

## Effect of CdCl<sub>2</sub> Treatment on Physical Properties of CdTe Films with Different Compositions Fabricated by Chemical Molecular Beam Deposition<sup>1</sup>

T. M. Razykov<sup>a, b</sup>, N. Amin<sup>b</sup>, B. Ergashev<sup>a</sup>, C. S. Ferekides<sup>c</sup>, D. Y. Goswami<sup>c</sup>, M. K. Hakkulov<sup>a</sup>, K. M. Kouchkarov<sup>a</sup>, K. Sopian<sup>b</sup>, M. Y. Sulaiman<sup>b</sup>, M. Alghoul<sup>b</sup>, and H. S. Ullal<sup>d</sup>

<sup>a</sup>Physical-Technical Institute, Scientific Association “Physics-Sun” Uzbekistan Academy of Sciences

<sup>b</sup>Solar Energy Research Institute, UKM, Bangi, Selangor Darul Ehsan, Malaysia

<sup>c</sup>University of South Florida, USA

<sup>d</sup>National Center for Photovoltaics, USA

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**Abstract**—CdTe films with different compositions (Cd-rich, Te-rich and stoichiometric) were fabricated by revolutionary novel and low cost chemical molecular beam deposition (CMBD) method in the atmospheric pressure hydrogen flow. Cd and Te granules were used as precursors. The films were deposited on ceramic (SiO<sub>2</sub> : Al<sub>2</sub>O<sub>3</sub>) substrates at 600°C. The growth rate was varied in the range of 20–30 Å/s. The composition of the samples was changed by controlling the molecular beam intensity (MBI) ratio Cd/Te. Effect of CdCl<sub>2</sub> treatment on morphology, photoluminescence and electrical properties of CdTe films was investigated by AFM, Raman, photoluminescence (PL) and Hall methods.

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Thin film solar cells that CdTe semiconductor absorber layers using are one of the primary contenders for large-scale commercialization of photovoltaics [1]. The two key properties of this material are its near ideal band gap for photovoltaic conversion efficiency of 1.45 eV, and its high optical absorption coefficient of 10<sup>4</sup>–10<sup>5</sup> cm<sup>-1</sup>. A thin film of CdTe with thickness of approximately 2 μm will absorb nearly 100% of the incident solar radiation. II–VI thin film solar cells based on CdTe have been the subject of intense research and development in the past few years. Substantial progress has been made thus far in the area of materials research, device fabrication and technology development and numerous applications based on CdTe have been deployed worldwide. Thin film CdS–CdTe solar cells with efficiency of 15.8–17.3% have been obtained [2–5].

Another advantage of the CdTe technology is the flexibility with regards to the method of manufacture [6, 7]. Many methods (close spaced sublimation [2–5], electrodeposition [8], sputtering [9], close spaced vapor transport [10], spray pyrolysis [11], metalorganic chemical vapor deposition [12, 13], etc.) were used for fabrication of CdTe layer. Successful results of around 16–17% efficiency were obtained on CdTe films deposited by close spaced sublimation [2–5]. Thin film CdS–CdTe solar cells have a potential to increase the efficiency to 20–25%. Before this happens,

it is necessary to develop a better understanding on the basic properties of the materials and processes involved in fabricating the photovoltaic device structure.

One of critical stages in thin film solar cell fabrication is the deposition of CdTe layer with controllable composition and stoichiometry. It has been pointed out that high efficient solar cells possess Te-rich CdTe surfaces with smooth interfaces of *p*-CdTe/*n*-CdS [13]. Another issue is fabrication of low resistivity *p*-CdTe film. This can be solved by intrinsic or extrinsic point defects [1, 14]. Intrinsic point defects strongly depend on the composition of CdTe films. Therefore, fabrication of CdTe films with controllable composition in growth process is very important.

One of key steps in fabrication of thin film CdS–CdTe solar cells is CdCl<sub>2</sub> treatment [15]. The efficiency of thin film CdS–CdTe heterostructure increases drastically after CdCl<sub>2</sub> treatment. This process gives several changes in thin film CdS–CdTe solar cells. It modifies the structure [16] and increases the grain size of CdTe films noticeably [17]. The grain growth and recrystallization reduce recombination losses and improve charge transport [18]. The promotion of interdiffusion between CdS and CdTe [19] helps reduce the lattice mismatch, which leads to reduction in microstress in CdTe [20]. Moreover, this treatment makes the CdTe film highly *p*-type with a significant improvement of minority-carrier lifetime [21].

Earlier, we had reported about revolutionary novel and low cost chemical molecular beam deposition

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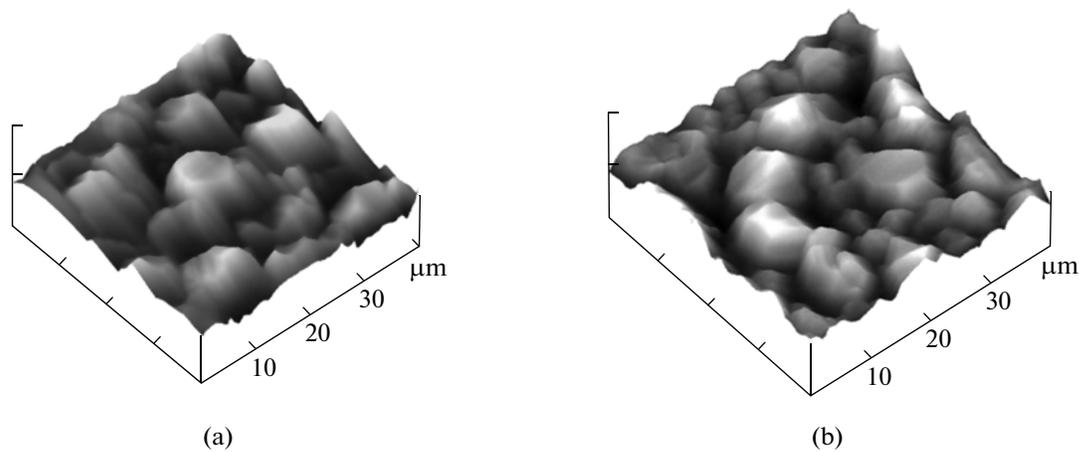
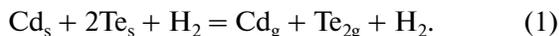


Fig. 1. AFM images of as deposited (a) and CdCl<sub>2</sub> treated (b) CdTe films fabricated at MBI ratios of Cd/Te = 1.0.

(CMBD) method in the atmospheric pressure gas flow for fabrication of binary, ternary and multinary II–VI films from separate metallic and chalcogenic precursors [22]. Some characteristics of CdTe films with different compositions fabricated by this method were discussed in [23–26]. Effect of CdCl<sub>2</sub> treatment on morphology, photoluminescence and electrical properties of CdTe films with different compositions fabricated by CMBD method were investigated by AFM, Raman, photoluminescence (PL) and Hall methods and is discussed in this paper.

CdTe films with different compositions were fabricated by a novel and low cost CMBD method in the atmospheric pressure under hydrogen flow [22]. Cd and Te granules of 99.999% purity were used as precursors. At the evaporation temperature the metallic Cd and Te components transfer into the vapor phase:



Cd and Te atoms reach the surface of the substrate and as a result of their interaction the CdTe film is formed:

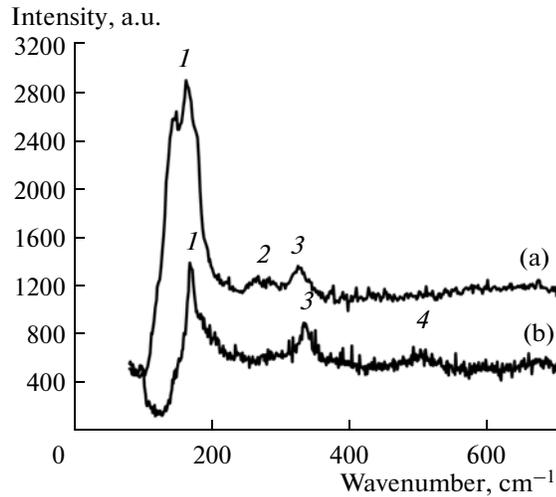


The composition of CdTe films were controlled by changing the molecular beam intensities (MBI) ratio of Cd and Te. Three samples fabricated at different MBI had Cd/Te ratios = 0.86, 1.0 and 1.1. Samples were deposited at substrate temperature of 600°C. All of the films were deposited on ceramic (SiO<sub>2</sub> : Al<sub>2</sub>O<sub>3</sub>) substrates. AFM measurements were performed with the Digital Instrument, Dimension 3000 microscope. SEM and EDX data were obtained with a Focused Ion Beam, Quanta 3D microscope. Hall measurements were done by four probe method. PL experiments were done with an Ar laser operating at  $k = 514$  nm with an output power of 0.5 W. The spectra were dispersed with a SPEX 500 spectrophotometer equipped with a Ge detector and InGaAs diode. The system settings were as follows; 2.0 ND, 1 mm slit,  $T = 20$  K, 655 nm inter-

ference filter in the range 655–1300 nm (PL1) and 1050 nm filter for the range 1300–1700 nm (PL2). Measurements were carried out at room temperature. The inelastic Raman scattering experiments were carried out at room temperature in a Labram Dilor-Horiba micro Raman spectrometer using an excitation line of 514.5 nm in backscattering configuration. In order to avoid sample modification due to laser heating effects, appropriate neutral density filters were employed. The Raman system uses a holographic notch filter that produces a sharp cut-off close to 155 cm<sup>-1</sup>. The signal was analyzed with an 1800 gr/mm grating and with the help of a thermoelectrically cooled CCD detector. PL experiments were performed at 20 K by 514 nm Ar laser line using with 5 W/cm<sup>2</sup> power density as an excitation source. PL spectra were dispersed by a SPEX 500, and recorded with N<sub>2</sub>-cooled Ge detector. CdCl<sub>2</sub> treatment was carried out in the atmospheric pressure He : O<sub>2</sub> (80 : 20%) at 390°C for 25 min.

The deposition rate and the thickness of films were 30 Å/s and 4–5 μm respectively. Surface morphology of all three CdTe films was examined by AFM. It is seen in Fig. 1a that deposited film contains high density and very well oriented cubic polycrystalline grains with the average grain size of 8–10 μm. After exposure to the CdCl<sub>2</sub> heat treatment (Fig. 1b) the film structure remained essentially unchanged. This result shows low stress in the structure of our samples.

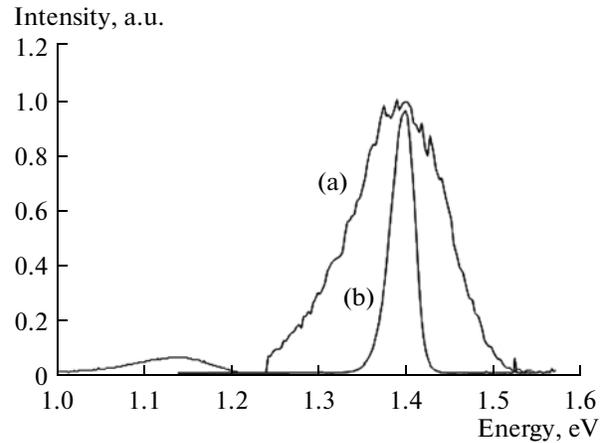
Figure 2a shows the Raman spectrum of an untreated stoichiometric CdTe sample. The broad band (peak 1) has the contributions of the longitudinal optic mode (LO) of CdTe at 165 cm<sup>-1</sup> [27] and the strong ETOTe mode at 145 cm<sup>-1</sup> [28]. It is known that Raman scattering is a powerful technique to detect Te microclusters or monolayers on CdTe [29] or on the other semiconductors [30]. In addition, due to the high Cd vapor pressure, CdTe samples may exhibit Te segregation that is readily detected through Raman



**Fig. 2.** Raman spectra of as deposited (a) and CdCl<sub>2</sub> treated (b) CdTe films fabricated at MBI ratio of Cd/Te = 1.0.

spectroscopy experiments [31]. In the same Fig. 2a peak 2 may be associated to a sum mode of the strongest Te modes  $A_1$  ( $120\text{ cm}^{-1}$ ) +  $E_{TO}$  ( $145\text{ cm}^{-1}$ ), while peak 3 corresponds to second harmonic of the LO phonon. The Raman spectrum of the film treated with CdCl<sub>2</sub>, Fig. 2b, presents important changes. The modes associated to pure Te have disappeared and a new mode (4) has arisen. These modifications in the spectrum indicate that the treatment has favored the redistribution of the formerly segregated Te atoms and that the overall crystalline quality has improved since now the spectrum presents up to the third LO overtone (peak 4). The appearance of phonon overtones is a measure of crystalline quality.

PL spectra at 20 K of all samples exhibited a near-band-edge peak at 1.41 eV and a deep level related emission band with a maximum at 1.12 eV. A typical low temperature PL spectrum is shown in Fig. 3. PL peak at 1.41 eV was also observed in [32, 33]. This peak is due to the transition of electrons from the conduction band to the acceptor level  $E_V + 0.15\text{ eV}$  and may be attributed to the vacancy of cadmium  $V_{Cd}^-$  related defect or the interstitial atoms of tellurium  $Te_i^-$  in CdTe films. Peak at 1.12 eV possibly caused owing to the transition of electrons from the donor level  $E_c$



**Fig. 3.** PL spectra at 20 K of as deposited (a) and CdCl<sub>2</sub> treated (b) CdTe films fabricated at MBI ratio of Cd/Te = 1.0.

–0.48 eV to the valence band. This donor level may be attributed to the vacancy of tellurium  $V_{Te}^{++}$  related defect or the interstitial atoms of cadmium  $Cd_i^{++}$ .

After CdCl<sub>2</sub> treatment the PL band located at 1.41 eV was still present; however the 1.12 eV band was annealed out. A tentative conclusion is that the 1.12 eV peak was associated with a tellurium vacancy ( $V_{Te}^{++}$ ) that was possibly substituted by oxygen following the CdCl<sub>2</sub> heat-treatment. Oxygen is present during the heat treatment and is most likely to occupy the tellurium vacancy (as compared to chlorine), since oxygen and tellurium are the same group elements.

Values of the resistivity, carrier concentration, mobility and conductivity type before and after CdCl<sub>2</sub> treatment are presented in the Table 1. The resistivity of the films was found to be in the range of  $10^3$ – $10^9\text{ Ohm cm}$ , the carrier concentration is in the range of  $10^7$ – $10^{13}\text{ cm}^{-3}$  and the mobility is in the range of  $1.8$ – $4.5 \times 10^2\text{ cm}^2/\text{V s}$  depending upon the composition. The CdCl<sub>2</sub> heat treatment did not lead to grain enhancement, in particular for large grain (8–10  $\mu\text{m}$ ) films, but it does have an effect on the point defects in CdTe films. The CdCl<sub>2</sub> heat treatment significantly decreased the resistivity of stoichiometric CdTe film

Parameters of CdTe films with different compositions before and after CdCl<sub>2</sub> treatment

Cd/Te	Resistivity, Ohm cm		Mobility, cm <sup>2</sup> /V s		Carrier concen., cm <sup>-3</sup>		Type of conduct.	
	before	after	before	after	before	after	before	after
0.5	$1.14 \times 10^6$	$8 \times 10^6$	410	67.6	$1.05 \times 10^{10}$	$1.16 \times 10^{10}$	<i>p</i>	<i>p</i>
1.0	$9.1 \times 10^8$	$4.71 \times 10^6$	35	44.7	$2.2 \times 10^8$	$2.97 \times 10^{10}$	<i>p</i>	<i>P</i>
1.16	$3.7 \times 10^6$	$4.2 \times 10^6$	26	35	$6.5 \times 10^{10}$	$4.3 \times 10^{10}$	<i>n</i>	<i>N</i>

from almost  $10^9$  Ohm cm to  $10^3$  Ohm cm owing to increasing of the carrier concentration from  $10^7$  to  $10^{12}$   $\text{cm}^{-3}$ . It is explained by the fact that oxygen occupies the tellurium vacancy  $V_{\text{Te}}^{++}$  as result the donor level  $E_C - 0.48$  eV passivates and the acceptor level  $E_V + 0.15$  eV activates. While the resistivity of Te-rich  $p$ -CdTe films was not essentially changed and remained at  $\sim 10^3$ – $10^4$  Ohm cm as before treatment. So, low resistivity  $p$ -CdTe films can be fabricated by the deviation of the composition of samples from the stoichiometry to Te-rich side.

CdTe films can be considered as compensated material containing the acceptor level  $E_V + 0.15$  eV and the donor level  $E_C - 0.48$  eV. Physical properties, in particular the resistivity of CdTe films is varied depending on the activity of these levels. The level  $E_C - 0.48$  eV is a predominant for Cd rich films and samples had  $n$ -type of conductivity. The level  $E_V + 0.15$  eV predominates for Te rich films and samples had  $p$ -type conductivity. We observed significant decreasing of the resistivity of CdTe films under the  $\text{CdCl}_2$  treatment. It is due to the priority of the level  $E_V + 0.15$  eV which caused by occupation of  $V_{\text{Te}}^{++}$  by oxygen. However, the decreasing of the resistivity of CdTe films under  $\text{CdCl}_2$  treatment is limited by the value of  $10^3$  Ohm cm. The increasing of the efficiency of thin film CdS–CdTe solar cells requires much less resistivity. The resistivity of CdTe films up to  $10^3$ – $10^4$  Ohm cm can be reached by the deviation of the composition from the stoichiometry to Te-rich side for  $p$ -CdTe films and Cd-rich side for  $n$ -CdTe films in growth process by CMBD.

Thus, all above mentioned 1–3 improvements and etching of CdTe in bromine methanol to form at the rear surface Te-rich layer can be done during growth process by CMBD method. So,  $\text{CdCl}_2$  heat treatment and the CdTe precursor are possibly not necessary for CdTe films fabricated by CMBD method. This novel and low cost method can successfully be used for fabrication of high efficiency thin film CdS–CdTe solar cells.

By the precise control of the MBI we were able to control the Cd/Te ratio in a revolutionary novel and low cost CMBD technique. Under atmospheric pressure hydrogen flow we succeeded in obtaining stoichiometric (Cd/Te = 1.0) CdTe films. It is also found that we can control the intrinsic point defects by deliberately changing the stoichiometry (Cd/Te = 0.86 and 1.1). AFM studies have shown that CdTe films have high quality and the average grains size is 8–10  $\mu\text{m}$  at 600°C. CdTe films have been considered as compensated semiconductor containing acceptor level  $E_V + 0.15$  eV ( $V_{\text{Cd}}^-$ ) and donor level  $E_C - 0.48$  eV ( $V_{\text{Te}}^{++}$ ).  $E_V + 0.15$  eV level dominates in Te-rich sam-

ples and  $E_C - 0.48$  eV level dominates in Cd rich films. We have fabricated  $p$ - and  $n$ -CdTe films by the deviation of the composition from the stoichiometry in growth process. The resistivity was varied between  $10^3$  and  $10^9$  Ohm cm depending on the composition of samples. The  $\text{CdCl}_2$  heat treatment significantly decreased the resistivity of stoichiometric CdTe film from almost  $10^9$  Ohm cm to  $10^3$  Ohm cm. While the resistivity of Cd-rich and Te-rich samples was not essentially changed. So, we can control the resistivity by the deviation of the composition of CdTe films from the stoichiometry. These results suggest that the  $\text{CdCl}_2$  heat treatment does not always lead to grain enhancement, in particular for large grain (8–10  $\mu\text{m}$ ) films, but it does have an effect on the point defects in CdTe films. These results are explained by the fact that oxygen is present during the heat treatment and is most likely to occupy the tellurium vacancy. Thus, all above mentioned improvements in  $\text{CdCl}_2$  treatment can be done in growth process by CMBD. Therefore,  $\text{CdCl}_2$  treatment is not necessary for CMBD method. This novel and low cost CMBD method can successfully be used for fabrication of high efficiency thin film CdS–CdTe solar cells.

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