Properties of Te-rich cadmium telluride thin films fabricated by closed space sublimation technique


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Abstract

Cadmium telluride (CdTe) thin films were prepared by the closed space sublimation (CSS) technique, using CdTe powder as evaporant onto substrates of water–white glass. In the next step, the same procedure was adopted by using tellurium as evaporant and already deposited CdTe film as substrate. Such compositions were then annealed at 300 °C for 30 min to obtain Te-enriched films. The samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), spectrophotometry, DC electrical resistivity, dark conductivity and activation energy analysis as a function of temperature by two-probe method. The electron microprobe analyzer (EMPA) results showed an increase of Te content composition in the samples as the mass of the Te-deposition increased in CdTe. The Hall measurements indicated the increase in mobility and carrier concentrations of CdTe films by addition of tellurium. A significant change in the shape and size of the CdTe grains were observed.

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1. Introduction

As a result of recent advances in the efficiency of CdTe-based solar cells [1–3], interest in this material for thin film terrestrial photovoltaic applications [4–6] is increasing. CdTe has a direct band gap of 1.5 eV at room
temperature, which is optimum for single junction solar cell efficiency [3]. CdTe can exhibit both types of conductivity, n and p, which makes diode technology [7] and field effect transistors [8] possible, and it can exhibit a semi-conducting state as well [9]. CdTe-based semi-magnets, like CdMnTe, display extremely exciting properties, which have not so far been completely exploited. Wu et al. [10] have reported on a CdTe/CdS solar cell with an efficiency of 16.5%. Because of its low sublimation temperature, CdTe polycrystalline films can be prepared by several techniques, such as thermal evaporation [11], metal organic chemical vapour deposition (MOCVD) [12], radio frequency (RF) sputtering [13], closed space sublimation (CSS) [14], screen printing [15], hot-wall flash evaporation [16], molecular beam deposition [17,18], hot-wall vacuum evaporation [19–21], etc. The CSS technique is one of the various techniques that have produced encouraging results. The CSS process offers the advantages of simple deposition apparatus and high transport efficiency conducted under low vacuum conditions at moderate temperatures, thus, simplifying scale-up for high-volume continuous processing [22,23]. It has been pointed out that high efficient solar cells possess Te-rich CdTe surfaces with smooth interfaces of p-CdTe/n-CdS [24].

The successful experimental approach will open a pathway for improving devices based on CdTe, such as solar cells, γ and IR detectors and field effect transistors [8]. The efficiency of these devices is strongly determined by the electrical and optical properties of the films. The systematic research on these properties in correlation with doping/excess of materials and with the film preparation conditions is still necessary for a more comprehensive understanding of this correlation and for the control of the properties of these films.

In the present work, we have fabricated Te-rich CdTe films using a home made CSS system and investigated the effects of Te addition on the crystal structure, morphology, electrical and optical properties such as film thickness, refractive index, absorption coefficient and optical band gap.

2. Experimental procedure

Usually, the deposition of CdTe films is based on the following reversible high-temperature process [25]:

\[
2\text{CdTe(s)} \leftrightarrow 2\text{Cd(g)} + \text{Te}_2(g).
\]

The CSS technique, however, offers the near-distance deposition without marked dissociation of the components. The CSS system used in our experiment is shown in Fig. 1.

Thin films of CdTe powder (99.99% pure) of Aldrich chemical company were prepared onto microscope slides of water–white glass substrates of size 25.4 mm × 76.2 mm. For that source material (14 mg) was put in the graphite boat of size 20 mm × 45 mm, heated by a halogen lamp (1000 W) connected to the main power through temperature controller with K-type thermocouple (Chromel & Alumel,—270–1350 °C). The substrate was fixed at a distance of about 4 mm from the source material. It was heated by a second halogen lamp (500 W), while the thermocouple was placed over the substrate to measure its surface temperature. Source and substrate temperatures were 400 and 300 °C, respectively. The substrate was fixed at a distance of about 4 mm from the source material. The chamber was evacuated down to \(10^{-3}\) mbar with the help of rotary pump. The deposition time for each film was 5 min at the source temperature of 400 °C. After that the source and substrate lamps were switched off for cooling down to 100 °C before opening the chamber.

In the next step, these CdTe films were covered with varying excess Te mass of 0.5, 1, 2, 3, 4 and 5 mg, respectively, which was evaporated onto them by CSS technique. These films were numbered 2–7 as given in Table 1. The temperature of the source and substrate was 200 and 100 °C, respectively. Again, the substrate was fixed at a distance of about 4 mm from the source material. The time of Te evaporation was 5 min for each sample. The vacuum of the system was \(10^{-3}\) mbar. After that all samples were annealed at 300 °C for 30 min under the same vacuum. Finally they were gold coated for ohmic contacting to perform Hall measurements. Table 1 compiles the samples denoted by Nos. 2–7 with successively varying Te content obtained after tellurium
deposition and annealing procedure by the above technique.

The structure of the films was studied by X-ray diffraction (XRD) using Cu-K$_\alpha$ (1.5418 Å) radiation with operating conditions voltage/current 40 kV/30 mA. The microstructure of the samples was checked using scanning electron microscope (SEM). The SEM accelerating voltage was 10 kV. The compositions of Cd and Te of all the samples were measured with the help of electron microprobe analyzer (EMPA) attached to the SEM. The optical properties such as film thickness, refractive index, absorption coefficient and optical band gap were calculated from the transmission spectra between 300 and 2500 nm recorded by Lambda 900 spectrophotometer.

The most direct and perhaps the simplest method for probing the band structure of semiconductors is to measure the absorption spectrum. A method for the calculation of the film thickness $d$ and refractive index $n$ from the transmission measurements was developed by Aqili and Maqsood [26] where $d$ can be determined from two maxima or minima. Thickness should be in nanometer range for good transmission spectra and other optical measurements. The values of $n$ and $d$, calculated from the above method are used as initial least-squares fitting parameters in the theoretical model [27] for the following equation:

$$ T = \frac{Ax}{B - Cx \cos(\phi) + Dx^2}, $$

where $A$, $B$, $C$, $D$ are constants and $T$ is the normal transmittance for the system consisting of a thin film on transparent substrate surrounded by air (refractive index $n = 1$) and taking all multiple reflections at the interface into account. In case of $k^2 \ll n^2$, which is true for this kind of semiconductor thin films, where $k$ is the extinction coefficient of the film, an empirical formula for the $n$ dependence of $\lambda$ as $n = a + b/\lambda^2$ can be used with $a$ and $b$ constants obtained from fitting the transmission spectra.

During the present investigation a two-point probe method was used to measure the sheet resistance $R_s$ of all the films by the relation $R_s =$
\[ V/I - R_i \]

where \( R_i \) is the internal resistance of the multimeter DM 350. The electrical properties such as sheet resistance, DC resistivity, dark conductivity and activation energy as functions of temperature (50–200 °C) were measured by the two-probe method at a pressure of \( 10^{-6} \) mbar in a 306 A Edward vacuum coating unit. Silver paste was used above the gold coatings for electrical contacts. The resistivity, mobility and carrier concentrations were determined by room temperature Hall measurements.

3. Results and discussion

The XRD patterns (arranged by XRD software) of the samples 1, 3, 5, 6 and 7 are compared in Fig. 2. The main reflections of four samples (1, 3, 6 and 7) are the same and can be indexed according to fcc CdTe lattice. The values of the lattice constant \( a_0 \) are for the sample (1) and for Te-enriched samples (3, 5, 6 and 7) 6.49, 6.44, 6.86(3), 6.57(2) and 6.54(3) Å, respectively. These values are calculated and averaged after comparison of respective experimental \( d \) values in agreement with the \( d \) standard values of the lattice constant according to 1999 JCPDS–International Centre for Diffraction Data 10-0207, 15-0770, 75-2086 and 75-2083 (PCPDFWIN v. 2.02). The increase in the lattice constant of the Te enriched samples can be explained as follows. During the annealing the diffusing Te atoms may replace the Cd atoms by a kick off mechanism besides its diffusion at interstitial position in the lattice, which results in an increase of the lattice constant. In sample 5 a new peak corresponding to 200 reflex appeared as shown in Fig. 2c. It matches with CdO mineral powder diffraction file (5-640) according to data book published by Joint Committee on Powder Diffraction Standards ICDD USA 1980, where-as the (1 1 1) plane disappeared completely. The presence of oxide is due to the heat treatment under low vacuum. It was observed in sample 3 that all the peaks were shifted by (0.4°) towards the higher range (right side). This shows that the lattice is in uniform strain due to expansion of the cell. The expansion of the cell can be explained on the basis

<table>
<thead>
<tr>
<th>Sl. no.</th>
<th>Te composition (at%)</th>
<th>Lattice constant ( a_0 ) (Å)</th>
<th>Thickness ( d ) (nm)</th>
<th>Refractive index ( n=\frac{a+b+c}{2} )</th>
<th>Energy gap ( E_g ) (eV)</th>
<th>Sheet resistance ( R_s ) at 200 °C (Ω sq)</th>
<th>Resistivity ( \rho ) at 200 °C (Ω cm)</th>
<th>Mobility ( \mu )</th>
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of radius of the Te atom, which is larger than that of the Cd atom. Thus, the incorporation of extra Te leads to the expansion of the CdTe lattice. A similar observation has been reported by Li et al. [14]. The change in intensities was also observed. The strongest (111) reflection in the pattern indicates a preferential orientation of [111] in the films as already reported [28]. Also the grains of the film became larger with the increase of Te content in the samples, which indicates that the crystallinity of the films can be improved by appropriate Te enrichment.

The Te content after its deposition and annealing determined by EMPA is shown in Table 1. The results show that the Te content in samples 1–7 is increasing. The ratio of at% of Cd and Te in as-deposited CdTe sample is 47.45:52.55, i.e. less than 1 which is considered the reason for CdTe films with slight p-type conduction due to the formation of Cd vacancies in CdTe lattice acting as acceptor centers. The Te content was increased up to 60.43% in sample 7, which is maximum Te-enriched. It is clear from these values that already the samples grown from the pure CdTe source have a deficiency in Cd, which can be almost 5 at%. On the other hand, the additional Te in the source leads to an increase of the Te content from 52.55 to 60.43 at%, as in samples 1–7. The lower Cd content gives rise to the formation of vacancies of Cd in the CdTe lattice. From Hall measurements samples 1–7 show p-type conductivity. The amount of excess Te in the films mainly affects their electrical properties. As can be seen from Table 1 the resistivity of the samples decreases with increasing Te content by two orders of magnitude.

SEM images in Fig. 3 show the main feature of the CSS technique, i.e. the Te-enriched films have larger grains. The crystallographic arrangements are related to the stress in the layer and to the application of annealing at high temperature. After optimization of annealing time, the average grain size of as-deposited film is under 540 nm while that of Te-enriched films in Figs. 3(b, c) are about 990 nm and 2 μm, respectively. The creation of larger grains is as a result of coalescence of small grains into bigger ones which can be seen from Fig. 3(c). This is consistent with the above results of XRD. Also a significant change of the grain shape was observed. It appears that the annealing in the presence of Te facilitates the grain growth in the CdTe films in such a way that some of the small grains coalesce together and
reorient themselves, which decrease the number of grain boundaries. As a result an improved different microstructure and morphology is created. Grain growth in CdTe is well known and reported for a solid-state recrystallization (SSR) method [29,30]. Usually CdTe films have a high absorption in the region of visible and near infrared. Indeed, the same was observed in the films deposited during this study. The transmission spectrum of the films did not change significantly after the optimization of heat treatment for 30 min, which ensured the diffusion of Te in the samples. The obtained thickness values are in the range of 264–730 nm. The transmittance slightly decreases with increase of Te content as shown in Fig. 4(a). Fig. 4(b) shows the resulting fit of Eq. (1) to experimental data. A good fitting in the transparent region is obvious.

Fig. 5. illustrates the change of refractive index $n$ with Te content. The increase in the refractive index is due to the change in the lattice constant. For the calculation of absorption coefficient $\alpha$ in the high absorption region the values of $n$ and $d$ from the fitted curve are used. A high absorption coefficient is important from both technological and economic considerations. Large absorption coefficient permits the absorber layer to be thin and hence less material is necessary for photovoltaic device fabrication. Since the region of high absorption in our films matches well with the solar spectrum, these films are optically well-suited for use as an absorber in solar cells.

For the bandgap determination the following relation can be used [31]:

$$\alpha h \nu = A (h \nu - E_g)^{N/2}. \tag{2}$$

Here $A$ is a constant, $h \nu$ the photon energy, $E_g$ the optical band energy gap and $N$ depends on the nature of the transition ($N = 1$ for direct band gap and $N = 4$ for indirect band gap transition). By extrapolating $(\alpha h \nu)^2$ vs. the incident photon energy ($h \nu$) plot the band gap can be obtained. The values
of energy gap, thickness and refractive index of all the sample series are listed in Table 1. The decrease in the energy gap is also due to tellurium diffusion into the CdTe films.

The sheet resistance in the present case for the as-deposited sample 1 was $5.58 \times 10^6 \Omega/\text{sq}$ at $200^\circ \text{C}$, while it dropped to $2.12 \times 10^5 \Omega/\text{sq}$ in Te-enriched sample 7 at the same temperature. For the resistivity determination by two-probe method the following relation could be used:

$$\rho = R_s d \frac{w}{\ell}, \quad (3)$$

where $R_s$ is the sheet resistance, $d$ the thickness, $w$ the width and $\ell$ the length of the film.

In general, as-prepared CdTe films, fabricated by various techniques, show a high electrical resistivity ($10^7$--$10^9 \Omega \text{cm}$) at room temperature [14]. The change in sheet resistance and resistivity of the samples as function of Te content at temperature $200^\circ \text{C}$ is shown in Table 1. As can be seen these values decrease with the increase of Te content.

The change of the electrical property of Te-enriched samples can be easily understood according to the above analysis of the sample microstructure. The grains of Te-rich samples become larger and the crystallinity improves which results in the decrease of the number of grain boundary and, hence, of the decrease in the grain barriers. All these changes are favorable for the transport of carriers. It is shown in Figs. 6 and 7 that the dark conductivity of the samples as a function of temperature ($50$--$200^\circ \text{C}$) is increasing. The dark conductivity activation energy ($E_a = E_f - E_v$) was deduced by linear fitting $\ln(\sigma)$ vs. $1/k_B T$ ($k_B$-Boltzmann constant). The slope gives the activation energy. The representative activation energy of one of the Te-rich sample 7 is shown in Fig. 7.

The resistivity of sample 7 with a van der Pauw geometry was $\sim 156 \Omega \text{cm}$ at room temperature, while the mobility and carrier concentration at room temperature were about $129.3 \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ and $3.09 \times 10^{14} \text{cm}^{-3}$, respectively. After Te addition the conductivity of the samples was markedly
improved. This improvement of the film conductivity could be attributed to the increased grain growth taking place in the CdTe films in presence of Te. As the concentration of Te increased the resistivity was reduced, probably due to the Te doping effect in CdTe. Similar results are reported by Turkevych et al. [32] for similar temperatures. It has been observed by Hall measurements that p-type doping is achieved in Te-enriched CdTe films prepared by CSS technique. This is caused by the excess of Te atoms replacing a part of the lattice that might create Cd vacancies, which increase the p-type carriers. Further work on this material is under progress and will be addressed in future.

4. Conclusion

In this work, Te-enriched CdTe films have been fabricated by the CSS technique with subsequent annealing. On the basis of the XRD, SEM and Hall measurements one can conclude that the post annealing strongly affects the morphology as well as electrical properties. The samples show large grains with size ~2 μm which can grow larger with increasing Te content. The values of refractive index increases with the increase of Te concentration. The transmission spectra showed a decrease of transmittance with increase of Te. The band gap values are also influenced by Te incorporation. The sheet resistance, DC electrical resistivity and activation energy of Te-rich samples were decreased but the dark conductivity, mobility and carrier concentration were increased significantly compared to pure CdTe samples. The increase of the film mobility could be due to the enlargement of the grains size, while the diffusion of Te in the CdTe films cause an increase in the number of the charge carriers.

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