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# Growth of Copper Telluride Thin Films using Electrodeposition

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***Abstract:*** *Copper Telluride thin films have been prepared on Fluorine doped Tin Oxide coated conducting glass substrates using electrodeposition technique. Cyclic voltammetric analysis has been carried out to analyze the growth mechanism of the deposited films. Thickness value of the deposited films has been estimated using Stylus profilometry. X-ray diffraction pattern revealed that the prepared films possess polycrystalline in nature. Microstructural parameters such as crystallite size, strain and dislocation density are evaluated using observed X-ray diffraction data. Optical absorption analysis showed that the prepared films are found to exhibit band gap value around 2.03 eV.*

*Keywords: Copper Telluride, Cyclic voltammetry, $SnO_2$, Optical absorption analysis*

## 1. INTRODUCTION

Semiconducting chalcogenides have attracted many researchers due to their interesting applications in solid-state devices. Recently, there has been considerable interest in copper chalcogenide thin films because of their applications in various devices such as solar cells, superionic conductors, photodetectors, photothermal converters, electroconductive electrodes, microwave shielding etc., [1-5]. Copper Telluride is found to exist in a number of phases such as $Cu_4Te_3$, $Cu_7Te_5$, $Cu_2Te$ and CuTe in between room temperature and 850 K [6-8]. Copper Telluride ($Cu_2Te$) is a p-type semiconductor with an energy gap value of 1.12 eV which make them interesting for the fabrication of solar cells [9]. Thin films of $Cu_2Te$ are found to be crystallized in hexagonal structure (File No.39-1061, JCPDS ICDD, 2003) with lattice constants (a = 4.237 Å; c = 7.274 Å), cubic structure (File No. 07-0106, JCPDS ICDD, 2003) with lattice constant (a = 6.11 Å) and in orthorhombic structure (File No. 45-1279, JCPDS ICDD, 2003) with lattice constants (a = 7.319 Å; b = 22.23 Å; c = 36.458 Å). $Cu_2Te$, CuTe powder and thin films are prepared by a number of techniques such as mechanical alloying [11], thermal evaporation [6,12], magnetron sputtering [13], pulsed laser deposition [14], modified chemical bath deposition [5] etc., Electrodeposition and chemical bath deposition techniques are particularly adapted for the preparation of chalcogenide materials [15,16]. When compared to the deposition techniques used for the preparation of $Cu_2Te$ and CuTe thin film electrodeposition appears to be attractive due to its low synthesis cost, low temperature processing, no need of vacuum facility, no contamination to the surrounding, control of growth rate, film thickness and morphology by controlling the deposition parameters as well as composition of the electrolytic bath etc., [17-20]. One obvious requirement in this technique is that the substrate utilized must be conductive [20].

The present work reports the preparation of $Cu_2Te$ thin films on Fluorine doped Tin Oxide coated conducting glass ($SnO_2$:F) substrates using an electrodeposition technique. Cyclic voltammetry analysis has been carried out to find out deposition potential and analyze growth mechanism of the deposited films. Stylus profilometric analysis has been carried out to find out the thickness value of the deposited films. X-ray diffraction studies have been carried out to determine the crystalline nature and phases of the deposited films. Optical absorption analysis has been carried out to determine the band gap value of the deposited films. The experimental observations are discussed in detail.

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## 2. EXPERIMENTAL DETAILS

The chemicals used in the present work were Analytical grade Reagents (99.5 % purity) purchased from Merck. Thin films of $Cu_2Te$ were deposited on $SnO_2$ substrates with sheet resistance of 20Ω/□ from a non-aqueous electrolytic bath, which consists of $CuSO_4$ and $TeO_2$. The working solution of $CuSO_4$ and $TeO_2$ was obtained by dissolving 0.99872 g $CuSO_4$ and 0.01596 g $TeO_2$ in 100 cc of double distilled water. Each 20 cc of the two solutions forms the reaction mixture and this reaction mixture is used as an electrolytic bath for all depositions. Before used for deposition the $SnO_2$ substrates were treated with ultrasonic waves in a bath of isopropanol for 10 minutes and then rinsed with acetone. Initially the pH of the electrolytic bath was 3.0 ± 0.1. By adding an adjustable amount of 1M NaOH the pH value of the solution was maintained at 4.0 ± 0.1. The electrochemical depositions were carried out with the help of SP 50 Potentiostat/Galvanostat unit (Bio Logic, France) using $SnO_2$ substrate as working electrode, Platinum electrode as counter electrode and Saturated Calomel Electrode as reference electrode, respectively. The SCE was introduced into the solution by Luggin capillary arrangement whose tip was placed as close as possible to the working electrode. All the experimental potentials were measured with respect to SCE. The electrolytic processes were monitored by cyclic voltammetry and governed potentiostatically. The temperature of the electrolytic bath was maintained at 80°C using magnetic stirrer - heater. The deposition potential was fixed as -550 mV versus SCE using cyclic voltammetry. The depositions were carried out for different intervals of time within the range between 5 and 60 minutes.

Cyclic voltammetric analysis has been carried out using the Potentiostat/Galvanostat unit (SP50 Bio Logic, France) Electrochemical analyzer employing three electrode cell configuration with $SnO_2$:F substrate as working electrode, platinum electrode as counter electrode and saturated calomel electrode as reference electrode, respectively. Thickness of the deposited films was measured using (Mitutoyo SJ 301, Japan) Stylus Profilometer. X-ray diffraction pattern of the prepared films was determined using an X-ray diffractometer (XPERT PRO PANalytical, Netherland) with $CuK_\alpha$ radiation with wavelength ($\lambda$ = 1.5418 Å). Optical absorption analysis has been carried out using an UV-Vis-NIR spectrophotometer (Schimadzu Model 2600, Singapore).

## 3. RESULTS AND DISCUSSION

### 3.1. Cyclic Voltammetry

The process of formation of alloys in electrodeposition is more complex, since they involve thermodynamic problem such as hydrogen evolution reaction leading to produce poor adhesion of film to the substrate, more acidic nature causes peel off of the film from the substrate [18]. In the formation of $Cu_2Te$ in electrodeposition process, deposition of less noble constituent (here formation of metallic alloy Te) takes place first at a potential which must be quite closer to the standard reduction of potential of -732 mV versus SCE according to Eq.(3). The formation of $Cu_2Te$ takes place according to the following Eq's. (1) to (4).

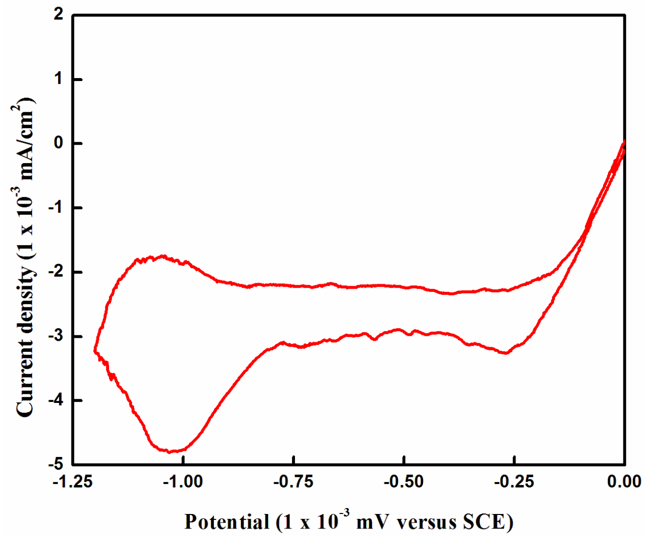

Figure 1. Cyclic voltammogram recorded for $Cu_2Te$ thin films obtained on $SnO_2$:F substrate from an electrolytic bath consists of $CuSO_4$ and $TeO_2$.

Figure 1 shows the cyclic voltammogram recorded for $Cu_2Te$ thin film from an electrolytic bath consisting of $CuSO_4$ and $TeO_2$ employing $SnO_2$:F substrate, Platinum electrode and SCE as working, counter and reference electrodes, respectively. All the voltammeteric curves are scanned in the potential range between 0 and -1200 mV versus SCE. It is observed from Figure 1 that the appearance of the peak at -127 mV versus SCE may correspond to the oxidation of $Cu(OH)_2$ to $Cu_2O$ according to Eq.(1). Further scanning towards more negative potential, the appearance of the second peak at -360 mV versus SCE may correspond to the reduction of $Cu_2O$ to Cu according to Eq.(2). In the reverse scan, the appearance of cathodic peak at -790 mV versus SCE may be ascribed to the formation Te according to the following Eq.(3) and Te be deposited first followed by charge transfer reaction [Eq.(3)]. The mechanism of formation of $Cu_2Te$ thin film on $SnO_2$:F substrate occurs at potential -550 mV versus SCE according to Eq.(4).

$$\begin{gathered} 2Cu(OH)_2+2e^- \rightarrow Cu_2O+2OH^- \\ E^0 = -0.08\ V \end{gathered} \tag{1}$$

$$\begin{gathered} Cu_2O+H_2O+2e- \rightarrow 2Cu+2OH- \\ E^0 = -0.36\ V \end{gathered} \tag{2}$$

$$\begin{gathered} Te+2H++2e^- \rightarrow H_2Te \\ E^0 = -0.79\ V \end{gathered} \tag{3}$$

$$\begin{gathered} 2Cu+Te+2H^++2e^- \rightarrow Cu_2Te \\ E^0 = -0.575V \end{gathered} \tag{4}$$

### 3.2. Film Thickness

Thickness of the deposited films is measured by using stylus profilometer. Two independent variables such as uniform growth and surface morphology have been controlled by the thickness of electrochemically deposited $Cu_2Te$ thin films [18, 20-21]. Thickness of the deposited films could be controlled by controlling the deposition potential, deposition time and bath temperature [21]. The temperature of the electrolytic bath is found to influence the deposition rate by increasing diffusion coefficient of the species and decrease in value of viscosity [21]. At lower bath temperature

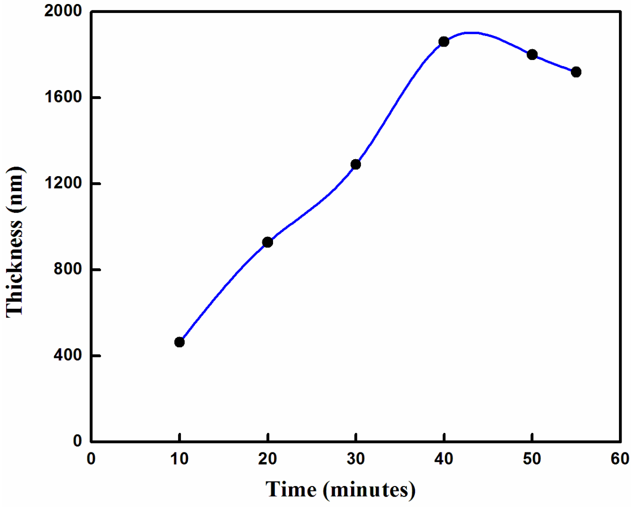

Figure 2. Variation of film thickness with deposition time for $Cu_2Te$ thin films obtained on $SnO_2$:F substrate.

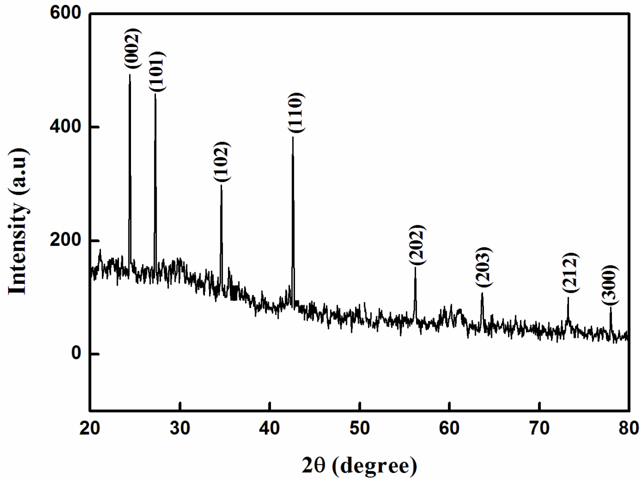

Figure 3. X-ray diffraction pattern recorded for $Cu_2Te$ thin films obtained on $SnO_2$:F substrate at bath temperature 80° C.

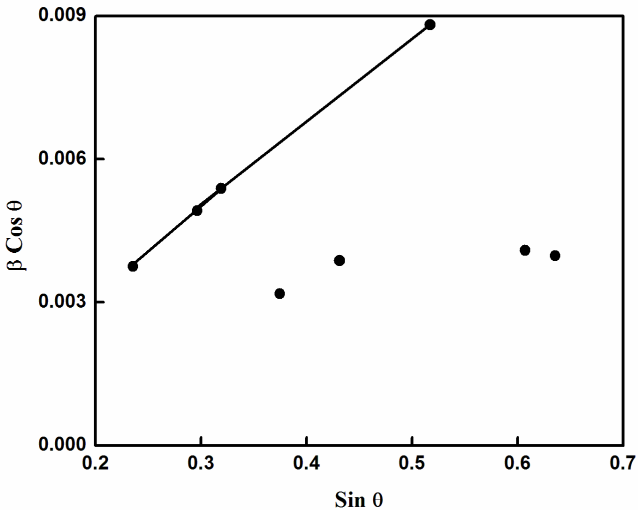

Figure 4. Williamson Hall plot of $Cu_2Te$ thin film electrodeposited on $SnO_2$:F substrate at bath temperature 80° C.

such as below 40° C, adherence of the deposited film to the substrate is very poor [21]. At higher bath temperature such as above 80ºC, the process of hydrogen evolution occurs, which hindered the process of deposition of $Cu_2Te$ [21]. Variation of film thickness with deposition time for $Cu_2Te$ thin films obtained on $SnO_2$ substrate at 80ºC is shown in Figure 2. It is observed that the film thickness increases with deposition time and attained its maximum value at 40 minutes of deposition. Further increasing deposition time above 40 minutes, there is decrease in film thickness value, which may be due to higher rate of dissolution than rate of deposition. Films with higher thickness value are obtained at a deposition time of 40 minutes of deposition.

### 3.3. X-ray Diffraction Analysis

X-ray diffraction pattern has been taken out to identify crystalline nature and phases of the deposited films. Figure 3 shows the XRD pattern recorded for $Cu_2Te$ thin films obtained on $SnO_2$:F substrate. XRD pattern showed that the prepared films possess polycrystalline in nature with hexagonal structure. The diffraction peaks of $Cu_2Te$ are found at 2θ values of angles 24.57, 27.24, 34.72, 42.67, 51.27, 56.37, 63.87, 73.37 and 77.87 corresponding to the lattice planes (002), (101), (102), (110), (201), (202), (203), (212), and (300),respectively. The observed peaks in the diffractogram are indexed and the corresponding values of interplanar spacing "d" are calculated and compared with the standard JCPDS ICDD file for hexagonal $Cu_2Te$ [22]. The height of (002) plane is found to be higher than all other peaks in the diffractogram indicating that the crystallites are preferentially oriented along (002) plane. The crystallite size value of the deposited film has been calculated using FWHM data and Debye Scherrer formula [18, 20-21, 23].

$$D = \frac{0.9\lambda}{\beta \cos\theta} \tag{5}$$

Strain is defined as the restoring force, which acts on the surface of the film to restrict the formation of crystallites on its surface [18,24]. The value of strain is calculated from the slope of β cos θ versus sin θ plot (Figure 4) using the following Eq. (6) by Williamson Hall plot method. Dislocation density is defined as the number of dislocation lines per unit volume of the crystal and it can be calculated using Eq.(7) [17-18,21].

$$\beta = \left( \frac{\lambda}{D\cos\theta} - \varepsilon \tan\theta \right) \tag{6}$$

$$\delta = \frac{1}{D^2} \tag{7}$$

The value of crystallite size, strain and dislocation density for

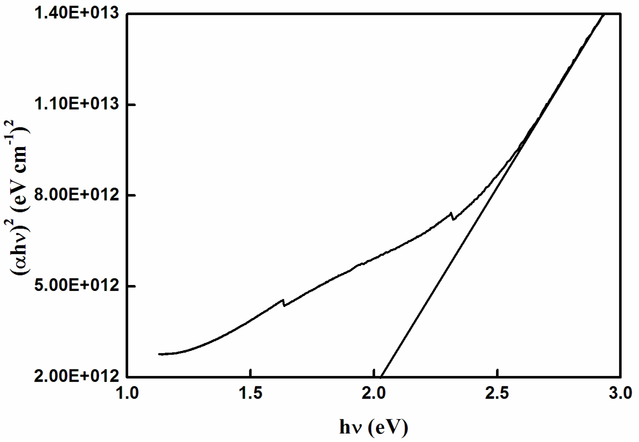

Figure 5. Plot of (hυ) versus $(\alpha h\upsilon)^2$ for $Cu_2Te$ thin film electrodeposited on $SnO_2$:F substrate at bath temperature 80º C.

films obtained on $SnO_2$:F substrate at bath temperature of 80º C are found to be 43.59 nm, 17.63 x $10^{-3}$ line$^{-2}$ metre$^{-4}$ and 5.262 x $10^{14}$ lines metre$^{-2}$, respectively.

### 3.4. Optical Absorption Analysis

Optical parameters such as absorption coefficient and band gap play an important role in recognizing optoelectronic properties of semiconducting material. Optical absorption and transmittance measurements of electrochemically deposited $Cu_2Te$ thin films on $SnO_2$:F substrate have been determined with the help of an UV-Vis-NIR spectrophotometer in the wavelength range between 300 and 1100 nm. If there is any substrate absorption occurs, it can be corrected by introducing an uncoated $SnO_2$:F substrate in the reference beam. An analysis of absorption spectrum in the energy range between 1.1 and 3.0 eV indicates that (α) follows the relation. The value of absorption coefficient (α) is determined by using the following Eq.(8).

$$\alpha = \frac{1}{t}\ln\left(\frac{A}{T}\right) \tag{8}$$

where α is the absorption coefficient in cm$^{-1}$, t is thickness value of the deposited film in nm, A is absorbance and T is transmittance in terms of percentage. The nature of transition present in the deposited film is determined by using the below mentioned Eq.(9).

$$\alpha h\nu = K(h\nu - E_g)^n \tag{9}$$

where K is an energy dependent constant, $E_g$ is band gap value of the deposited films in eV, hν is photon energy in eV. A plot of (hυ) versus $(\alpha h\upsilon)^2$ is drawn for films prepared at bath temperature 80°C is shown in Figure 5. Linear portion of the plot is extrapolated to energy (hυ) axis (X-axis) to get the band gap value of the material. The band gap value of films obtained in the present work is found to be 2.03 eV. The band gap value of the deposited films obtained in the present work, which must be quite closer to the value, reported earlier for $Cu_2Te$ thin films.

## 4. CONCLUSIONS

$Cu_2Te$ thin films were deposited on $SnO_2$:F substrates using an electrodeposition technique. Growth mechanism of the deposited films was analyzed using cyclic voltammetry. Films with maximum thickness value were obtained at a deposition time of 40 minutes. X-ray diffraction analysis showed that the prepared films possess polycrystalline in nature with hexagonal structure with most prominent reflection along (002) plane. Optical absorption analysis showed that the prepared films possess direct band gap value of 2.03 eV, which must be quite closer to the value reported earlier.

## 5. ACKNOWLEDGEMENT

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