2+} and $SO_4{}^{2-}$ ions were adsorbed on the surface of the substrate. The substrate was rinsed in distilled water to remove loose Cu^{2+} and $SO_4{}^{2-}$ ions. The substrate was then immersed in an anionic precursor solution i.e. in the Na_2S solution, where HS^-, S^{2-}, OH^- and Na^+ ions diffuse from the anionic bath into the few surface layers of solid solution interface in order to balance the concentration in the diffusion layer with bath solution. As a result the HS^- and S^{2-} ions diffuse into the outer Helmoltz layer to react with Cu^{2+} to form CuS layer. This is followed by rinsing again in ion exchange water to remove Cu^{2+}, S^{2-} ions, unreacted and loosely bounded CuS material and other byproducts. This completes one deposition cycle for the deposition of CuS film. The overall reaction can be written as,
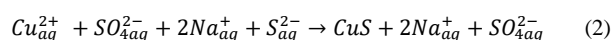
$$Cu_{aq}^{2+} + SO_{4aq}^{2-} + 2Na_{aq}^+ + S_{aq}^{2-} \rightarrow CuS + 2Na_{aq}^+ + SO_{4aq}^{2-} \qquad (2)$$

Table 1.3. Comparison of observed and standard XRD data of CuS thin films. JCPDS Cards: 75-2233 of CuS.

Film No	Standard 2θ (degree)	Observed 2θ value (degree)	hkl
(A) CuS without Complex	27.367	27.509	100
	44.716	44.42	008
(C) CuS with TEA	29.542	29.203	102
	56.474	56.864	200
(D) CuS with NH_3	29.542	29.261	102
	33.153	33.507	006
	56.474	56.826	200

Table 1.4. Variation of grain size with film thickness of CuS.

| Film No.	Thickness (nm)	Crystallite Size (nm)
(A) CuS without Complex	430	32
(B) CuS with Hydrazine hydrate	261	-
(B) CuS with TEA	274	61
(D) CuS with NH_3	481	53

When the value of ionic product overreach the solubility product film can be deposited on the substrate, otherwise it is precipitated out. The copper ions are usually complexed by a suitable complexing reagent, which would then slowly release copper ions throughout the reaction. The generation of cu-complex ion controls the rate formation of solid metal hydroxides which causes to the evolution of solid film. The complexing reagent should not be too weak or too strong in ordered to prevent bulk precipitation or to deposition of the desired film. This concentration is controlled by the formation of metal complex species given by the reaction.

$$X(Y)^{2+} \leftrightarrow X^2 + Y \qquad (3)$$

When TEA Complex was added in cationic precursor, copper sulphate is broken down by TEA to form a copper complex ion as,

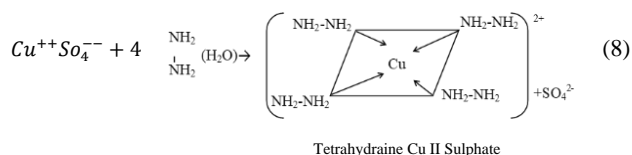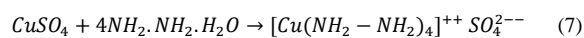$$Cu^{2+} + SO_4^{2-} + TEA \rightarrow Cu[TEA]^{+2} + SO_4^{2-} \qquad (4)$$
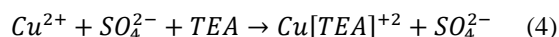
In reaction vessel i.e. in anionic precursor, metal complex TEA further breaks down to release copper (II) ions;

$$Cu[TEA]^{+2} \rightarrow Cu^{+2} + TEA \qquad (5)$$
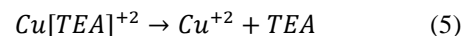
And then copper ions react ionically with sulphide ions to form copper sulphide as;

$$Cu^{2+} + S^{2-} \rightarrow CuS \downarrow \qquad (6)$$
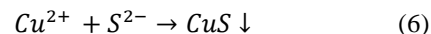
In second case, when hydrazine hydrate complex was added in cationic precursor, it first forms square planer complex with Cu^{2+} as,

$$CuSO_4 + 4NH_2.NH_2.H_2O \rightarrow [Cu(NH_2 - NH_2)_4]^{++} SO_4^{2--} \qquad (7)$$

$$Cu^{++}So_4^{--} + 4 \ \overset{NH_2}{\underset{NH_2}{|}} (H_2O) \rightarrow \qquad (8)$$

Tetrahydraine Cu II Sulphate

This square planner Cu (II) complex, decomposes in reaction vessel to give Cu^{2+}, which then reacts with S^{2-} to produce CuS,

$$Cu^{2+} + S^{2-} \rightarrow CuS \downarrow \qquad (9)$$
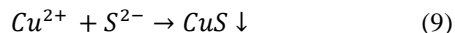
In third case, when ammonia is added to a solution of copper (II) cation, a deep blue color is formed immediately. The blue color is due to the complex ion Cu $(NH_3)_4^{2+}$.

$$Cu^{2+}So_4^{2-} + 4NH_3 \rightarrow [Cu(NH_3)_4]^{2+} + SO_4^{2-} \qquad (10)$$
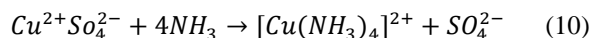
This adsorbed complex further dissociates in anionic precursor, where Cu^{2+} and S^{2-} reacts to produce,

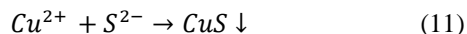$$Cu^{2+} + S^{2-} \rightarrow CuS \downarrow \qquad (11)$$
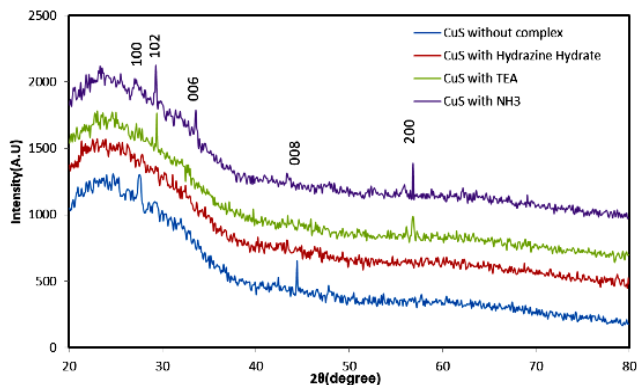
Fig. 1.1. XRD Patterns of CuS films.

The structural properties of the CuS thin films with and without complexing reagent were studied by X-ray diffractometer (Regaku Miniflex 600) with CuKα radiation of wavelength 0.154 nm. **Fig. 1.1** shows the XRD patterns of CuS films deposited with and without complexing agent. It is observed that the CuS films deposited using complex hydrazine hydrate are amorphous in nature. Other films are nanocrystalline in nature with hexagonal lattice and covellite phase. The crystallinity of CuS is more when TEA complex was used. The crystallite orientation is highly affected by complex used in deposition process. The average crystallite size of film was determined by using Debye-Scherrer formula,

$$D = \frac{K\lambda}{\beta Cos\theta} \qquad (11)$$

where λ is the wavelength, β is the angular line width at half maximum intensity in radians, θ is the Braggs angle. It is observed that the crystallite size changes with complexing reagent. It is of the order of 32 nm for film without complex and becomes 61 and 53 nm for TEA and NH_3 SEM results of thin films deposited on substrates were performed using FE-SEM (JEOL JSM-7500F). The film surface of film deposited using hydrazine hydrate is very smooth as compared to other samples supporting its amorphous character as suggested by XRD results. The SEM morphology of this film **Fig. (1.2 C)** shows uniform distribution of smaller grains along the entire substrate surface. However the film deposited using NH_3 complex has higher terminal thickness with agglomeration of grains at various places on the substrate surface **Fig. (1.2 D)**. This suggests that in the growth process the square planner metal

ion complex [TEA –Cu] decomposes easily as that of [NH_3- Cu] complex. As a result [NH_3- Cu] complex lowers the growth rate giving higher terminal thickness with uniform distribution of grains as suggested by SEM image. However, the films deposited by using [Tea –Cu] square planner complex shows lower thickness, but higher grain size due to higher growth rate but lower thickness due to less adhesive nature of depositing material. The film deposited using hydrazine hydrate complex is amorphous with low thickness, as this Cu-hydrazine hydrate complex decomposes very slowly and gives smaller thickness and no grain structure is developed for 60 number of SILAR cycles.
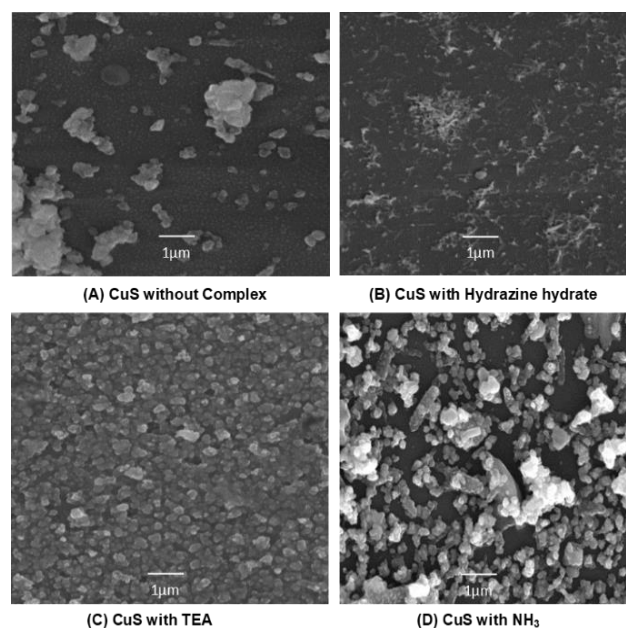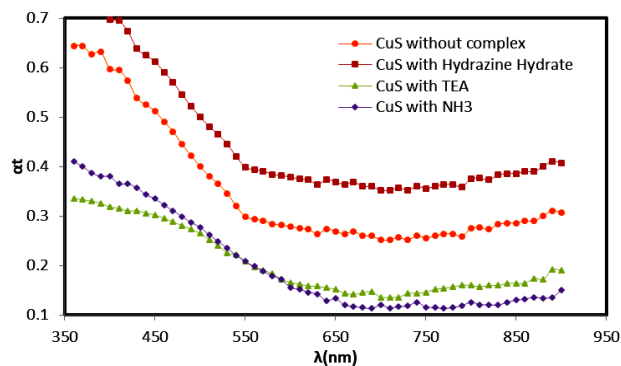

Fig. 1.2. FESEM micrographs of CuS film.

Fig. 1.3. Plots of optical absorption versus wavelength for CuS film.

The optical absorption measurements were carried out to estimate band gap energy of deposited material using a UV–Vis spectrophotometer (UV-1800) in the wavelength range 350–950 nm. **Fig. 1.3** shows the variation of optical density with wavelength for CuS thin film. It was observed that SILAR grown CuS exhibits higher absorbance in visible region. The type of transition estimated by using relation,

$$\alpha = A(h\upsilon - Eg)^n /h\upsilon \qquad (12)$$

where Eg is the band gap energy, hν is the energy of incident photon, and A and n are constants.

Fig 1.4 shows the plots of $(\alpha h\nu)^2$ Vs. *hν* for CuS films. It was observed that the optical band gap energy of CuS varies with complexing reagent used. It is maximum for hydrazine hydrate i.e. 2.21 and lowest for CuS deposited with TEA as complexing reagent i.e. 2.01 eV. Thus band gap of CuS can be engineered by using suitable complexing agent in growth process.
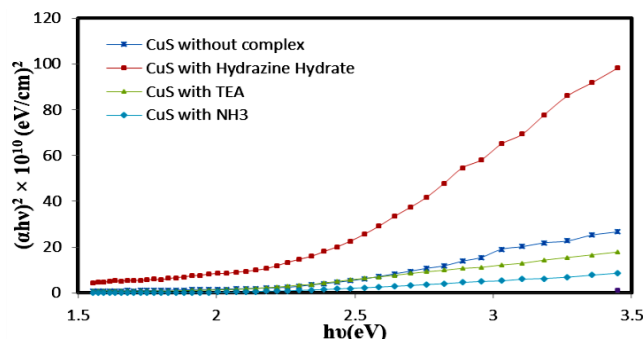

Fig. 1.4. Comparison of Plots of $(\alpha h\nu)^2$ Vs hν for CuS films.

The electrical resistivity measurements were carried out using the dc two point probe method in the temperature range 303–493 K. The electrical resistivity measurements showed that films are semiconducting in nature. **Fig. 1.5** shows the variation of log ρ with reciprocal of temperature. The thermal activation energy 'E$_a$' was calculated by using relation,

$$\rho = \rho o \, exp \, (-Ea \, / \, KT) \qquad (13)$$

where, ρ_o is a parameter depending on the sample characteristics (thickness, structure etc.), E$_a$ denotes the thermal activation energy of electrical conduction, K is Boltzmann's constant and T is absolute temperature. The activation energy of CuS deposited without complex is of the order of 0.74 eV and decreases of 0.51 eV for film deposited using NH$_3$ complex.
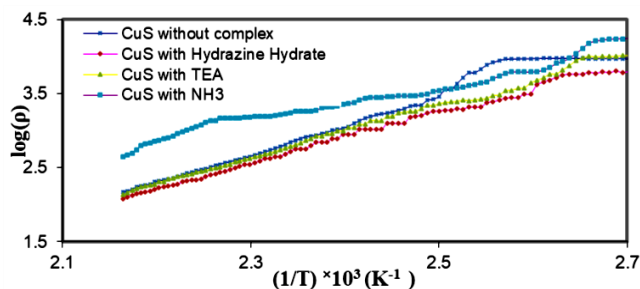

Fig. 1.5. The Variation of log (ρ) with reciprocal of temperature (10^3/T) of CuS.

The **Fig 1.6** shows variation in magnitude of thermo-emf with complexing reagent. The temperature difference applied across the length of sample causes the transport of carriers from hot end to cold end and thus creates electric field, which gives thermal voltage. From the measurement of thermo-emf, it was observed that as the temperature difference across the films increases, thermo-emf also increases, and it is maximum for CuS film deposited using NH$_3$. It was observed that the polarity of

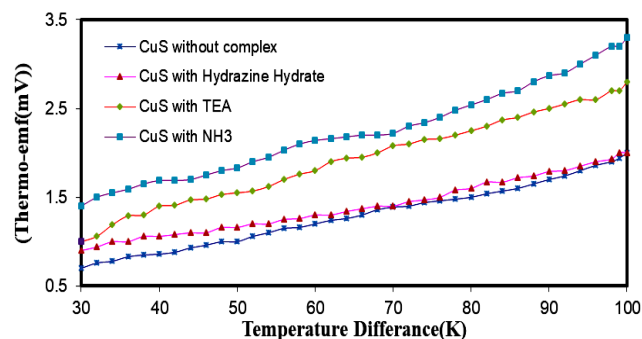thermally generated voltage at the cold end is positive, indicating that the deposited films are of p-type.

Fig. 1.6. Variation of thermo emf with temperature difference of CuS film.

Conclusions

CuS thin film are successfully deposited using complexing reagents hydrazine hydrate (H$_6$N$_2$O(N$_2$H$_2$)), tri ethanol amine (C$_6$H$_{15}$NO$_3$) and ammonia (NH$_3$). This investigation shows that the growth rate of CuS can be controlled by selecting suitable complexing reagent. It is observed that, hydrazine hydrate gives amorphous morphology, TEA gives agglomerated porous morphology, however NH$_3$ complex shows better control on the growth process with uniform distribution of grains. The complexing reagent used which affects the growth mechanism and grain size of deposit. As a result band gap energy of the deposit changes depending upon complexing agent used. The activation and band gap energy can also be engineered by using suitable complexing agent.

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