



Comparative study of electrical properties of Cd and Te-enriched CdTe thin films at cryogenic temperature

Nazar Abbas Shah*

Thin Films Research Laboratory, Department of Physics, COMSATS Institute of Information Technology, Park Road, Islamabad 45320, Pakistan

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ABSTRACT

Cd and Te-enriched cadmium telluride (CdTe) polycrystalline thin films were grown on corning glass substrates by Close Spaced Sublimation (CSS) technique. The structural investigations performed by means of X-ray diffraction (XRD) technique, scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDX) showed that the deposited films exhibit a polycrystalline structure with (1 1 1) as preferred orientation. The optical transmittance for Te-enriched CdTe sample was above 0.8 in the range of 1500–2500 nm, which was significantly below 0.8 for Cd-enriched CdTe sample. The electrical properties of these samples were analyzed as a function of the Cd and Te concentration at cryogenic temperature. The electrical resistivity dropped several orders of magnitude. These properties are significantly changed at cryogenic temperature. The comparative study revealed that using this deposition technique, *n*-type, and *p*-type Cd and Te-enriched CdTe polycrystalline films can be produced.

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1. Introduction

Search for efficient photo-receiving materials is a long standing demand of scientific community. CdTe is II–VI semiconductor material quite appropriate for applications to solar energy conversion devices [1–3]. Though this semiconductor has been focused as solar cell material but could not get much attention commercially due to its cost factors. An important reduction in the cost of solar cells can be achieved by preparing doped polycrystalline thin films of appropriate quality. CdTe thin films have been prepared by several growth techniques [4–19]. However, the best CdTe thin films based solar cells have been fabricated using CSS method which is one of the various techniques with large area manufacturing potential due to its high throughput and efficient material utilization [20]. Thin films prepared by the CSS method have distinct novel features such as large grain sizes, well-defined preferential orientation and relatively high absorption coefficients needed in the fabrication of solar cells material [20].

In this paper we present some of the electrical properties of Cd and Te-enriched CdTe thin films prepared by the CSS method. The experiments were carried out by taking Hall measurements at cryogenic temperature. Furthermore, comparative analysis of measured physical properties is presented. To our knowledge the comparative study of Hall measurements on Cd and Te-enriched CdTe thin films at liquid nitrogen temperature are not reported earlier.

2. Experimental

The deposition of CdTe thin films by the CSS technique is based on the following reversible dissociation of CdTe at high temperature:



The schematic diagram of Close Space Sublimation (CSS) experimental set up is shown in Fig. 1, where a small distance of about 5 mm separates the CdTe source from a corning glass substrate. The source temperature was kept higher than that of the substrate, because the source CdTe dissociates into its constituent elements, i.e. Cd and Te and then recombines on the substrate surface, which was kept at a lower temperature. The source and substrate could be maintained at the desired temperature as they were heated and controlled separately. Two K-type thermocouples were used to monitor the temperatures of the source and the substrate during the evaporation process. The temperatures of the source and substrate were maintained at 500 and 400 °C, respectively.

The source material (CdTe 99.999% purity) was placed in a graphite sublimation cast as shown in Fig. 1. The substrate was first cleaned with IPA bath in an ultrasonic cleaner for about 60 min and further cleaned by lint free tissues with the help of tweezers and finger cots to avoid fingerprints on the glass substrate. The substrate was then supported by the cast which was made of heat insulating mica sheet and kept in a close proximity to the source material. Initially the vacuum chamber was allowed to evacuate by a rotary vane pump. The chamber was kept for evacuation for about an hour each time to reach approximately 10^{-3} mbar.

The optimized time for deposition was 5 min for each thin film. The thin film was then kept at substrate temperature until the temperature of source became lower than the substrate temperature after that the substrate heater was switched off to allow cooling to ~ 40 °C before opening the vacuum chamber. By using the automatic temperature controller for heating the source and substrate, the quality of the thin film was optimized.

In the next step, these as-deposited CdTe thin films were used as substrate for varying excess Cd mass (99.99% purity) deposition by the same technique to get Cd-enriched samples. The source (Cd) and substrate (CdTe) temperatures were kept at 350 and 250 °C, respectively.

* Tel.: +92 519235036; fax: +92 514442805.

E-mail address: nabbasqureshi@yahoo.com.

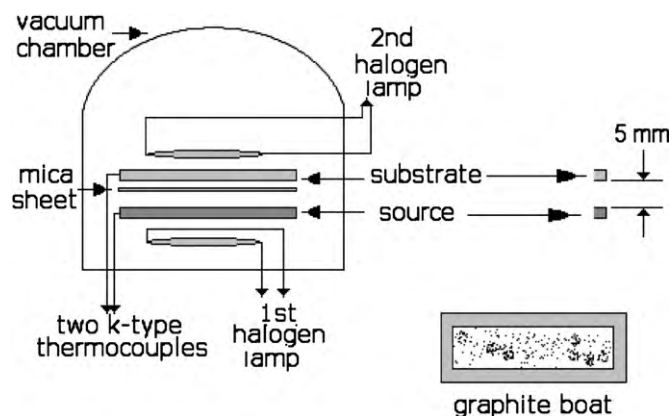


Fig. 1. Schematic diagram of Close Space Sublimation (CSS) experimental set up.

Similarly the CdTe thin films were covered with varying excess Te mass, which was evaporated onto them by CSS technique under the same vacuum conditions to get Te-enriched samples. This time the temperature of the source (Te) and substrate were kept at 200 and 100 °C, respectively. The time of Te evaporation was 5 min for each thin film. After that all the Cd and Te-enriched thin films were annealed at 300 °C for about 30 min under the same vacuum. The annealed samples were characterized and their electrical properties were studied at cryogenic temperature.

The structure of the samples was studied by XRD technique. The compositional analysis of the samples was determined by EDX attached with the SEM. Transmission spectra of Cd and Te-enriched samples were taken by the UV–vis–NIR spectrophotometer. Resistivity, mobility and carrier concentration of samples were measured by Hall Effect measurements system HMS 3000 Ecopia at liquid nitrogen temperature.

3. Results and discussions

3.1. X-ray diffraction studies

The structural analysis of the samples were carried out by using X-ray diffraction technique with Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$). The XRD patterns of the as-deposited and Cd and Te-enriched CdTe samples are similar in the main reflection and can be indexed based on a cubic CdTe lattice. The strong (1 1 1) reflection in the patterns indicates a preferential orientation of [1 1 1] in thin films as already reported for thermally evaporated CdTe thin films [18,19]. The position of (1 1 1) crystalline line shifts slightly to a higher angular position by increasing Cd concentration. There is an inverse relationship between lattice constant and Cd concentration; lattice constant decreased on increasing Cd concentration. The incorporation of extra Cd reduces the lattice constant which is due to reduction in the bond length produced by the interstitial Cd atoms in CdTe lattice. While the increase in the lattice constant of the

Table 1
Composition of Cd and Te in Cd-enriched CdTe samples.

Sample no.	Cd (at.%)	Te (at.%)	Lattice constant (Å)
1 (as-deposited)	45	55	6.48
2	46	54	6.46
3	48	52	6.45
4	51	49	6.43
5	52	48	6.42

Table 2
Composition of Cd and Te in Te-enriched CdTe samples.

Sample No.	Cd (at.%)	Te (at.%)	Lattice constant (Å)
1 (as-deposited)	47	53	6.48
2	46	54	6.49
3	43	57	6.56
4	41	59	6.57
5	40	60	6.54

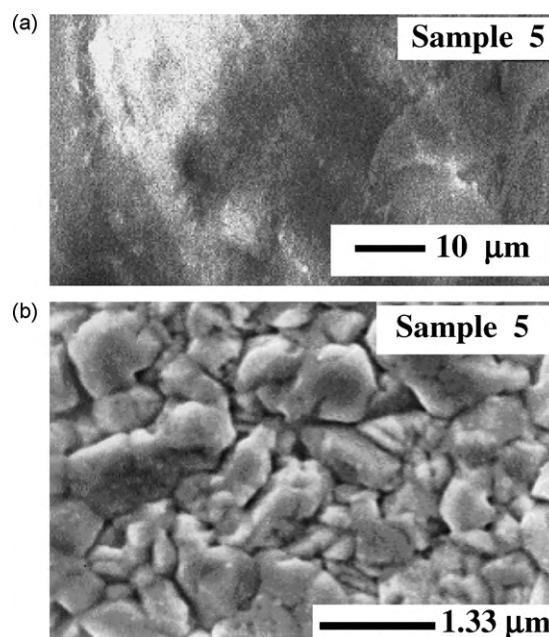


Fig. 2. (a) SEM image of the Cd-enriched sample 5. (b) SEM image of the Te-enriched sample 5.

Te-enriched samples can be explained as follows. The diffusing Te atoms may replace the Cd atoms by a kick off mechanism besides its diffusion at interstitial position in the lattice, during the annealing process. This may result in an increase of the lattice constant [19].

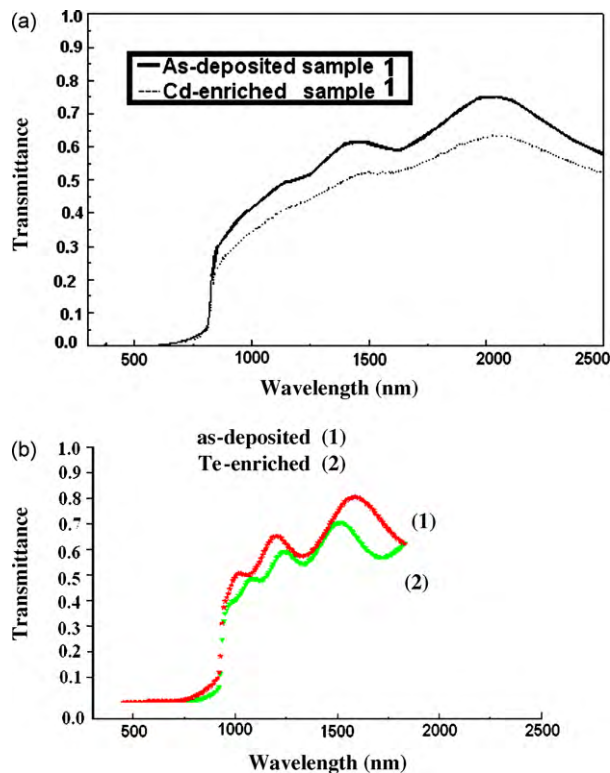


Fig. 3. (a) Transmittance spectra of as-deposited and Cd-enriched sample 1. (b) Transmittance spectra of as-deposited and Te-enriched sample 1.

3.2. Morphology studies

JEOL JSM scanning electron microscope along with energy dispersive X-ray spectroscopy attachment (INCA 200; Oxford Instruments, UK) was used to investigate the elemental composition of Cd-enriched CdTe samples. The EDX analysis of the Cd-enriched and Te-enriched CdTe samples showing actual contents of Cd and Te are given in Tables 1 and 2, respectively. The EDX results showed that the increase in Cd contents in sample 1–5 indicating Cd-enriched into CdTe thin films.

The Te contents after its deposition and annealing was determined by EDX and given in Table 2. The results show increase in the Te contents in the samples 1–5. The ratio of at.% of Cd and Te in as-deposited CdTe sample is 47:53, i.e. less than 1 which is considered as the reason for CdTe films with slight *p*-type conduction, due to the formation of Cd vacancies in CdTe lattice acting as acceptor centers. It is clear from these values that already grown thin films from pure CdTe source have a deficiency in Cd, which are about 6 at.%. On the other hand the additional enrichment of Te in the source leads to an increase of the Te contents from 53 to 60 at.%, as in samples 1–5. The lower Cd contents give rise to the formation of vacancies of Cd in the CdTe lattice. From Hall measurements samples 1–5 show *p*-type conductivity. The amount of excess Te in the samples mainly affects their electrical properties.

The morphology and microstructure of samples analyzed by SEM revealed that the Cd-enriched CdTe samples by using CSS have a significant change in the shape and size. As a result, different

microstructure and morphology are created. SEM images of Cd and Te-enriched CdTe samples are given in Fig. 2a and b, respectively.

In case of Te-enriched samples, the grains of the samples became larger with increasing Te content in the samples, which indicates that the crystallinity of the films can be improved by appropriate Te enrichment. SEM images of 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 the annealing time, average grain size of as-deposited CdTe thin film was under 500 nm while that of Te-enriched sample was about 2 μm , respectively. The creation of larger grains was the results of coalescence of small grains into bigger ones. This is consistent with the results of XRD. It appeared that the annealing process in the presence of Te facilitates the grain growth in the CdTe thin films, and the number of grain boundaries are reduced due to coalesce and reorientation. As a result an improved different microstructure and morphology is created.

3.3. Optical analysis

The transmittance spectra in the range of 300–2500 nm were recorded for as-deposited CdTe, Cd and Te-enriched CdTe samples using Perkin-Elmer, Lambda 900, UV-vis/NIR spectrophotometer with UV-Winlab software. The examination of the CdTe as-deposited samples in the larger wavelength span is possible because our substrates show transmittance above 0.9 from visible to far infrared region. The transmittance spectrum of the Cd-enriched samples did not change significantly after the optimization of heat treatment at 300 °C for about 30 min ensuring the

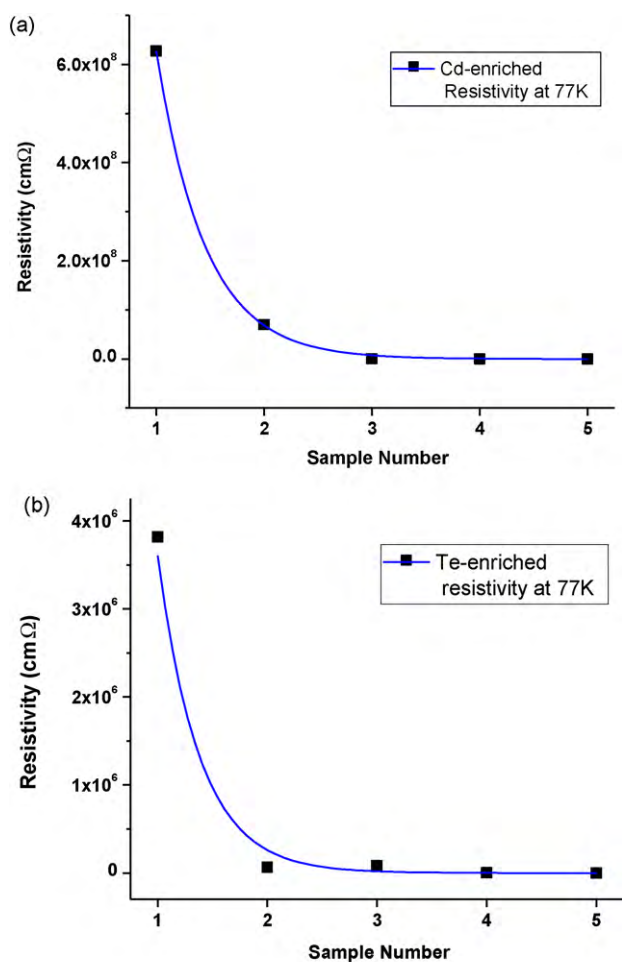


Fig. 4. (a) Electrical resistivity of Cd-enriched samples at cryogenic temperature. (b) Electrical resistivity of Te-enriched samples at cryogenic temperature.

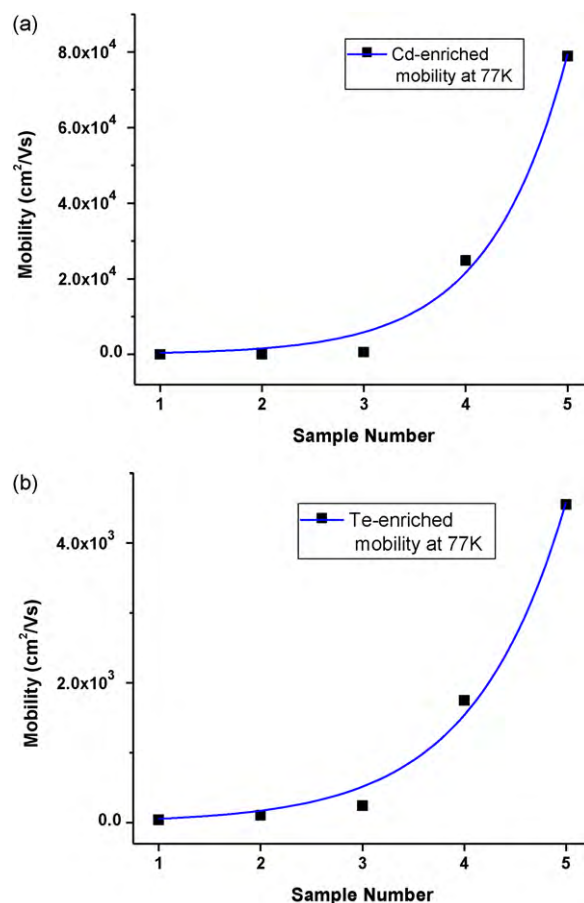


Fig. 5. (a) Mobility of Cd-enriched samples at cryogenic temperature. (b) Mobility of Te-enriched samples at cryogenic temperature.

diffusion of Cd in the samples. The transmittance decreased with the increase of Cd contents as shown in Fig. 3a. It is cleared that the presence of Cd has strongly affected the transmittance. The Cd present in the samples shows high absorption in the respective region.

The optical transmittance for Te-enriched CdTe sample was above 0.80 in the 1500–2500 nm range whereas it was significantly below 0.80 for Cd-enriched CdTe sample. The transmittance decreased with increase of Te contents as shown in Fig. 3b.

3.4. Electrical analysis

Resistivity, mobility and carrier concentration of all Cd and Te-enriched samples were measured by Hall Effect measurements system at liquid nitrogen temperature. For these measurements very low resistance silver wires and silver paste for ohmic contacts were used and all the measurements were performed at cryogenic temperature.

Due to the formation of Cd vacancies in CdTe lattice, acting as acceptor centers, CdTe thin films prepared by different techniques have generally higher electrical resistivity (10^6 – 10^9 Ω cm) with slightly *p*-type conductivity. On the other hand, an excess of Cd atoms located interstitially can produce *n*-type CdTe samples [18]. The resistivity for the Cd-enriched sample 5 was dropped to about 60 Ω cm on Cd concentration reaching 52 at.% as shown in Fig. 4a. The results show that samples having excess of Te contain a small amount of crystalline Te which is embedded into the CdTe structure and gradually disappears with increasing presence of Cd.

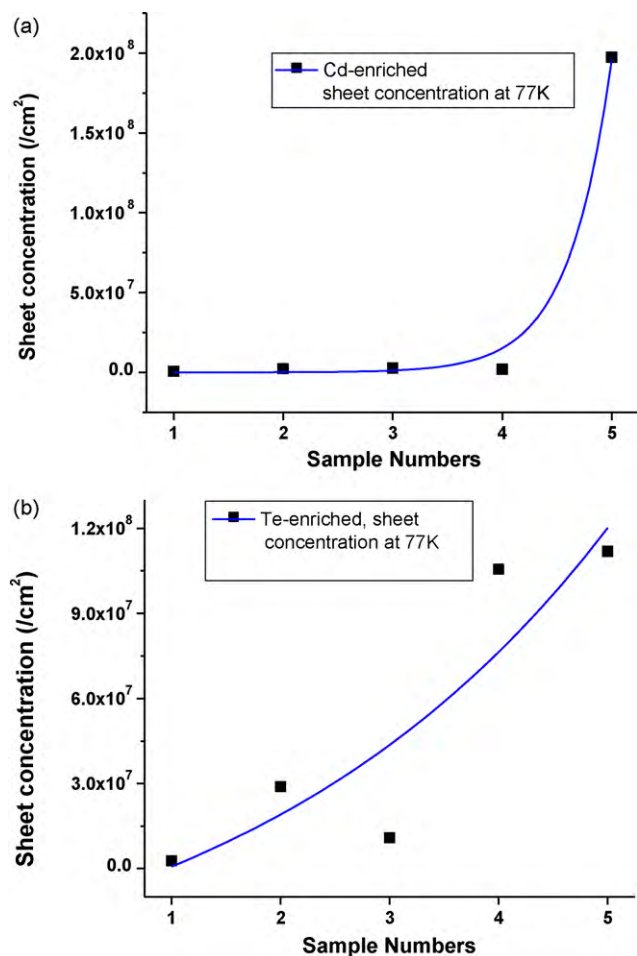


Fig. 6. (a) Carrier concentrations of Cd-enriched samples at cryogenic temperature. (b) Carrier concentrations of Te-enriched samples at cryogenic temperature.

It is also known that CdTe structure in these samples contains Cd vacancies accounting for *p*-type conductivity and therefore, making it difficult for *n*-type doping of this material. The electrical resistivity of these samples changed with increasing Cd concentration. It is clear that the incorporation of Cd, first prevents the formation of crystalline Te and then inhibits the formation of Cd vacancies. At about 50 at.% of Cd, the vacancies have been drastically reduced and on further incorporation of Cd probably go to the interstitial positions in the CdTe lattice. It means that the electrical parameters change as soon as the Cd exceeds the stoichiometric composition indicating an effective enrichment by the interstitial Cd. The mobility of these samples varies from 4.5 to 7.9×10^4 (cm²/Vs) as shown in Fig. 5a for the samples 1–5, respectively. The carrier concentrations for the samples 1–5 were observed in the range of 5.4×10^5 – 1.9×10^8 /cm², respectively at cryogenic temperature, as shown in Fig. 6a.

In the case of Te-enriched samples, the electrical resistivity measured by using Hall Effect was found in the range from 3.8×10^6 to 8.9×10^2 (Ω cm), while mobility was in range of 44– 4.5×10^3 (cm²/Vs) as shown in Figs 4b and 5b for the samples 1–5, respectively. The carrier concentrations for the same samples were recorded in the range of 2.7×10^6 – 1.1×10^8 /cm², respectively as shown in Fig. 6b.

4. Conclusions

The XRD results show the position of (1 1 1) crystalline line shifts slightly to higher angular position as Cd concentration has been increased. While the lattice constant decreases as Cd concentration has been increased. In case of the Te-enriched samples, the lattice constant is increased due to diffusion of Te atoms. A significant change in the shape and size of the grains are observed in Cd as well as Te-enriched samples. The EDX results show the Cd and Te contents in samples are increased indicating the enrichment of Cd and Te into CdTe thin films. Similarly the presence of Cd and Te strongly affect the transmittance of the thin films. The electrical resistivity of CdTe samples with an excess of Cd atoms dropped several orders of magnitude, i.e. 6×10^8 –60 Ω cm and the conductivity has been changed from *p* to *n* type as the composition of the thin films change from Te-enrich to Cd-enrich along with high mobility. It is also showed that Te-enriched CdTe samples have electrical resistivity $\approx 9 \times 10^2$ Ω cm and slightly *p*-type conductivity which is due to the formation of Cd vacancies in the CdTe lattice acting as acceptor centers. The results presented here indicate that *n*-type doping can be achieved when interstitial Cd atoms are incorporated in the CdTe lattice.

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