Preparation and Characterization of Copper Telluride Thin Films

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Abstract

Copper telluride thin lms were deposited using a modi ed chemical technique with copper(II) sulphate pentahydrate [$CuSO_45H_2O$] and sodium tellurite [Na_2TeO_3] as cationic and anionic sources, respectively. The modi ed chemical technique is based on immersing the substrate in distinct cationic and anionic precursors. The preparative parameters, such as concentration, pH, immersion time, immersion cycles, and so on, were tuned to produce high-quality copper telluride thin lms at room temperature. X-ray di raction (XRD), scanning electron microscopy (SEM), and energy dispersive X-ray analysis (EDAX) were used to study the lms' structural, compositional, optical, and electrical transport properties.

Keywords: Cupric telluride, thin lm, sodium tellurite, cationic,XRD, EDMAX,SEM.

1 Introduction

Because of their vast range of applications in numerous domains of science and technology, semi-conducting copper chalcogenide thin lms have sparked increased attention in recent decades. Copper chalcogenide thin lms are used in a variety of devices, including solar cells, super ionic conductors, photodetectors, photothermal conversion, electroconductive electrodes, microwave shielding coatings, and so on. Copper telluride is a copper chalcogenide (compound from groups I-VI). Depending on the value of x ($1 < x < 2$), copper telluride (Cu_2Te) has distinct crystal forms (see[1-15]). The optical band gap of Cu_2Te is ≈ 1.1 eV.

Thin lm deposition by a modi ed chemical approach has recently piqued the interest of researchers since it o ers numerous advantages over the more recognized synthetic route to semiconductor materials. Controlling lm thickness and deposition rate by adjusting pH, reagent concentration, and complexing agent are combined with the ability to coat a vast surface at a reasonable cost. The modi ed chemical approach can be employed for aqueous solution deposition at room temperature.The growth mode is the primary distinction between chemical bath deposition (CBD) and modi ed chemical methods. In CBD, all of the precursors are present in the reaction vessel at the same time, but in the modi ed chemical technique, each precursor is treated separately on the substrate, and rinse separates these treatments. As the separate stages are isolated by washing, the adsorbed species on the substrate surface govern the reactions and lm formation occurs. The number of deposition cycles directly controls the thickness of the layers(see[16-35]).

The modi ed chemical approach is based on a sequential reaction at the surface of the substrate. Each reaction is followed by rinsing, which allows for heterogeneous interaction between the solid phase and the solvated ions in the solution. The goal is to produce thin lms of water-insoluble ionic or ion covalent compounds of the KpAa type by a heterogeneous chemical reaction at the solid solution interface between adsorbed cations pK^{a+} and anion $aAp-$

$$pK_{aq}^{a+} + qX_{aq}^{b-} + b'Y_{aq}^{q'+} + aA^{p} \rightarrow KpAs_s \downarrow + qX_{aq}^{b-} + b'Y_{aq}^{q'+}$$

with $ap = bq = b'q$.Where K represents the cation (Cd_2^+, Zn_2^+,Fe_3^+, Cu^+, etc.), p the number of cations, a the numerical value of charge on cation, X an ion in cationic precursors having negative charge (X = SO_4^2 , Cl^2 , NO_3^2 etc.), q the number of X in cationic precursors, b the numerical value of charges on X,

b' the number of Y in the anionic solutions, q' the numerical value of charge on Y, Y the ion which is attached to chalcogen ion, A the anion (O, S, Se and Te) and a the number of anions.

A number of attempts have been made to deposit Cu_xS and Cu_xSe thin lms using a modi ed CBD technique; however, no report on the deposition of copper telluride thin lms is published. In this study, semi-conducting copper telluride thin lms were formed onto glass substrates at room temperature using a modi ed chemical technique. X-ray di raction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDAX), Rutherford back scattering (RBS), optical absorption, electrical resistivity, and thermoemf measurements were used to characterize the lms' structural, surface morphological, compositional, optical, and electrical properties(see[36-51]).

2 Experimental

2.1 Copper telluride thin lm formation

The deposition was carried out on 75 mm × 25 mm × 1mm commercially available glass microslides. The microslides were boiled in chromic acid for 30 minutes before being washed with detergent, rinsed with acetone, and ultrasonically cleaned with double distilled water.The following process was used to deposit copper telluride lms from an aqueous solution: Copper telluride's cationic precursor was 0.1 M copper sulphate pentahydrate [$CuSO_45H_2O$] at a pH of 5. The telluride ion was obtained from 0.05 M sodium tellurite with a pH of 9. For 20 seconds, a clean glass substrate was immersed in a copper sulphate solution, where copper ions were adsorbed on the surface of the glass substrate. To remove weakly bound or excess copper ions from the glass substrate, it was washed in deionized water for 50 seconds.The glass substrate was then immersed for 20 seconds in an anionic precursor (Na_2TeO_3) solution, where telluride ions reacted with pre-adsorbed copper ions on the glass substrate to generate a copper telluride layer on the glass's surface. The optimum deposition conditions for copper telluride are listed in table 1. a TEA: triethanolamine. b HH: hydrazine hydrate.

	Precursor	$CuSO_4$(2 NTEA[a] + 2 NHH[b])	Na_2TeO_3
1	Concentration(M)	0.1	0.05
2	pH	5	9
3	Immersion time(s)	20	20
4	Number of immersions	60	60
5	Deposition temperature (K)	300	300

Table 1: Conditions for deposition of copper telluride thin lms using a modi ed chemical technique.

2.2 Characterization of the copper telluride thin films

The weight di erence approach was used to determine the thickness of the copper telluride layer. The X-ray di raction pattern of copper telluride lms was obtained using a Philips model PW 1710 in the scanning angle range of 20 60 (2θ) with CuKα radiations at 1.5418 $^{-}$. The copper telluride thin lm's microstructure and chemical composition were determined using scanning electron microscopy and energy dispersive X-ray analysis on a Philips XL-30 SEM and an EDAX analyzer, respectively.1.8 MeV He^+ ions were used in the Rutherford back scattering study of lms on glass substrate. The ion beam was incident on the surface of the lm, and a semiconductor detector (implanted Si detector, solid angle of 3.4×10^{-3} sr) was installed at a scattering angle of 170 . The energy resolution exceeded 20 keV. To achieve a statistical error of 1 , about (1 - 3) × 10^5 counts per peak were sampled. The composition of the lm can be established by recreating the lms' Rutherford back scattering spectra with software and tting them to experimental data.To investigate the optical characteristics, optical absorption and transmission were measured using a Hitachi 330 spectrophotometer in the wavelength range of 350 850 nm. The electrical resistivity of the lm was measured in the temperature range of 300 500 K using a dc two-point probe method. The temperature

di erence was measured using a chromel alumel thermocouple and a brass block as a sample holder. The polarity of the thermally generated voltage at the hot end of the lm was used to determine the type of electrical conductivity of the lm.

3 Results and discussion

3.1 Thickness measurement

Thickness of the copper telluride lms for di erent number of deposition cycles was measured using weight di erence method given by

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

where m is the mass of the lm, A is the area of the lm and ρ (7.303 g/cm^3) the mean density (Cu_2Te: 7.27 g/cm^3; CuTe: 7.10 g/cm^3; $Cu_{1.4}Te$: 7.54 g/cm^3 of deposited material, as discussed in Section 3.2.The change of copper telluride lm thickness for the number of deposition cycles with optimum deposition circumstances is shown in Fig. 1. For 50 deposition cycles, a nal thickness of 0.36 m was discovered. The rate of growth was determined to be 7.2 nm per cycle.

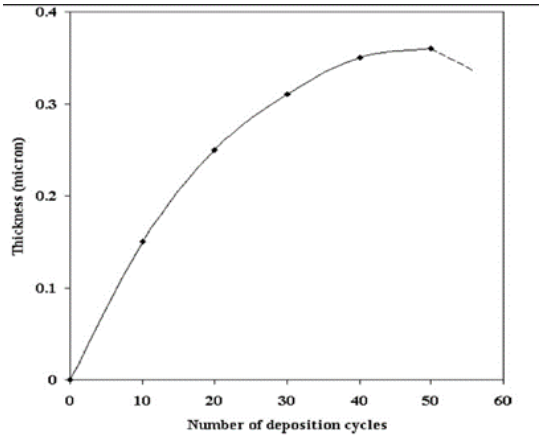

Figure 1: Thickness vs deposition cycle count for copper telluride thin lm.

The lms got powdery and aked o the glass substrate after 50 cycles. Previously, similar behavior was observed in Bi2S3 thin lms created by modi ed chemical bath deposition (M-CBD).

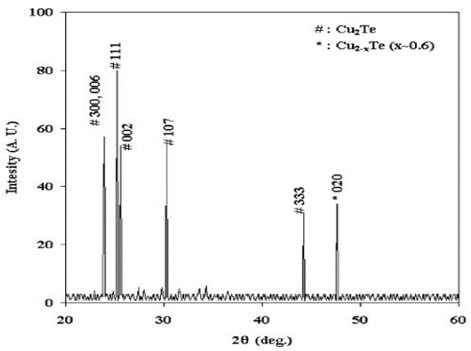

Figure 2: XRD pattern of copper telluride thin lm placed on glass substrate.

	Observed 'd'	Standard 'd'	Plane hkl	Phase
1	3.61	3.61	3 0 0,0 0 6	Cu_2Te
2	3.52	3.51	1 1 1	Cu_2Te
3	3.47	3.47	0 0 2	CuTe
4	2.94	2.99	1 0 7	Cu_2Te
5	2.04	2.04	0 2 0	CuTe
6	1.91	1.939	0 2 0	$Cu_{2-x}Te$
7	1.51	1.52	1 0 4	Cu_2Te

Table 2: Composition of XRD and ASTM data from copper telluride thin lms formed using a modi ed chemical technique.

3.2 Structural studies

Fig. 2 depicts the XRD pattern of a copper telluride lm on a glass substrate. Table 2 compares observed interplaner distance 'd' values to standard 'd' values from ASTM data. The deposited material is copper telluride with mixed cubic and tetragonal crystal structure [mixed phases of Cu_2Te,CuTe, and $Cu_{2-x}Te$x] based on a comparison of measured 'd' values with standard 'd' values.

No further phases of Cu and Te were found in the XRD pattern, which could be owing to the amorphous structure or a low fraction of the same.

3.3 Scanning electron microscopy (SEM) and energy dispersive Xray analysis (EDAX)

SEM is a handy technique for studying the surface microstructure of thin lms. Scanning electron micrographs of copper telluride thin lms produced on glass substrates at 1000 and
10,000 magni cations are shown in Figs. 3*a* and *b*. According to Fig. 3, the copper telluride thin lm is uniform, smooth, and homogeneous, and it is well covered to the substrate. Fine-grained surface

particles of copper telluride lm are seen in Fig. 5.3*b*. Copper telluride thin lm on glass substrate was analyzed using energy dispersive X-rays. According to the results of the investigations, the average at % composition of the lm is Cu:Te 67 : 33.

3.4 Rutherford back scattering

The Rutherford back scattering spectrum of a copper telluride lm on a glass substrate is shown in Fig. 4. It plots the number of detected back-scattered He ions as a function of their energy alongside simulated copper telluride spectra. The solid curve depicts the computed RBS spectra of Cu Te on glass. Cu and Te were considered to be homogeneously distributed in thin lm for calculation purposes. The presence of oxygen is also indicated by a tiny peak with an edge energy of 650 keV.The presence of oxygen and Si peaks in RBS spectra is due to the substrate's amorphous glass (SiO_2). The presence of oxygen has been discovered in numerous chemically formed lms using the RBS approach. The integrated counts under curves (peak and tail) coincide with the counts under simulated peaks, showing that the lm is Cu Te.

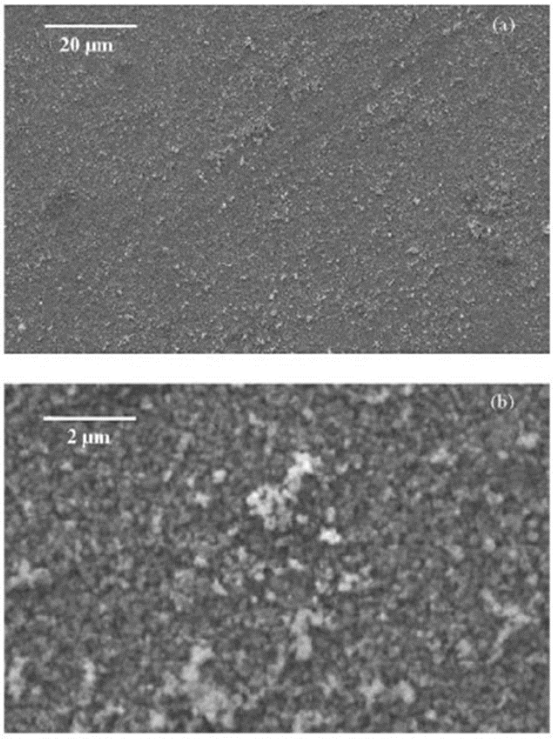

Figure 3: Scanning electron microscopy (SEM) of copper telluride thin lm at (a) 1000X and (b) 10,000X magni cations.

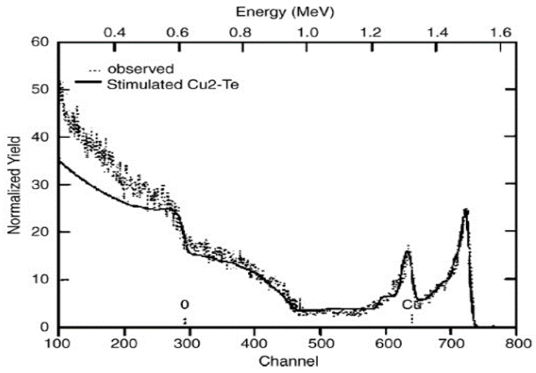

Figure 4: Spectra of RBS for a copper telluride thin lm on a glass substrate.

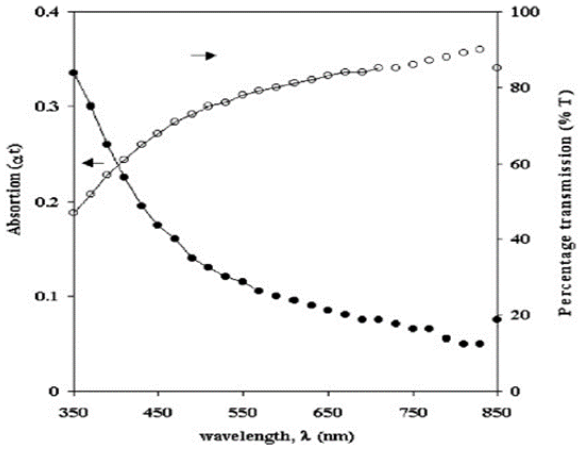

Figure 5: Absorption (at) and transmittance (T %) plots against wavelength (λ) for copper telluride thin lm.

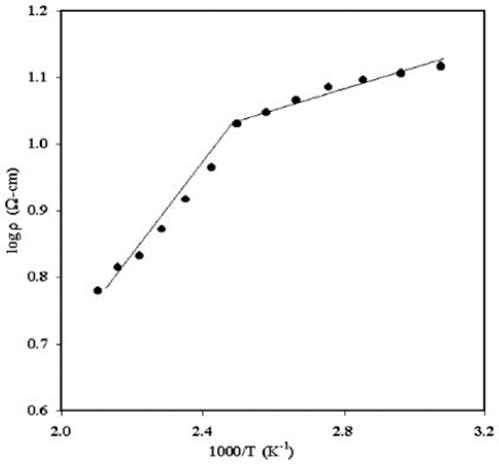

Figure 6: The plot of logρ versus 1000/T for thin lm of copper telluride.

3.5 Optical studies

The optical absorption and transmission spectra [Fig.5]of a copper telluride thin lm coated on a glass substrate (thickness∼ 0.2 mm) were measured using a spectrophotometer (Hitachi Model 330) in the wavelength range 350 850 nm . According to these spectra, the lm shows a high absorbance ($10^4\,cm^{-1}$) indicating a direct band gap transition. However, the maximum percentage transmission (90%) occurs at λ = 830 nm .

3.6 Electrical resistivity and thermoemf measurement

A dc two-point probe approach was used to test the dark electrical resistivity (ρ) of the copper telluride lm. Figure 6 depicts the variance of log*r* versus 1000/*T* for the lm. The resistance reduces with increasing temperature, showing that the copper telluride coating is semi-conducting. At room temperature, the dark electrical resistivity was on the order of 10^1
Ω·cm , which is the same as the value (10^1Ω·cm) reported previously for electrodeposited Cu_xTe thin lms.The variation is also shown to be non-linear. The gure is divided into two sections that correlate to low and high temperatures. Similar results have already been reported for copper sulphide thin lms. The temperature dependency drives carrier transfer from the hot to cold end, giving birth to the thermal voltage. Thermoemf was measured for copper telluride thin lms at temperatures ranging from 300 500 K. The thermally generated voltage at the hot end had a negative polarity, indicating that the material is p-type. The rise in thermoemf with temperature di erence could be due to an increase in the mobility of charge carriers as temperature di erence rises.

4 Conclusions

A modi ed chemical approach can be used to generate copper telluride thin lms on glass substrates.

The lm is made up of various phases of copper telluride (CuTe, Cu_2Te, and $Cu_{2-x}Te$. The absence of Cu_xO, TeO, and other oxides observed may be attributable to their amorphous nature or a low fraction of them. The electrical resistivity at room temperature was measured to be on the order of 10^1 Ω·cm. Cu_xTe lms deposited with M-CBD exhibit p-type electrical conductivity.

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