5.1 Introduction

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 nanoscience and nanotechnology. Copper telluride forms different phases viz. CuTe, Cu$_2$-xTe, Cu$_2$Te etc. Cu$_x$Te thin films have been found to possess near ideal solar control characteristics. Generally, the films are blackish gray-blue-purple-red in color. Copper telluride nanowires are fabricated by a microwave-assisted solvothermal method using a self-sacrificial template due to their electrical conductivity [1-6]. Controlled hydrothermal synthesis and growth mechanism of various nanostructured films of copper and silver tellurides is explained [7]. Deposition of metal chalcogenide thin films by SILAR method is reported [8]. Preparation and characterization of copper telluride thin film by M-CBD method is also reported [9]. Hydrophilic nature of electrodeposited copper telluride and stress, mass, fringe width and thickness of CuTe thin film is reported [10]. Copper telluride (Cu$_2$Te) nanoparticles have been synthesized in a single reaction at 70°C within 9 hours by a wet chemical method [11], this method ensures almost complete utilization of the precursors with a very high productive yield. Polycrystalline Cu$_7$Te$_4$ dendritic microstructures were synthesized by simple galvanostatic electrochemical deposition method [12]. Cu$_7$Te$_4$ microstructure constructed by nanoparticles, with defined sizes of 25–30 nm is also reported [11, 12]. The electrodeposition of Cu, Te and Cu-Te thin films on BDD electrodes was investigated [13].

The structural and electronic properties of the novel semiconductor alloy Cd$_{1-x}$Cu$_x$Te is determined [14]. Copper telluride nanowires of 100 nm diameter have been fabricated using electrodeposition method [15]. Cu$_2$Te synthesis and copper telluride
(Cu$_{1.75}$Te) nanowires of diameter 100 nm and 50 nm have been synthesized with band gap 3.092 eV is reported [16, 17]. By the electrochemical technique films can be fabricated on large and irregular surfaces. The deposition occurs closer to equilibrium than in many high temperature methods, there is no problem with inter element diffusion. 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.

5.2 Experimental

5.2.1 Thin film deposition

5.2.1.1 Preparation of solution

Preparative parameters such as, deposition time and concentrations of precursor were optimized. In the typical synthesis, copper sulfate (CuSO$_4$) and sodium telluride (Na$_2$TeO$_3$) are used as source of copper and telluride respectively while triethanolamine is used as complexing agent. Solutions are prepared in double distilled water.

- **bath (1)** 0.05M CuSO$_4$, 0.01M Na$_2$TeO$_3$ and 5 mL of 0.25M triethanolamine
- **bath (2)** 0.1M CuSO$_4$, 0.02M Na$_2$TeO$_3$ and 5 mL of 0.25M triethanolamine
- **bath (3)** 0.15M CuSO$_4$, 0.03M Na$_2$TeO$_3$ and 5 mL of 0.25M triethanolamine
- **bath (4)** 0.20M CuSO$_4$, 0.04M Na$_2$TeO$_3$ and 5 mL of 0.25M triethanolamine

30 ml prepared solution is used as electrolyte for deposition.

5.2.1.2 Reaction Mechanism

At the beginning of reaction, copper sulfate in water gets dissociated as follows,

\[ \text{CuSO}_4 \rightarrow \text{Cu}^{2+} + \text{SO}_4^{2-} \quad (5.1) \]

In the present research work unstirred reactions are carried out at room temperature. In next step reduction of telluride takes place as follows
Na₂TeO₃ + H₂O \rightarrow 2Na⁺ + TeO₃²⁻ \hspace{1cm} (5.2)

2Cu²⁺ + TeO₃²⁻ + 6e⁻ + 6H⁺ \rightarrow Cu₂Te + 3H₂O \hspace{1cm} (5.3)

In present case the copper telluride thin films are adhesive to the substrate though the deposition was carried out for prolonged time intervals.

5.2.1.3 Cyclic Voltammetry

Fig. 5.1 shows the cyclic voltammograms recorded onto stainless steel substrate from electrolytic solutions containing 0.05M of CuSO₄·5H₂O, 0.01M of Na₂TeO₂·5H₂O, triethanolamine is used as complexing agent in order to find the suitable reduction potentials of copper telluride. The deposition potential of copper telluride was found to be -0.7 V/SCE.

![Cyclic voltammogram](image)

**Fig. 5.1** Cyclic voltammogram onto stainless steel substrate for copper telluride thin film

The electrodeposition of copper telluride thin films was carried out at the deposition potential -0.7 V/SCE and current density is 1.5-2.0 mA/cm², for various deposition times.
by keeping bath concentration fixed and vice-versa. Films are deposited at room temperature. Blackish-gray colored, uniform and copper telluride thin films were deposited by potentiostatic mode onto stainless steel and ITO coated glass substrates for optimized preparative parameters. After the deposition, the films were washed with double distilled water. The pH of the plating bath ranges between 3 to 4.

5.3 characterizations

The various characteristics such as structural, compositional and optical properties of the electrodeposited copper telluride thin films were studied by various techniques are discussed in section 3.3.

5.4 Results and discussion

5.4.1 Optimization of bath concentration

5.4.1.1 X-ray Diffraction study

The XRD patterns of the as-prepared copper telluride samples for bath (1, 2, 3, 4) with deposition time of 15 min. are shown in Fig. 5.2 (a, b, c, d). Figure indicates the formation of polycrystalline copper telluride and all of them can be indexed as the reported hexagonal copper telluride (JCPDS card No. 39-1061). The phases of copper telluride can be easily distinguished by the powder X-ray diffraction patterns, all of the peaks can be indexed as (103), (201), (300) and (302) in the hexagonal copper telluride structure. Diffraction peaks of other phases or impurities were not detected. Table 5.1 shows the comparison of measured and standard ‘d’ values of the films for bath (1, 2, 3, 4) with deposition time of 15 min. They are in good agreement with standard d values. Hence the copper telluride present in the structure of hexagonal. We conclude that the films are composed of pure copper telluride.
Fig. 2 The XRD patterns of copper telluride thin films for, (a) bath (1); (b) bath (2); (c) bath (3) and (d) bath (4), with deposition time of 15 min.

Table 5.1 Standard and measured 'd' values of copper telluride thin films for bath (1, 2, 3, 4); with 15 min. deposition time

<table>
<thead>
<tr>
<th>(hkl) plane</th>
<th>Standard 'd' values (Å)</th>
<th>Measured 'd' values (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>hkl plane</td>
<td>bath 1</td>
<td>bath 2</td>
</tr>
<tr>
<td>(103)</td>
<td>2.023</td>
<td>2.025</td>
</tr>
<tr>
<td>(201)</td>
<td>1.780</td>
<td>1.787</td>
</tr>
<tr>
<td>(300)</td>
<td>1.225</td>
<td>1.220</td>
</tr>
<tr>
<td>(302)</td>
<td>1.158</td>
<td>1.156</td>
</tr>
</tbody>
</table>

Peak intensity goes on decreases with increases in bath concentration indicates decrease in crystallinity of material shown in Fig. 5.2 (a, b, c). With bath (4) again there is increase in peak intensity indicates increase in crystallinity of material. For bath (1);
crystal size is 14 nm with film thickness of 526 nm, for bath (2); crystal size is 11 nm with film thickness of 637 nm, for bath (3); crystal size is 9 nm with film thickness of 685 nm and for bath (4); crystal size is 12 nm with film thickness of 610 nm. This change in crystallite size and film thickness with bath concentration is explained in section 3.4.1.1.

5.4.1.2 Scanning electron microscopy

Fig. 5.3 (a, b, c, d) shows that different copper telluride nanostructures were obtained by varying bath concentration.

![SEM images](image)

**Fig. 5.3** The SEMs of copper telluride thin films, (a) bath (1); (b) bath (2); (c) bath (3) and (d) bath (4); with deposition time 15 min.
The morphology and nanostructure of the resulting copper telluride films were investigated by using scanning electron microscopy and field emission scanning electron microscopy. The resulting film is composed of regular nanograins, these nano-sized grains possess over whole surface, having 32-55 nm in diameter shown in Fig. 5.3 (f).

Fig. 5.3 FESEM of copper telluride thin films for bath (3); with deposition time 15 min.

(e) (x50K mag.) (f) (X100K mag.)

These results indicate that the chemical reaction of copper foils and telluride can selectively produce various copper telluride nanostructures with the addition of triethanolamine and distilled water. From these images it seen that with increase in bath concentration grain size increases with increase in film thickness, for bath (3); film thickness is 687 nm. Furthermore with still increase in bath concentration the grain size goes on decreases with decrease in film thickness, for bath (4); it is 610 nm. The well developed and matured copper telluride grains (onion flower like structure) growths were shown in FESEM images Fig. 5.3 (e-f) with different magnification. This growth process is explained in section 3.4.1.2.
5.4.1.3 Compositional analysis

The compositional analysis of copper telluride is as shown in Fig. 5.4 (a, b, c, d).

![EDAX patterns of copper telluride thin films](image)

**Fig. 5.4 EDAX patterns of copper telluride thin films (a) bath (1); (b) bath (2); (c) bath (3); (d) bath (4); with deposition time of 15 min.**
The compositional analysis of copper telluride was carried out from energy dispersive X-ray analysis. From the graph it is noted that for bath (1); the atomic percentage of copper is 75.23, while that of telluride is 24.77, for bath (2); the atomic percentage of copper is 67.19, while that of telluride is 32.81, for bath (3); the atomic percentage of copper is 64.27, while that of telluride is 35.73 and for bath (4); the atomic percentage of copper is 68.36, while that of telluride is 31.64.

With increase in bath concentration atomic percentage of copper decreases and that of telluride increases and for further increase in bath composition at% of copper again increases. Table 5.2 shows comparison of chemical composition with different bath compositions.

**Table 5.2** Chemical composition of Cu and Te of copper telluride thin films for different bath composition

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Cu (at %)</th>
<th>Te (at %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>bath 1</td>
<td>75.23</td>
<td>24.77</td>
</tr>
<tr>
<td>bath 2</td>
<td>67.19</td>
<td>32.81</td>
</tr>
<tr>
<td>bath 3</td>
<td>64.27</td>
<td>35.73</td>
</tr>
<tr>
<td>bath 4</td>
<td>68.36</td>
<td>31.64</td>
</tr>
</tbody>
</table>

**5.4.1.4 Optical properties**

The optical band gap of copper telluride films estimated from the Fig. 5.5 (a, b, c, d) is 2.52 eV for bath (1); having crystal size of 14 nm, 2.77 eV for bath (2); with crystal size 11 nm, 2.90 eV for bath (3); with crystal size of 9 nm and decreases with further increase in bath composition, these optical band gap energy values are nearly equal with reported values [11, 16]. There is a tendency that more telluride-rich films have a higher band gap.
The change in the band gaps with crystal size shows the blueshift in copper telluride which can be attributed to the quantum size effect [16, 19].

![Graph showing optical band gap of copper telluride thin films](image)

**Fig. 5.5** Optical band gap of copper telluride thin films, (a) bath (1); (b) bath (2); (c) bath (3); (d) bath (4); with deposition time of 15 min.

Fig. 5.6 (a, b, c, d) represents the absorption spectra in the range of 300-800 nm of the as-prepared copper telluride nanomaterials of nanograins patterns, onion flower like crystals structure. It is seen that the four copper telluride nanostructures have two absorption regions. First absorption region is within the range of 350-400 nm, second absorption region is from 450-550 nm. Differently, the absorption ranges of the copper telluride for bath (3) are narrower and more obvious than those of the copper telluride
with bath (1, 2). The blueshifts in the absorption spectra might be caused by nanosize effects and structural defects of nanocrystals [11, 19].

![Figure 5.6](image)

**Fig. 5.6** Optical absorption spectra of copper telluride thin films (a) for bath (1); (b) bath (2); (c) bath (3); (d) bath (4); with deposition time of 15 min.

**Table 5.3** Chemical composition, optical band gap energy, crystallite size and film thickness of copper telluride thin film with different bath composition

<table>
<thead>
<tr>
<th>Bath concentration</th>
<th>Cu (at %)</th>
<th>Te (at %)</th>
<th>Band gap (eV)</th>
<th>Crystal size (nm)</th>
<th>Film thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>bath 1</td>
<td>75.23</td>
<td>24.77</td>
<td>2.52</td>
<td>14</td>
<td>526</td>
</tr>
<tr>
<td>bath 2</td>
<td>67.19</td>
<td>32.81</td>
<td>2.77</td>
<td>11</td>
<td>637</td>
</tr>
<tr>
<td>bath 3</td>
<td>64.27</td>
<td>35.73</td>
<td>2.90</td>
<td>9</td>
<td>685</td>
</tr>
<tr>
<td>bath 4</td>
<td>68.36</td>
<td>31.64</td>
<td>2.82</td>
<td>12</td>
<td>610</td>
</tr>
</tbody>
</table>
5.4.2 Optimization of deposition time

5.4.2.1 X-ray Diffraction study

The XRD patterns of the as-prepared copper telluride samples for bath (3) with deposition time of 5, 10, 15, 20 min. is shown in Fig. 5.7 (a, b, c, d). Figure indicates the formation of polycrystalline copper telluride, and all of them can be indexed as the reported hexagonal copper telluride (JCPDS card No. 39-1061).

![XRD patterns](image)

**Fig. 5.7** The XRD patterns of copper telluride thin films for bath (3); with deposition time of (a) 5 min., (b) 10 min., (c) 15 min., (d) 20 min.

The phases of copper telluride can be easily distinguished by the powder X-ray diffraction patterns, all of the peaks can be indexed as (103), (201), (300) and (302) in the hexagonal copper telluride structure. We conclude that the films are composed of pure copper telluride. Peak intensity goes on decreases with increases in deposition time.
indicates decrease in crystallinity of material shown in Fig. 5.7 (a, b, c). Again in Fig. 7 (d) there should be increase in peak intensity indicates increase in crystallinity of thin films with increase in deposition time. Crystallite size for copper telluride thin films are 15 nm; with 5 min. deposition time, 12 nm; with 10 min. deposition time, 9 nm; with 15 min. deposition time and it becomes 11 nm; with further increase in deposition time of 20 min.

5.4.2.2 Scanning electron microscopy

The morphology and nanostructure of the resulting copper telluride films were investigated by scanning electron microscopy.

Fig. 5.8 The SEMs of copper telluride thin films for bath (3); with deposition time of (a) 5 min., (b) 10 min., (c) 15 min., (d) 20 min.
Fig. 5.8 (a, b, c, d) shows that different copper telluride structures were obtained by varying the deposition time. The resulting film is composed of regular grains, these grains possess over whole surface. The well developed and matured copper telluride grains with onion flower like structure growths were shown in SEM images Fig. 5.8 (b-c). For films with higher deposition time the growth occurs with multiple nucleation centres resulting in higher grain size. The grain size increases upto 15 min. deposition time and then decreases with further increase in deposition time.

5.4.2.3 Compositional analysis

The compositional analysis of copper telluride was carried out by Energy-Dispersive X-ray analysis (EDAX), as shown in Fig. 5.9 (a, b, c, d). From the graph it is noted that for bath (3); with deposition time of 5 min. the atomic percentage of copper is 59.14, while that of telluride is 40.86, for deposition time 10 min. the atomic percentage of copper is 62.28, while that of telluride is 37.72, for deposition time of 15 min. the atomic percentage of copper is 64.27, while that of telluride is 35.73 and for deposition time of 20 min. the atomic percentage of copper is 72.33, while that of telluride is 27.67. As deposition time increase the atomic percentage of copper decreases and that of telluride increases. Table 5.3 shows comparison of chemical composition and optical band gap energy with different deposition time.
Fig. 5.9 EDAX patterns of copper telluride thin films for bath (3); with deposition time of (a) 5 min, (b) 10 min, (c) 15 min, and (d) 20 min.
5.4.2.4 Optical properties

Optical band gap energy values for copper telluride thin films for bath (3) with different deposition times are shown in Fig. The optical band gap of copper telluride films estimated from the Fig. 5.10 (a, b, c, d) is 2.54 eV for 5 min. deposition time, 2.65 eV for 10 min. deposition time, 2.90 eV for 15 min. and decreases to 2.80 eV with further increase in deposition time of 20 min., these optical band gap energy values are nearly equal with reported values [11, 16]. The band gap energy value goes on increases with decrease in crystallite size for increase in deposition time. The change in the band gap with crystal size is explained in section 3.4.2.4 and 4.4.2.4. There is a tendency that more telluride rich films have a higher band gap.

![Graph showing optical band gap energy values](image)

**Fig. 5.10** Optical band gap of copper telluride thin films for bath (3); with deposition time of (a) 5 min., (b) 10 min., (c) 15 min., (d) 20 min.
Fig. 5.11 (a, b, c, d) represents the absorption spectra in the range of 300-800 nm of the as-prepared copper telluride nanomaterials. It is shown that the three copper telluride nanostructures have two absorption regions shown in Fig. 5.11 (a, b, c). First absorption region is within the range of 350-400 nm, second absorption region is from 500-570 nm. Differently, the absorption ranges of the copper telluride onion flower like structure are narrower and more obvious than those of the copper telluride nanograins patterns. For bath (3); with 20 min. deposition time shows one absorption region ranges from 475-575 nm shown in Fig. 5.11 (d). The results suggest that the variety in the morphology of the materials can lead to some subtle distinction in their optical absorption but overall absorption spectrum is not affected by the shapes of the products.

![Absorption spectra](image)

**Fig. 5.11** Optical absorption spectra of copper telluride thin films for bath (3); with deposition time of (a) 5 min., (b) 10 min., (c) 15 min., (d) 20 min.
Table 5.4 Chemical composition, optical band gap energy, crystallite size and film thickness of copper telluride thin film with different deposition time

<table>
<thead>
<tr>
<th>Deposition time (min.)</th>
<th>Cu (at %)</th>
<th>Te (at %)</th>
<th>Band gap (eV)</th>
<th>Crystal size (nm)</th>
<th>Film thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>59.14</td>
<td>40.86</td>
<td>2.54</td>
<td>15</td>
<td>524</td>
</tr>
<tr>
<td>10</td>
<td>62.28</td>
<td>37.72</td>
<td>2.65</td>
<td>12</td>
<td>599</td>
</tr>
<tr>
<td>15</td>
<td>64.27</td>
<td>35.73</td>
<td>2.90</td>
<td>9</td>
<td>685</td>
</tr>
<tr>
<td>20</td>
<td>72.33</td>
<td>27.67</td>
<td>2.80</td>
<td>11</td>
<td>458</td>
</tr>
</tbody>
</table>

5.4.2.5 Raman spectroscopy

A feature of Raman scattering is that each line has a characteristic polarization, and polarization data provide additional information about molecular structure.

Fig. 5.12 Raman spectrum of copper telluride thin film for bath (3); with deposition time of 15 min.
The lattice vibrational modes of the copper telluride compound have been obtained at room temperature by the Raman spectra. In Fig. 5.12 peak observed at 268 cm\(^{-1}\) assigned to the E or B\(_2\) modes, agree quite well with the peaks observed in Raman spectrum of reported literature [18] of copper telluride samples. On the other hand, the peak that appears at 255 cm\(^{-1}\), which is only Raman active, is assigned to the A\(_1\) mode. Four peaks at 327, 351, 380, 423 cm\(^{-1}\), probably having the E symmetry, are also observed.

**5.4.2.6 Thickness measurement**

Fig. 5.13 shows the film thickness versus deposition time for copper telluride. It is seen that the film thickness increases with increasing deposition time from 5-15 min. attains maximum value at 15 min. (685 nm), from 20 min. deposition time it decreases.

![Graph showing film thickness vs deposition time](image)

**Fig. 5.13** Film thickness of copper telluride deposited at various deposition time for bath [3]
This can be explained as follows: initially, at lower deposition time, e.g. 5 min. the deposition time may not be sufficient to deposit the copper and telluride ions from the solution on substrate therefore, results in low thickness. At a particular deposition time, reduction of copper and telluride occurs at the optimum rate resulting maximum thickness. A noticeable decrease of the film thickness with increasing the deposition time is observed after 20 min. Hence copper telluride thin film with deposition time 15 min. and bath (3) is optimized with thickness.
References