Research Article

Electrodeposition and Characterization of CuTe and Cu₂Te Thin Films

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An electrodeposition method for fabrication of CuTe and Cu₂Te thin films is presented. The films' growth is based on the epitaxial electrodeposition of Cu and Te alternately with different electrochemical parameter, respectively. The deposited thin films were characterized by X-ray diffraction (XRD), field emission scanning electronic microscopy (FE-SEM) with an energy dispersive X-ray (EDX) analyzer, and FTIR studies. The results suggest that the epitaxial electrodeposition is an ideal method for deposition of compound semiconductor films for photoelectric applications.

1. Introduction

Semiconducting compounds such as I–VI copper chalcogenides are widely used in the fabrication of photoconductive and photovoltaic devices [1]. Copper based chalcogenides exhibited the characteristics of a p-type semiconductor for the vacancies of copper and are potential materials for wide applications. Thin films of copper chalcogenides especially have been a subject of interest for many years mainly because of their wide range of applications in solar cells [2], superionic conductors [3], photodetectors, photothermal [4] converters [5], electroconductive electrodes [6], and so forth.

Of these copper chalcogenides, copper telluride compounds have gained great interest owing to its superionic conductivity [7], direct band gap between 1.1 and 1.5 eV [8], and large thermoelectric power. In the literature, a number of methods for preparation of Cu_xSe [9] and Cu_xS [10, 11] thin films have been reported. However, fabrication of CuTe thin films is much less studied to date. Copper telluride compounds (Cu_xTe, where $x = 1, 2$ or between 1 and 2) were known to exist in a wide range of compositions and phases whose properties are controlled by the Cu:Te ratio [12] and can be grown by chemical bath deposition, coevaporation, and fusion method [13].

Electrochemical atomic layer deposition is considered as a controllable and simple deposition technique [14] for homogeneous compound semiconductors on conductive substrates without annealing [15]. The electrochemical atomic layer deposition was based on the alternated underpotential deposition which was a phenomenon of surface limited [16] so that the resulting deposit was generally limited to one atomic layer [17]. Thus, each deposition cycle formed a single layer of the compound [18, 19], and the number of deposition cycles controls the thickness of deposits [20]. In this paper, an epitaxial electrodeposition method for preparation of CuTe and Cu₂Te thin films on ITO substrates by controlling the solution conditions in contact with the deposit and the potential of the electrode is reported. The crystallographic structures of the obtained films are discussed on the basis of X-ray diffraction data. Field emission scanning electronic microscopy (FE-SEM) with an energy dispersive X-ray (EDX) analyzer shows investigation of morphology. Optical characteristics of the films are studied by FTIR.

2. Experimental

Electrochemical experiments were carried out using a CHI 660A electrochemical workstation (CH Instrument, USA).

The deposition was performed in a three-electrode cell with a platinum wire as counter electrode and Ag/AgCl/sat. KCl as reference electrode. Indium doped tin oxide (ITO) glass slide ($\approx 20 \Omega/\text{cm}$) was used as a working electrode. Prior to electrodeposition, the ITO substrate was ultrasonic cleaned with acetone, ethanol, and water sequentially.

All solutions were prepared with nanopure water purified by the Milli-Q system (Millipore Inc., nominal resistivity $18.2 \text{ M}\Omega \text{ cm}$), and all chemicals were of analytical reagent grade. The oxygen was removed by blowing purified N_2 before each measurement, and the whole experiments were conducted at room temperature.

The crystallographic structures of the thin films obtained were determined by XRD (Rigaku D/max-2400). The morphology is investigated by FE-SEM (Kevex JSM-6701F, Japan) equipped with an EDX analyzer. Glancing angle absorption measurements were performed using an FTIR spectrophotometer (Nicolet Nexus 670, USA).

3. Results and Discussion

3.1. Thin Film Deposition

3.1.1. CuTe Thin Film Deposition. Figure 1 shows the cyclic voltammograms of ITO electrode in blank and Cu solution, respectively. For CuTe film growth, H_2SO_4 was used as supporting electrolyte. From Figure 1(b), only one pair of redox peaks was observed at -0.34 V (C1) and 0.30 V (A1), corresponding to Cu^{2+} reduction to Cu, as reaction (1) shows

Figure 2 shows the cyclic voltammograms of Cu-covered ITO electrode in $0.1 \text{ M H}_2\text{SO}_4$ and in $5 \text{ mM H}_2\text{TeO}_3 + 0.1 \text{ M H}_2\text{SO}_4$ solutions. In these experiments, the potential scanning was started at 0 V to avoid the oxidative stripping of Cu. Similar to most literatures, two reduction peaks are seen: peak C2 at about -0.21 V based upon the four-electron process for Te reduction shown in reaction (1) and peak C3 at about -0.46 V , which should be corresponded to bulk Te (0) reduction to Te^{2-} , as reaction (2) shows

Therefore, we applied -0.30 V as the electrodeposition potentials for Cu and -0.20 V for Te. Repeat electrodepositing Cu at -0.30 V and Te at -0.20 V for 15 s alternately as many times as desired to grow epitaxial nanofilms of CuTe on ITO substrate.

3.1.2. Cu_2Te Thin Film Deposition. For Cu_2Te film growth, KNO_3 was used as supporting electrolyte because Cu^{+} ions cannot exist in a strong acid solution like $0.1 \text{ M H}_2\text{SO}_4$. Figure 3 shows the cyclic voltammograms of ITO electrode in blank KNO_3 and Cu solution, respectively. In Figure 3(b), two well-defined cathodic peaks are located at -0.23 V (C4) and -0.51 V (C5), which are related to the formation of Cu_2O

FIGURE 1: Cyclic voltammograms of ITO electrode in (a) $0.1 \text{ M H}_2\text{SO}_4$; (b) $0.1 \text{ M H}_2\text{SO}_4$ with 5 mM CuSO_4 (scan rate: 10 mV/s).

FIGURE 2: Cyclic voltammograms of Cu-covered ITO electrode in (a) $0.1 \text{ M H}_2\text{SO}_4$; (b) $0.1 \text{ M H}_2\text{SO}_4$ with 5 mM TeO_2 (scan rate: 10 mV/s).

and reduction of Cu on the ITO substrate, as reaction (4) and (1) show [14]:

Figure 4 shows the cyclic voltammograms of Cu_2O -covered ITO electrode in 0.1 M KNO_3 and in $5 \text{ mM H}_2\text{TeO}_3 + 0.1 \text{ M KNO}_3$ solutions. From Figure 4(b), two reduction peaks are also seen: peak C6 at about -0.35 V based upon the H_2TeO_3 reduction to Te and peak C7 at about -0.60 V corresponding to Te reduction to H_2Te , which immediately react with the underlying Cu_2O layer to form Cu_2Te , as reaction (5) shows

FIGURE 3: Cyclic voltammograms of ITO electrode in (a) 0.1 M KNO_3 ; (b) 0.1 M KNO_3 with 5 mM CuSO_4 (scan rate: 10 mV/s).

FIGURE 4: Cyclic voltammograms of Cu_2O -covered ITO electrode in (a) 0.1 M KNO_3 ; (b) 0.1 M KNO_3 with 5 mM TeO_2 (scan rate: 10 mV/s).

Therefore, we applied -0.20 V as the electrodeposition potentials for Cu and -0.60 V for Te. Repeat electrodepositing Cu at -0.20 V and Te at -0.60 V for 15 s alternately as many times as desired to grow epitaxial nanofilms of Cu_2Te on ITO substrate.

3.2. Thin Film Characterization

3.2.1. X-Ray Investigations. Identification of the obtained thin films was carried out using the X-ray diffraction method. The recorded XRD patterns of deposited CuTe and Cu_2Te are presented in Figure 5. Figure 5(a) shows the XRD patterns of deposited CuTe film. The observed peak positions of the deposited CuTe film are in well agreement with those due to reflection from (0 1 1), (1 0 1), and (1 1 2) planes of the reported CuTe data with an orthorhombic structure

FIGURE 5: XRD patterns of deposited CuTe (a) and Cu_2Te (b) films.

(JCPDS 22-0252). The XRD pattern of deposited Cu_2Te film is presented in Figure 5(b). As can be seen, the analysis indicates that the deposited Cu_2Te film is in hexagonal structure, with the preferential orientation of (0 0 6) plane (JCPDS 49-1411).

The average crystal size was estimated using the well-known Debye-Scherrer relationship:

$$d = \frac{0.9 \cdot \lambda}{\beta \cdot \cos \theta}, \quad (6)$$

where θ is the Bragg angle, λ is the X-ray wavelength, and β is the full width at half-maximum. It was found that the average crystal size of the deposited CuTe film is 92.11 nm and Cu_2Te film was found to be about 36.84 nm, which are consistent with the SEM observation.

3.2.2. SEM Observations. The SEM micrographs of deposited CuTe and Cu_2Te films are shown in Figures 6(a) and 6(b), respectively, at 30,000x magnification. In deposited CuTe film (Figure 3(a)), the grains are more distinct and of bigger size, while, in Cu_2Te film (Figure 3(b)), the grains are of smaller size, more compact with densely packed microcrystals. The EDX analysis was carried out only for Cu and Te. The average atomic percentage of Cu:Te in deposited CuTe film was 50.4:49.6. It is close to 1:1 stoichiometry. Similar results for Cu_2Te were 67.3:32.7, close to 2:1 stoichiometry.

3.2.3. Optical Measurements. For optical characterization, FTIR spectra of deposited CuTe and Cu_2Te thin films were recorded. The optical band gap (E_g) for deposited CuTe and Cu_2Te thin films was calculated on the basis of the FTIR spectra, using the well-known relation

$$\alpha h\nu = A (h\nu - E_g)^{1/2}, \quad (7)$$

where A is the constant, E_g is the band gap, and $h\nu$ is the photon energy. Figure 7 shows the variation of $(\alpha h\nu)^2$ with $h\nu$ for deposited CuTe and Cu_2Te . By extrapolating straight line portion of $(\alpha h\nu)^2$ against $h\nu$ plot to $\alpha = 0$, the optical

FIGURE 6: SEM micrograph of deposited CuTe (a) and Cu₂Te (b) films.

FIGURE 7: The dependence of $(\alpha h\nu)^2$ on $h\nu$ for deposited CuTe (a) and Cu₂Te (b) films.

band gap energy was found to be 1.51 eV for CuTe and 1.12 eV for Cu₂Te films, comparable with the value reported earlier for CuTe and Cu₂Te thin film [1, 15].

4. Conclusion

In this work, the Cu/Te ratio has been successfully controlled to prepare crystalline CuTe and Cu₂Te thin films on the ITO electrode via electrodeposition. The copper-tellurium films were epitaxial electrodeposited under layer-by-layer, potentiostatic conditions. XRD, SEM, and IR studies of the deposited CuTe and Cu₂Te thin films confirm the high quality of the deposits and demonstrate that the epitaxial electrodeposition is applicable to the deposition of stoichiometric nanofilms of copper-tellurium films of good quality.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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