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MEASUREMENT OF PROPERTIES OF COPPER TELLURIDE THIN FILMS USING HOLOGRAPHY

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Abstract—Holography is a technique employed to make three dimensional images using electromagnetic waves. Holographic interferometry is one of the most important applications of holography. It is concerned with the formation and interpretation of fringe patterns, which appears when a wave generated at some earlier time and stored in a hologram is later reconstructed by interfering with comparison wave. We report a technique, which uses double exposure holographic interferometry together with simple mathematical interpretation, which allows immediate finding of stress, mass, fringe width and thickness of thin film. We tested different normalities of solutions. It is observed that increase in deposition time increases thickness and mass of thin film but decreases stress to substrate. The thin films are prepared using electrodeposition technique. The structural, optical and surface wettability properties of the deposited films have been studied using X-ray diffraction (XRD), optical absorption and contact angle measurement, respectively.

1. INTRODUCTION

Holography is a well-known optical technique which can provide valuable information on the location and distribution of small particles in three-dimensional space. Holography is an interference method of recording the light waves diffracted by an object illuminated with coherent light. The diffracted waves are caused to interfere with a phase-related reference wave. If the waves are highly coherent, the relative phase between subject and reference wave remains constant in time producing an observable effect on the intensity distribution

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of the resulting interference pattern. The photographic record of this pattern, called as hologram, contains sufficient information about both amplitudes (heights) of waves and phases (relative positions) of the waves reflected from the object [1, 2].

There has been increasing interest during the past few decades in semi-conducting copper chalcogenide thin films because of its wide range of applications in various fields of science and technology. Copper chalcogenide thin films have a number of applications in various devices such as solar cells, super ionic conductors, photo-detectors, photothermal conversion, electroconductive electrodes, microwave shielding coating, etc. [3–6]. Copper telluride belongs to copper chalcogenide (groups I–VI compound) materials. Copper telluride (Cu_xTe) has different crystal structures depending upon the value of x ($1 < x < 2$) [7, 8].

Several methods have been employed to prepare CuTe thin films. Among them, the electrochemical technique provides numerous advantages, including: It involves relatively simple and inexpensive equipment; films can be fabricated on large and irregular surfaces; the deposition occurs closer to equilibrium than in many high temperature methods, and inter element diffusion is not a problem; the process can be rather precisely controlled because of its electrical nature; the toxic gaseous precursors are not used unlike in chemical gas phase methods. But studies on electrodeposited CuTe thin films have not been done so far using Double Exposure Holographic Interferometry (DEHI) technique.

2. EXPERIMENTAL STUDIES

2.1. Electrodeposition Technique

Copper telluride (CuTe) thin films were prepared by using electrodeposition method, from aqueous electrolytic bath containing $CuSO_4$ and Na_2TeO_3 as precursor sources of Cu and Te ions, and Triethanolamine (TEA) is used as a complexing agent. The stainless steel (s) and fluorine doped tin oxide (FTO) were used as substrates.

Stainless steel substrate was mirror polished by zero grade polish paper, and FTO substrate was cleaned with 10% HCl for 15 min and then cleaned with double distilled water. Electrodeposition study of CuTe thin films was made using potentiostat (Princeton Perkin-Elmer, Applied Research Versa-stat-II; Model 250/270) in three electrode configurations. Pure graphite plate was used as an anode; stainless steel and FTO were used as cathode; saturated calomel electrode (SCE) was used as reference electrode. Bluish-black colored, smooth, uniform CuTe thin films were obtained.

2.2. Double Exposure Holographic Interferometry (DEHI) Technique

The double exposure holographic interferometry (DEHI) technique was used for the thickness and stress measurement of CuTe thin film at the time of film deposition. The experimental setup for recording hologram of the thin film is shown in Fig. 1. Initially, steel substrate was recorded on the holographic plate, and then holographic plate was exposed after depositing CuTe for few minutes. It was reconstructed in the same angle as that of the recording one [9].

While recording the hologram, the substrate is illuminated with a beam of light making an angle θ_1 with normal, and it is viewed at an angle θ_2 during reconstruction; the reconstructed image has a superimposed fringe pattern corresponding to a displacement of the surface. The displacement in the normal direction is given by

$$d = \frac{n\lambda}{\cos\theta_1 + \cos\theta_2} \tag{1}$$

where, n is the total number of fringes, and λ is wavelength of light.

The angles θ_1 and θ_2 are sufficiently smaller. Therefore,

$$d = \frac{n\lambda}{2} \tag{2}$$

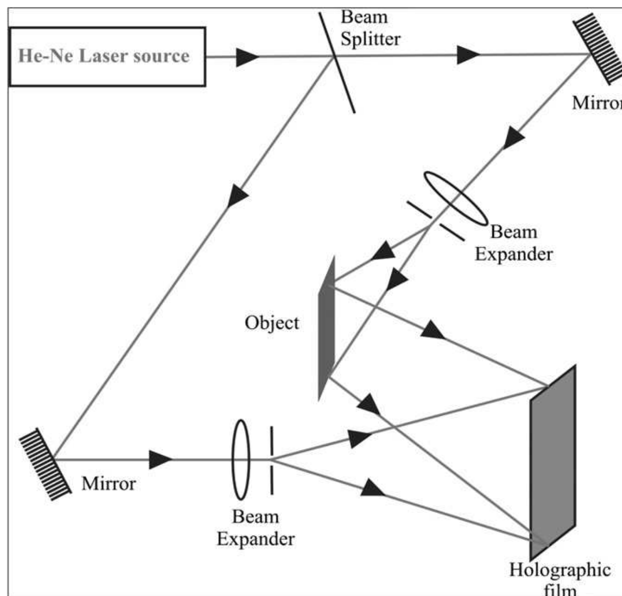

Figure 1. Experimental set up for recording hologram.

After counting relative number of fringes n, deformation of object surface was calculated, using Eq. (2).

The mass of the film was calculated using the following relation.

$$\text{mass} = \text{density} \times \text{volume} \tag{3}$$

The stress to substrate is given by the formula [10, 11]

$$\overline{S} = \frac{t_s^2 Y_s \Delta}{3l^2 t_f} \tag{4}$$

where, $\overline{S}$ is stress in dyne/cm^2; t_s is substrate thickness; t_f is film thickness; Δ is deflection of substrate $= 4\lambda/2$; Y_s is young's modulus; l is length of the substrate on which the film is deposited.

Table 1. Thickness, mass, stress and fringe width of CuTe thin films to the substrate for various deposition times and concentrations.

Bath Concentration	Deposition Time (s)	Number of fringes	Thickness of CuTe film	Mass deposited (mg)	Stress, 10^9 (dyne/cm ^{2})	Fringe Width (cm)
(T_1)	10	1	0.316	0.795	0.303	0.282
	15	2	0.632	1.591	0.151	0.153
	20	3	0.949	2.387	0.101	0.087
	25	5	1.582	3.979	0.060	0.082
	30	7	2.214	5.571	0.043	0.071
(T_2)	10	2	0.632	1.591	0.151	0.150
	15	3	0.949	2.387	0.101	0.106
	20	4	1.265	3.183	0.075	0.079
	25	6	1.898	4.775	0.050	0.066
	30	8	2.531	6.367	0.037	0.054
(T_3)	10	4	1.265	3.184	0.075	0.127
	15	5	1.582	3.979	0.060	0.089
	20	6	1.898	4.775	0.050	0.068
	25	8	2.531	6.367	0.037	0.057
	30	10	3.164	7.959	0.030	0.045

Using Eqs. (2), (3), (4), we estimated the values of the thickness, mass and stress of CuTe thin film, which are given in Table 1.

For the structural study, the X-ray diffraction pattern scanned out in the range of angle 10° to 100° by employing Philips PW-1710 diffractometer. The films deposited on the FTO substrate are used for optical absorption studies by employing UV-VIS-NIR spectrophotometer in the wavelength range 350–850 nm.

3. RESULTS AND DISCUSSION

3.1. Double Exposure Holographic Interferometry

Figures 2, 3 and 4 show recorded holograms of CuTe thin films developed on the holographic film for (a) 4 mM $CuSO_4$ + 2 mM Na_2TeO_3 + TEA, i.e., T_1, (b) 8 mM $CuSO_4$ + 4 mM Na_2TeO_3 +

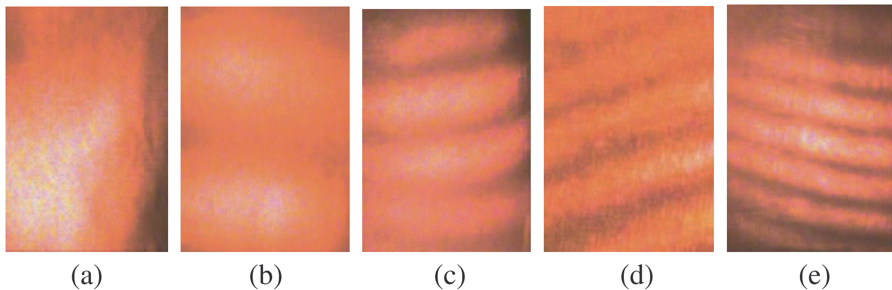

Figure 2. Holograms of CuTe thin film for a bath concentration T_1, for deposition time (a) 10 min; (b) 15 min; (c) 20 min; (d) 25 min; (e) 30 min.

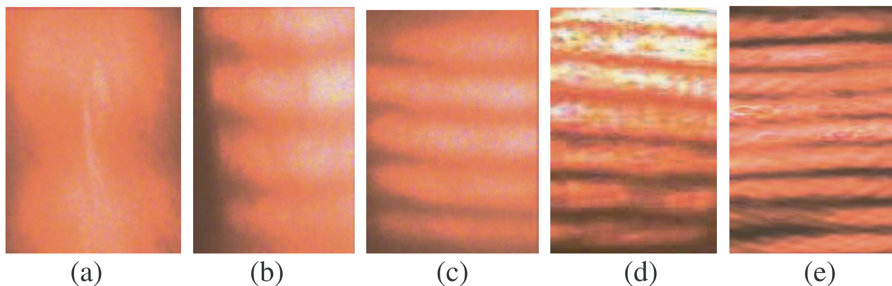

Figure 3. Holograms of CuTe thin film for a bath concentration T_2, for deposition time (a) 10 min; (b) 15 min; (c) 20 min; (d) 25 min; (e) 30 min.

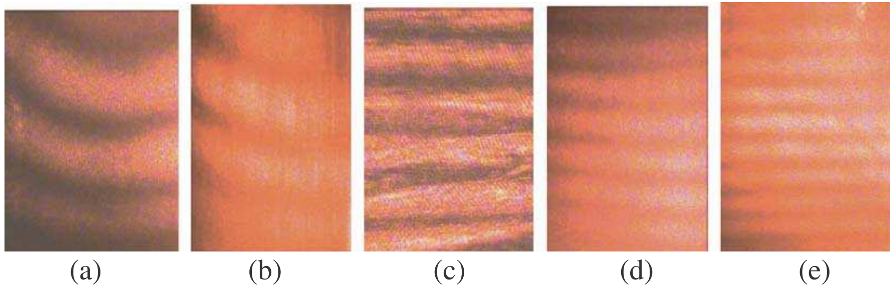

Figure 4. Holograms of CuTe thin film for a bath concentration T_3, for deposition time (a) 10 min; (b) 15 min; (c) 20 min; (d) 25 min; (e) 30 min.

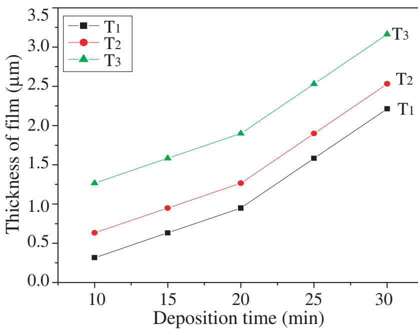

Figure 5. The variation of thickness against time of deposition of CuTe film for T_1, T_2, and T_3 bath concentration.

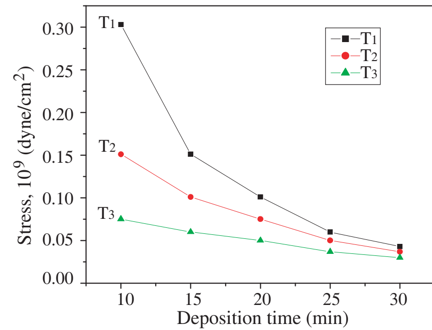

Figure 6. The variation of stress against time of deposition of CuTe film for T_1, T_2, and T_3 bath concentration.

TEA, i.e., T_2, (c) 12 mM $CuSO_4$ + 6 mM Na_2TeO_3 + TEA, i.e., T_3 bath concentration for 10 min, 15 min, 20 min, 25 min, 30 min deposition time. From the hologram study, it is observed that the time of deposition increases; the number of fringes localized on the surface of stainless steel substrate increases; consequently the fringe width decreases [12]. The variation of CuTe film thickness with deposition time is specified in Fig. 5. The variation of stress with deposition time of CuTe thin film is given in Fig. 6. The variation of fringe width of CuTe thin film with deposition time is shown in Fig. 7. It is seen that as time of the film deposition increases, stress developed in the film decreases [13].

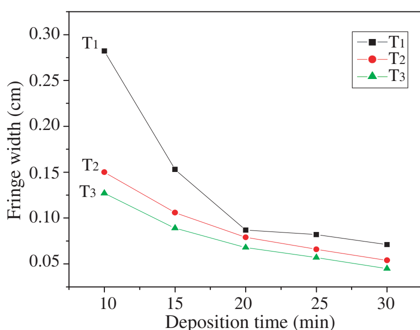

Figure 7. The variation of fringe width against time of deposition of CuTe film for T_1, T_2, and T_3 bath concentration.

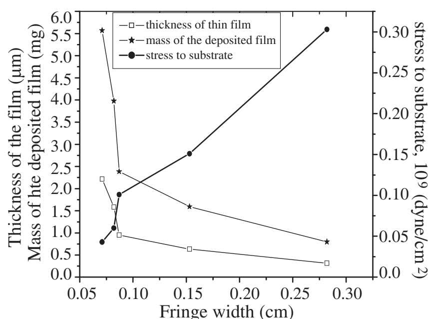

Figure 8. The variation of thickness of film, stress to substrate and mass of the film against fringe width of deposited CuTe film for T_1 bath concentration.

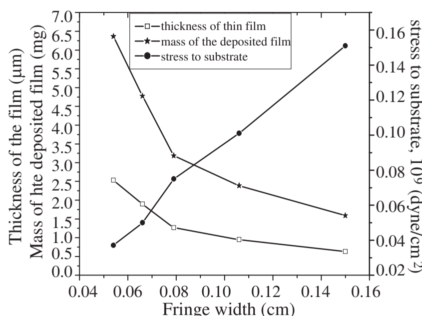

Figure 9. The variation of thickness of film, stress to substrate and mass of the film against fringe width of deposited CuTe film for T_2 bath concentration.

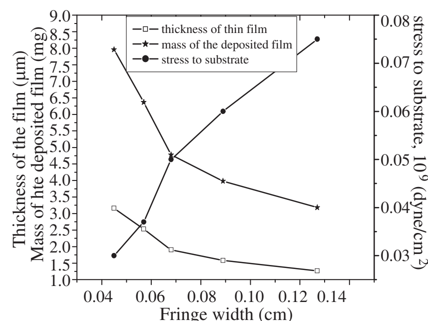

Figure 10. The variation of thickness of film, stress to substrate and mass of the film against fringe width of deposited CuTe film for T_3 bath concentration.

3.2. Fringe Width

The fringe width of recorded holograms of as-deposited CuTe thin films was measured by traveling microscope and is given in Table 1. From the table it is clear that, as the deposition time as well as bath concentration increases, fringe width decreases. The variation of thickness, mass of the deposited film and stress to substrate against fringe width of as-deposited CuTe thin films is shown in Figs. 8, 9 and 10 for T_1, T_2, T_3 bath concentrations.

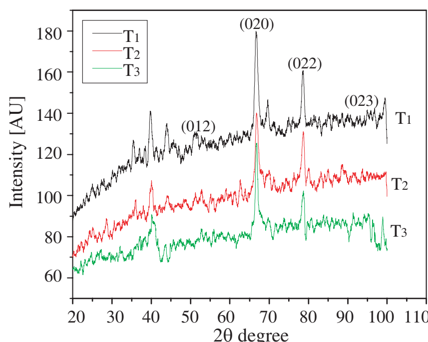

Figure 11. X-ray diffraction pattern of CuTe thin film deposited on to stainless steel substrate for T_1, T_2, and T_3 bath concentration.

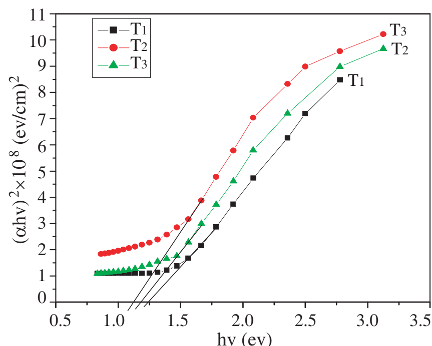

Figure 12. Plot of $(\alpha h\upsilon)^2$ against $h\upsilon$ for CuTe thin film for bath concentrations T_1, T_2, T_3.

Table 2. Comparison of observed and standard '*d*' values of CuTe thin film.

Ob. No.	Standard '*d*' values (A)	Reflecting (*hkl*) Plane	Observed '*d*' values
1	2.64	012	2.67
2	2.04	020	2.08
3	1.76	022	1.79
4	1.53	023	1.53

3.3. Structural Studies

X-ray diffraction pattern of CuTe thin films for bath concentration T_1, T_2, T_3 on stainless steel substrate is shown in Fig. 11. The comparison between the observed interplaner distance '*d*' value and the standard '*d*' value [14] is given in Table 2. It is concluded that the deposited material is copper telluride. Film is polycrystalline with orthorhombic in nature.

3.4. Optical Studies

Optical absorption spectra (Fig. 12) of the copper telluride thin film deposited on FTO glass substrate for T_1, T_2, T_3 bath concentrations. An optical study was carried out by using spectrophotometer (Hitachi Model 330) in the wavelength range 350–850 nm. A plot of $(\alpha h\upsilon)^2$

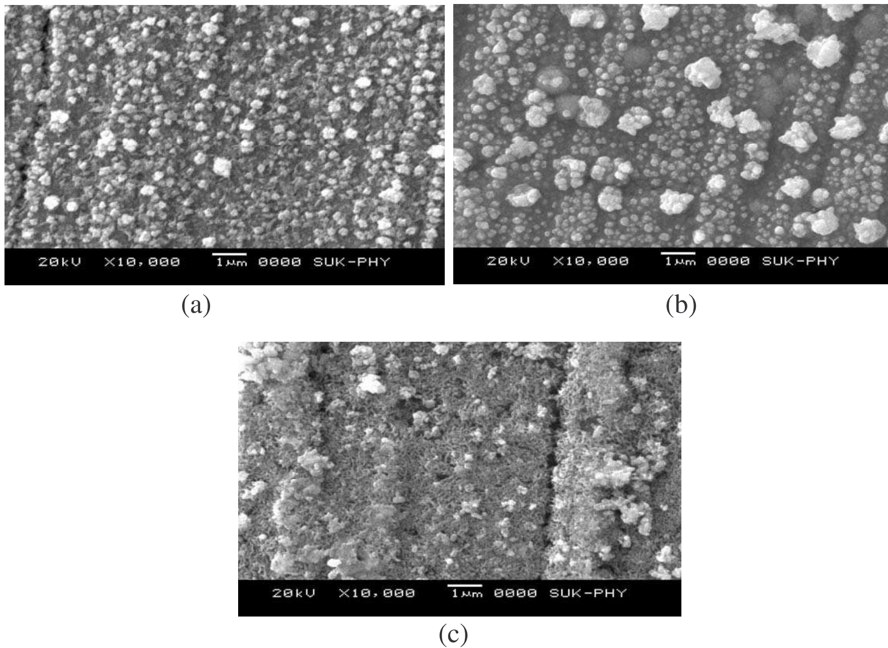

Figure 13. SEM of CuTe thin film for (a) T_1, (b) T_2, and (c) T_3 bath concentrations.

against hv gives optical band gap energy Eg value ranging from 1.1 eV to 1.3 eV which is comparable to the value reported earlier [15].

3.5. Scanning Electron Microscopy (SEM)

Scanning electron microscopy is a convenient technique for surface microstructure studies of thin films. Fig. 13 shows scanning electron micrographs of copper telluride thin films for T_1, T_2, and T_3 bath concentrations, deposited on stainless steel substrate. It is observed that copper telluride thin film is uniform, smooth and homogeneous and well covered to the substrate.

3.6. Surface Wettability Study

Wettability involves the interaction between a liquid and a solid in contact. The wettability behavior is characterized by the value of the contact angle, a macroscopic parameter. For bath concentrations T_1, T_2, and T_3 the contact angles are 62°, 70° and 75° respectively, which is shown in Fig. 14. It is concluded that the increase in concentration

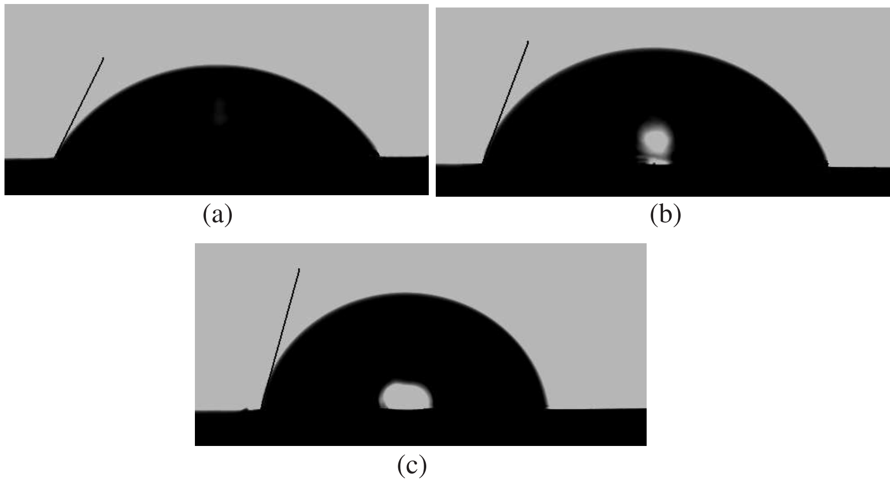

Figure 14. Contact angle of CuTe thin film for (a) T_1, (b) T_2, and (c) T_3 bath concentration.

increases the contact angle [16]. The contact angle of CuTe thin film with water is less than 90°, so the film nature is hydrophilic.

4. CONCLUSION

CuTe thin films were deposited by electrodeposition in aqueous acidic bath using potentiostatic mode. DEHI technique is very good for the characterization of CuTe thin films deposited onto a stainless steel substrate, which shows that as the deposition time increases, the number of fringes localized on the surface of stainless steel increases. From the holographic study, it is clear that the increase in deposition time increases the thickness of the film, but stress to the substrate decreases. Increase in concentration of precursors increases thickness and decreases stress to the substrate. The water contact angle of CuTe thin films increases as bandgap energy decreases with the increase in bath concentrations.

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