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CHARACTERIZATION AND HOLOGRAPHIC STUDY OF NANOSTRUCTURE COPPER SULPHIDE THIN FILMS GROWN AT ROOM TEMPERATURE

V. P. Malekar, V. J. Fulari and V.P Kothavale

[1]Department of Physics, Bhogawati Mahavidyalaya, Kurukali-416004, (MS) India
[2]Department of Physics, Shivaji University, Kolhapur-416004, (MS) India.
[3]Department of Physics, Bhogawati Mahavidyalaya, Kurukali-416004, (MS) India.
vpyash07@gmail.com

Abstract:

Nanostructure Copper Chalcogenide thin film**s** are prepared using electrodeposition technique. The structural, morphological and surface wettability properties of the as deposited Copper Sulphide thin films have been studied using XRD, SEM and contact angle measurement. FT-Raman and FT-IR spectral properties of the deposited films have been studied by FT Raman and FT-IR spectrophotometer. Optical band gap energy (Eg value) for Copper Sulphide thin films ranges from 2.1 eV to 2.3 eV. Using as deposited holographic thin films fringe width, thickness of thin film, stress to substrate and mass deposited can be calculated. It is observed that, increase in deposition time thickness of thin film and mass deposited increases but fringe width as well as stress to substrate decreases.

Keywords: FT Raman; Copper Sulphide; Fringe width; Nanostructure; Wettability

1.Introduction:

The CuS thin films have solar control characteristic, due to this, CuS thin films have been used in air-glass tabular solar collectors as absorber coating in photoelectron and photovoltaic applications [1]. CuS thin films are used in solid junction solar cells, that have many applications as, it is a direct conversion device [2]. In comparison with chemical bath deposition (CBD), the electrochemical method is very simple and because of its electric nature, the process can be controlled [3].

Surface deformation study of electrodeposited copper chalcogenide thin films was first carried out by Double Exposure Holographic Interferometry (DEHI). DEHI technique is used to record the hologram of same object at two different conditions, one is unstressed condition and other is stressed condition [4]. This technique is used to study stress-strain relation, non-destructive testing, fluid mechanics, phase shifting and deformation measurement etc [5]. Here this technique used for determination of thickness, mass, stress to substrate of deposited film and fringe width by recorded holograms.

2. Experimental Setup

2.1 Electrodeposition of CuS Thin FILM: Electrolytic bath for CuS thin films were prepared by AR grade copper sulphate $CuSO_4$, Sodium thiosulphate ($Na_2S_2O_3$) and Ethylene Diamine Tetra acetic Acid (EDTA) chemicals dissolved in double distilled water. The equimolar bath solution of 0.10 M $CuSO_4$, 0.10 M Sodium thiosulphate ($Na_2S_2O_3$) and 0.10 M (in preparation 1:3:1) Ethylene Diamine Tetra acetic Acid (EDTA) used as a complexing agentand were prepared in double distilled water. The experimental setup are as shown in Fig. 1 and Fig. 4 shows Photograph of electrodeposited CuS thin films for various deposition times.

2.2 Hologram Recording By Dehi: Dehi is one of the easier technique used to measure thickness, mass and stress to substrate at the time of film deposition. The experimental setup for recording hologram of the thin film is shown in Fig. 2. Recorded holograms of CuS thin film for bath concentration 0.10 M ($CuSO4+Na_2S_2O_3$+EDTA) by varying time of deposition from (a)5 sec, (b)10 sec, (c)15 sec, (d)20 sec and (e)25 sec, the number of fringes increases (Fig.3). As the deposition time increases, number of fringes localized on the surface of substrate increases, consequently the fringe width decreases [6].

3. Results and Discussion

3.1 X-Ray Diffraction: Fig. 5 shows X-ray diffraction patterns, the observed 'd' values are in good agreement with standard'd' values [7] arranged in Table 1. CuS thin films have polycrystalline orthorhombic crystal structure. The enhancement of particle size with deposition time is due to increase in thickness and growth mechanism in thin film [8]

3.2 Optical Absorption: Optical absorption in as-deposited and annealed CuS thin film is carried out in the wavelength range of 350-800 nm. The Fig.6, Plots of $(\alpha h\upsilon)^2$ against $h\upsilon$ gives optical band gap energy ranging from 2.1 eV to 2.3 eV (Table 2) which is comparable to value reported earlier [9].

.3.3 Surface Wettability Study: The presence of local inhomogenities, chemical composition and surface morphology in thin film is directly related

to the surface of water contact angle [10]. The wettability behavior is characterized by the value of the contact angle, a macroscopic parameter [11]. By increase in concentration, increases the contact angle because of roughness of the surface of film [12]. The contact angle of CuS film with water is less than 90^0 (Fig. 7).

3.4 Surface Morphology Study: Microstructure of CuS thin films on to stainless steel substrate was analyzed by scanning electron microscope technique. From the SEM images (Fig. 8), it is seen that small size grains are uniformly distributed over smooth homogenous background [13].

3.5 Ft-Raman and Ft-Ir Spectroscopy: Raman spectra of the films were collected on a combination system including research grade FT-IR model VERTEX 70 with model- Ram- II FT Raman spectrometer equipped with Nd- YAG laser at 1064nm wavelength. The Raman spectra of CuS thin film are as shown in Fig. 9, sharp peak was observed at about ~3234 cm^{-1} [14].

FT-IR spectra (Fig. 10) were recorded on a spectrophotometer (Perkin Elmer FT-IR Spectrum-GX) [15]. The FT-IR bands are at around wave numbers 621.8, 1017.69, 1101, 1380.62 and 1623 cm^{-1} [16].

3.6 Calculation of Thickness of Thin Films: DEHI technique used to study electrodeposited CuS thin films reveals that as deposition time increases, number of fringes on substrate increases causing increase in thickness of the film. Calculated values of thickness of thin films of as deposited thin films are specified in Table 3, thickness of film varies from 0.632 to 1.898 µm [17].

3.7 Measurement of Mass Deposited: Holographic interferometry technique used to study electrodeposited CuS thin films reveals that as deposition time increases mass of deposited film increases. The deposition time increases from 5 to 25 sec, the mass deposited onto the stainless steel substrate varies from 1.243 to 3.731 mg.

3.8 Determination of Stress To Substrate: As the time of deposition increases from 5 to 25 sec 0.10 M ($CuSO4+Na_2S_2O_3$+EDTA) bath concentration stress to substrate of the deposited films decreases from 0.151 x 10^9 to 0.050 x 10^9 dyne/cm^2.

3.9 Calculation of fringe width: The fringe width of the recorded hologram of CuS thin film is measured using travelling microscope. As the time of deposition increases from 5 to 25 sec, the fringe width of the recorded hologram decreases from 0.123 to 0.059 cm.

The variation of optical band gap energy, contact angle and Particle size of CuS film with deposition time is shown in the Fig.11 and Table.2.

The variation of stress to substrate, mass of the deposited film, and thickness of the thin film versus fringe width are shown in the Fig.12 and Table.3.

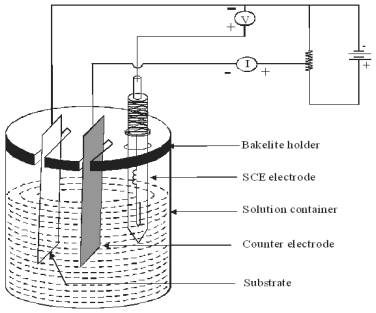


Figure 1 Experimental setup of CuS thin film deposited by electrodeposition technique

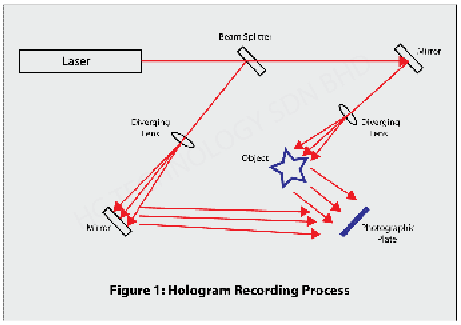


Figure 2 Experimental setup for recording for hologram of the thin film

(a) 5 sec (b) 10 sec (c) 15 sec (d) 20 sec (e) 25 sec

Figure 3 Holograms of CuS thin films

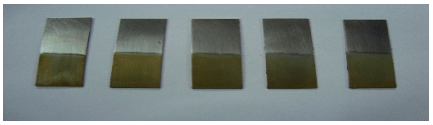


Figure 4 Photograph of electrodeposited CuS thin films for various deposition times

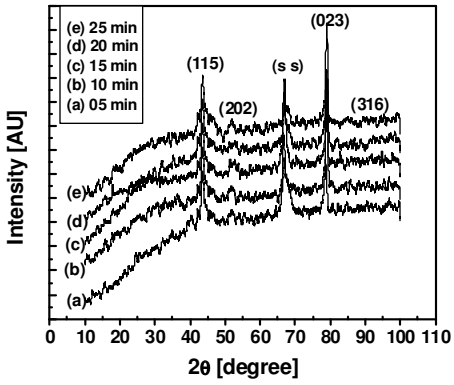


Figure 5 X-ray diffraction patterns

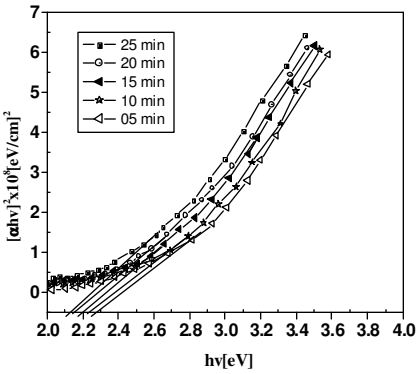
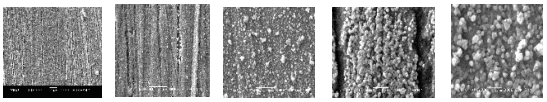


Figure 6 Plot of $(\alpha h\nu)^2$ versus $h\nu$

a) 54⁰ b) 59⁰ c) 66⁰ d) 75⁰ e) 83⁰

Figure 7 Water contact angles



(a) 5 sec (b) 10 sec (c) 15 sec (d) 20 sec (e) 25 sec

Figure 8 SEM images of CuS thin films

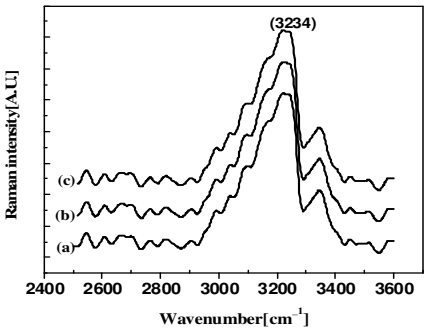


Figure 9 FT-Raman Spectra of CuS thin films

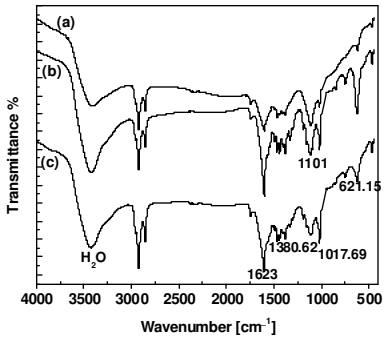


Figure 10 FT-IR spectra of CuS films

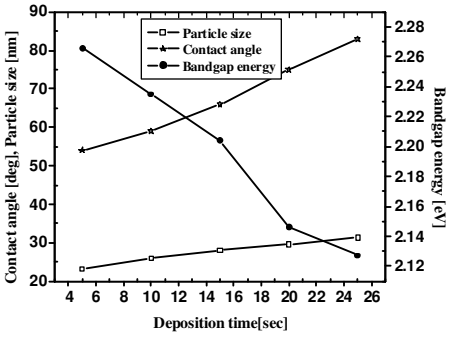


Figure 11 Variation of particle size, Band gap energy and contact angle versus deposition time

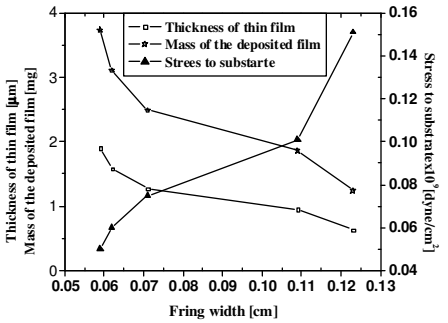


Figure 12 Stress to substrate, thickness and mass of deposited films vs. fringe width

Table.1 Comparison of observed and standard 'd' values of CuS thin films

Sr.No.	Observed 'd' (A^0)	Standard 'd' (A^0)	(hkl) plane
1	2.069	2.074	115
2	1.815	1.844	202
3	1.799	1.788	023
4	1.085	1.095	316

Table.2 Particle size, Contact angle and Band gap energy of CuS thin films

Bath concentration	Deposition Time (sec)	Particle size (nm)	Contact angle (deg)	Band gap energy (eV)
0.10 M ($CuSO_4$ + $Na_2S_2O_3$ + EDTA)	5	23.07	54	2.26
	10	25.90	59	2.23
	15	28.08	66	2.20
	20	29.48	75	2.14
	25	31.34	83	2.12

Table.3 Mass, stress, thickness, fringe width and number of fringes of CuS films

Bath conc.	Deposition time (sec)	Fringe No.	Thickness of CuS film (μm)	Mass deposited (mg)	Stress×10^9 (dyne/cm^2)	Fringe width (cm)
0.10 M ($CuSO4+Na_2S_2O_3$+EDTA	5	2	0.632	1.243	0.151	0.123
	10	3	0.949	1.865	0.101	0.109
	15	4	1.265	2.487	0.075	0.071
	20	5	1.582	3.109	0.060	0.062
	25	6	1.898	3.731	0.050	0.059

4. Conclusions:

CuS thin films have polycrystalline orthorhombic crystal structure. The enhancement of particle size with deposition time is due to increase in thickness. The grain size increases by increasing time. The film nature is hydrophilic. From the study it is clear that by increase in deposition time, particle size and contact angle increases but band gap energy decreases, similarly thickness, Mass and number of fringes increases but stress to substrate and Fringe width decreases.

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