ISSN 0003-701X, Applied Solar Energy, 2015, Vol. 51, No. 4, pp. 314–318. © Allerton Press, Inc., 2015.
Original Russian Text © K.M. Kuchkarov, T.M. Razykov, Chris Ferekides, B.A. Ergashev, R.T. Yuldoshov, M.A. Zufarov, 2015, published in Geliotekhnika, 2015, No. 4, pp. 87–92.

HELIOTECHNICAL MATERIALS SCIENCE

Research of the Morphological and Structural Properties of CdTe Films Obtained by Chemical Molecular Beam Deposition for Thin Film Solar Cells

K. M. Kuchkarov[a], T. M. Razykov[a, c], Chris Ferekides[d], B. A. Ergashev[a], R. T. Yuldoshov[a], and M. A. Zufarov[b]

[a] *Physical-Technical Institute of SPA Physics–Sun, Uzbekistan Academy of Sciences, Tashkent, Uzbekistan*
[b] *Institute of Material Sciences of SPA Physics–Sun, Uzbekistan Academy of Sciences, Tashkent, Uzbekistan*
[c] *Solar Energy Research Institute, National University of Malaysia, Bangi, Malaysia*
[d] *University of South Florida, Tampa, United States*
e-mail: k.kuchkarov@mail.ru

Received March 26, 2015

Abstract—CdTe films of different composition were obtained by chemical molecular beam deposition (CMBD). Their morphological and structural properties before and after heat treatment were investigated. The study of pictures of a scanning electron microscope and X-ray diffraction analysis showed that CdTe films have a well-oriented polycrystalline structure with a preferred orientation (111), size of film grains of 3–5 μm, and the structure of the (grains) films is denser. This conditions the possibility of growing CdTe films of different composition suitable for the manufacture of photovoltaic devices.

DOI: 10.3103/S0003701X15040143

Cadmium telluride is the most suitable material for the manufacture of thin film solar cells due to two main physical properties. Firstly, it has the optimum band-gap width, covering the entire spectrum of the visible region of sunlight. The second feature is its high absorption coefficient in which the incident solar radiation is absorbed at a depth of a few microns.

Recent advances in the efficiency of thin film solar cells based on cadmium telluride are presented in Table 1. As shown in Table 1, every year the effectiveness of a film solar cell increases. The leading company in this field is FirstSolar, which received the highest value of the efficiency of solar cells in laboratory conditions (21.5%) and in modules (18.6%) [2]. As can be seen from Table 1, the short-circuit current and fill factor reached its practical maximum. A further increase in the efficiency of solar cells can be achieved by increasing the open-circuit voltage, which has varied slightly in the range of 50 mV over the past 20 years. Solution of this problem requires a deep study of the physical properties of the absorbing layer of CdTe, particularly its structural and morphological properties. Many scientific works are devoted to the study of the physical properties of CdTe films obtained by different methods. The morphological and structural properties of the films of cadmium telluride, obtained by the low-temperature method of electrodeposition and vapor deposition, are studied in [3, 4]. The efficiency of thin-film solar cells based on CdTe, obtained by low-temperature methods, is lower than 15%, and of those obtained by high-temperature methods is more than 15% of [4, 5].

Previously, we reported on the proposed low-cost methods of chemical molecular beam deposition for the production of films of $A^{II}B^{VI}$ compounds and binary compounds at atmospheric pressure in a gas flow [6]. Also a linear relationship was found between the ratio of the intensity of molecular beams in the vapor phase and the film composition [7]. The influence of chloride heat treatment on the electrophysical properties of CdTe films of different compositions obtained by the method of chemical molecular beam deposition was studied [8]. The results showed that after chloride heat treatment the specific resistance of films decreased from $10^8\ \Omega$ cm to $10^3\ \Omega$ cm, depending on the ratio of the elements in Cd/Te.

In the article, the morphological and structural properties of films of cadmium telluride obtained by chemical molecular beam deposition, controlling the ratio of the metal and chalcogenide components in the vapor phase of the process of growth, are studied.

CdTe films were obtained by chemical molecular beam deposition at atmospheric pressure in a stream of hydrogen. The elements Cd and Te (with purity of 99.999%) were used as starting substances. The composition of the films of cadmium telluride was controlled by varying the intensity of molecular beams (IMBs) of metal and chalcogenide in the vapor phase [9]. The films were deposited on both glass (borosilicate glass) and metal (molybdenum foil with purity of

Table 1. Achievements on the efficiency of solar cells based on CdS/CdTe, obtained by different methods and companies [1]

Year	Type	CdS and CdTe/process	Activation process	V_{xx} (mV)	I_{sc} (mA/cm^2)	FF (%)	η (%)	Area (cm^2)	Group
1991	Glass/SnO_2:F/CdS/CdTe/Au	PM/CSS	$CdCl_2$ heat treatment	840	21.9	72.6	13.4	1.20	USF
1992	Glass/SnO_2:F/CdS/CdTe/Au	PM/CSS	$CdCl_2$ heat treatment	850	24.4	70.5	14.6	1.05	USF
1993	Glass/SnO_2:F/CdS/CdTe	CBD/CSS	$CdCl_2$ heat treatment	843	25.1	74.5	15.8	1.05	USF
2001	Glass/CTO/ZTO/CdS/CdTe	CBD/CSS	Thermal evaporation of $CdCl_2$	845	25.9	75.5	16.5	1.03	NREL
2013	Glass/CTO/ZTO/CdS/CdTe	CBD/CSS	Thermal evaporation of $CdCl_2$	875	28.9	78.0	19.7	1	First Solar
2014	Glass/CTO/ZTO/CdS/CdTe	CBD/CSS	Thermal evaporation of $CdCl_2$	872	29.5	79.5	20.4	1	First Solar
2014	Glass/CTO/ZTO/CdS/CdTe	CBD/CSS	Thermal evaporation of $CdCl_2$	903	30	79.8	21.5	1	First Solar*

PM is the Printing method; CSS is Closed space sublimation; CBD is Chemical bath deposition; USF refers to University of South Florida; NREL is the National Renewable Energy Laboratory.

99.96%) substrates at a substrate temperature of 600°C. The samples obtained in ratios of the intensity of molecular beams Cd/Te of 0.8, 0.88, 0.94, 1.01, 1.05, and 1.08 were studied.

The obtained CdTe films were investigated with a scanning electron microscope and X-ray diffraction analysis, which were performed in the laboratory of the University of South Florida (United States).

The process of depositing the $CdCl_2$ solution onto the surface of the CdTe was carried out in a high vacuum. In the process of spraying, $CdCl_2$ layers of varying thickness were deposited onto the surface of the cadmium telluride films. The thickness of $CdCl_2$ was controlled by the deposition time and was 200–300 nm. To prevent surface oxidation of the samples, slow cooling under a high vacuum was carried out. After depositing a layer of $CdCl_2$, the samples were heat-treated in an installation of chemical molecular beam deposition at the temperature of 390–400°C for 30 minutes in an atmosphere of pure argon. After annealing, the residual precipitate of $CdCl_2$ was washed with deionized water and dried in a stream of nitrogen.

Figure 1 shows SEM pictures for all samples obtained at a temperature of 600°C. As can be seen from Fig. 1, the microstructure (grain size and shape) of the samples, with close to a stoichiometric composition, prior to treatment has a similar appearance, except for two films having a composition ratio of Cd/Te of 0.79 and 0.88. These samples (Cd/Te of 0.94, 1.01, 1.05, 1.08) have a well-oriented polycrystalline structure and a grain size of 2–3 μm, but the structure of the (grains) films is not closely packed. At the same time, films enriched with tellurium (a composition ratio of Cd/Te of 0.79 and 0.88) also had a well-oriented polycrystalline structure and a grain size of 3–5 μm, but the texture of the (grains) films is denser. This conditions the possibility of growing CdTe films enriched with tellurium, which are suitable for the manufacture of photovoltaic devices.

Figures 2a and 2b show pictures of SEM samples with a near-stoichiometric composition after heat treatment. The samples were obtained on glass and molybdenum substrates. According to the SEM pictures (Figs. 2a, 2b) after treatment in a solution of $CdCl_2$, the morphology of the film structure changed and the presence of a uniform surface was observed.

Analysis of the results shows the following:

(a) During the measurement of the morphology of the films by a scanning electron microscope a well-oriented polycrystalline structure with a grain size of 2–5 μm was observed;

(b) After treatment in a solution of $CdCl_2$, morphological changes of the properties were observed.

This is due to the fact that at treatment in an environment of $CdCl_2$ recrystallization, the morphology of the film structure and alignment of the grain size take place. At the same time, the disappearance of small grains is observed, large grains break down into

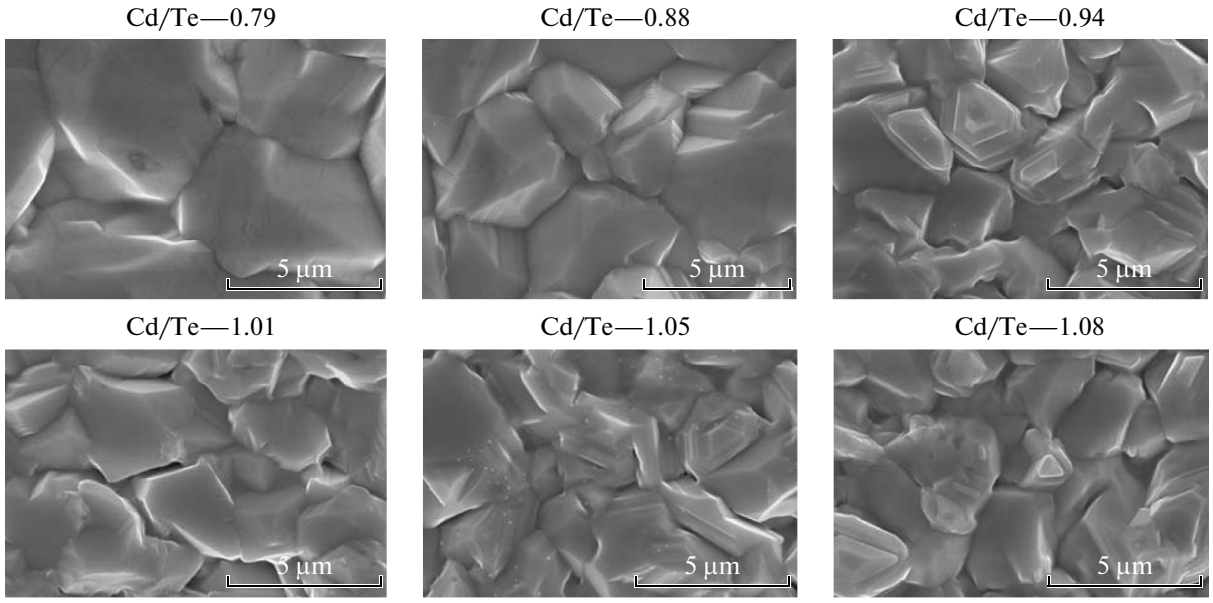

Fig. 1. Pictures obtained on a scanning electron microscope for CdTe films of different composition: before treatment at 600°C.

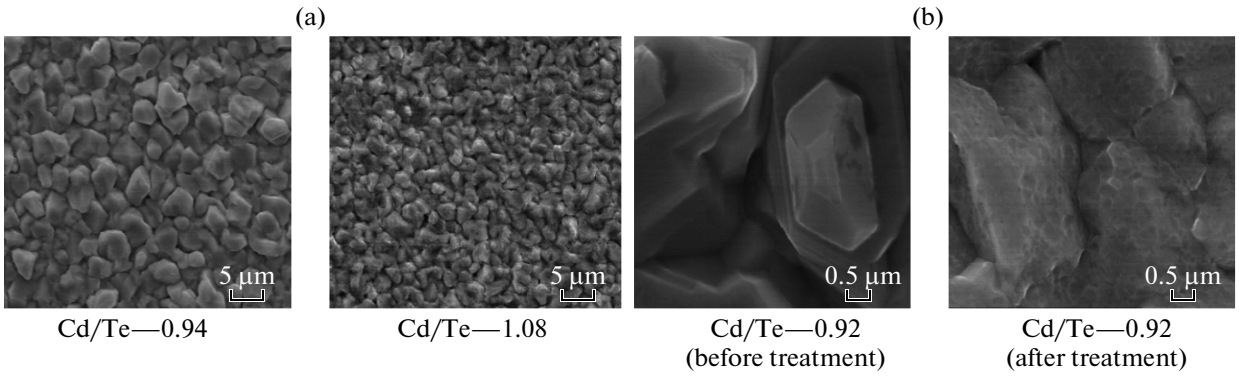

Fig. 2. Pictures of the film structures obtained by a scanning electron microscope: after treatment in a solution of $CdCl_2$; (a) glass substrate; (b) Mo substrate.

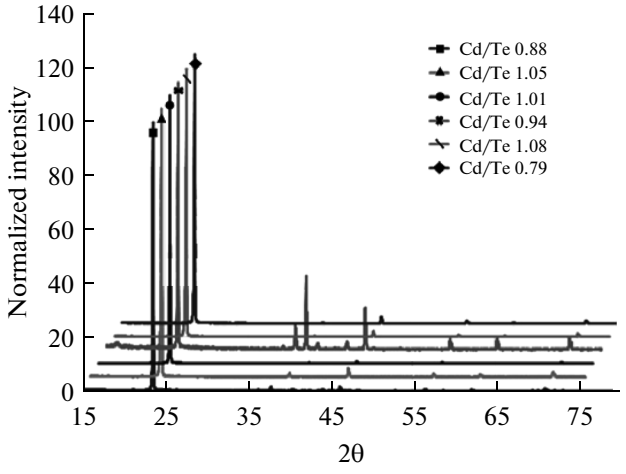

Fig. 3. X-ray spectra for CdTe films of different composition before treatment, obtained on a glass substrate.

smaller ones, and the film structure becomes more closely packed.

Diffractograms for the CdTe films grown in a hydrogen stream with different ratios (Cd/Te of ~0.79, 0.88, 0.94, 1.01, 1.05, 1.08) are shown in Fig. 3. The values of the crystal orientation are indicated above the respective peaks.

X-ray diffraction spectra for all samples have an intense peak at $2\theta = 23.7°$, which corresponds to the crystallographic axis (111). This shows that all of the CdTe films have a sphalerite structure and are oriented along the axis (111). Also, weak peaks were observed at $2\theta = 39.2°$, $46.4°$ and $71.2°$, corresponding to the crystallographic orientation (220), (311), and (422) (Fig. 3). As can be seen from Fig. 3, the intensities of the X-ray peaks corresponding to the crystallographic orientation (220), (311), and (422), for samples hav-

ing a composition of Cd/Te of 0.94, slightly increased. This may be due to the different thickness of the CdTe films. This dependence of the intensity peaks from the film thickness was observed in [10]. On all films produced in a stream of hydrogen and having different composition peaks with the orientation (111) were predominant (Fig. 4). These samples of CdTe had lattice constant $a = 6.487$ Å.

Figure 5 shows the X-ray diffraction spectra of samples prepared on glass substrates after the heat treatment and on metal substrates before and after heat treatment. As can be seen from Fig. 5, all of the samples also have a maximum peak at $2\theta = 23.7°$, which corresponds to the crystallographic axis (111). The observed weak peaks corresponding to the crystallographic orientation (220), (311), and (422) change after the heat treatment. These peaks for samples, having a composition of Cd/Te of 0.94 almost disappear and for films with a composition of Cd/Te of 0.93 are manifested slightly. At the same time, the weak peaks for films close to the stoichiometric composition (Cd/Te of 1.08) did not change. Similar results were observed for the films obtained on metal substrates. Also, additional weak peaks were observed on radiographs which are related to a molybdenum substrate.

The results obtained by X-ray diffraction were analyzed to determine the preferred orientation of the grains of CdTe films using the following formula [11]:

$$C_i = \frac{I_i/I_{oi}}{\left(\frac{1}{N}\right)\sum_{i=1}^{N} I_i/I_{oi}}, \quad (1)$$

where C_i is the texture coefficient; I_i is the total peak intensity in the spectrum; I_{0i} is the intensity of a randomly selected total peak; and N is the number of reflections considered in the analysis. The texture coefficient determines the orientation of each reflection in a plane. When the value of C_i is less than or equal to 1, then the film grains grow in a random orientation, and if the value of $C_i > 1$, then the grains have a preferred orientation in this direction. As can be seen from Table 2 and Fig. 4, all the films obtained by chemical molecular beam deposition exhibit the preferred orientation (111). The same results were also obtained in [12], when films were obtained by elemental vapor transmission.

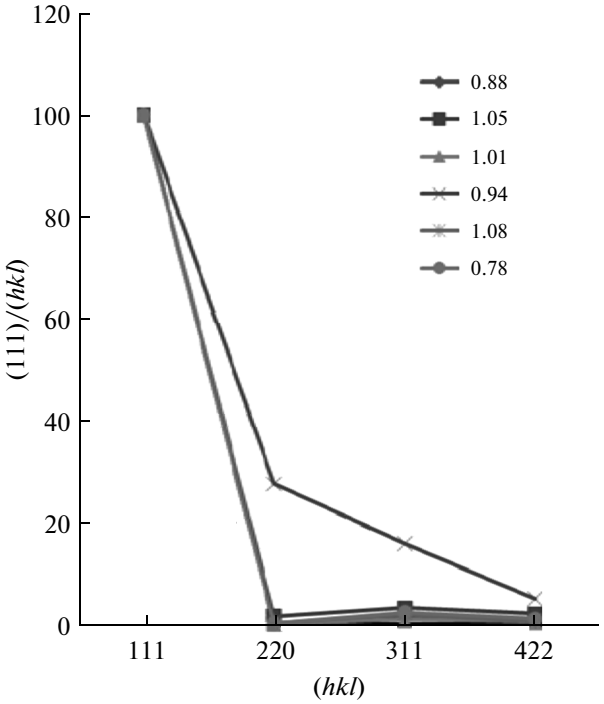

Fig. 4. Ratios of the intensities of X-rays for CdTe films of different composition.

CdTe films of different composition were obtained, deposited by the method of chemical molecular beam deposition. It is shown that the chloride heat treatment at a temperature of 400°C for 30 min in an argon atmosphere results in a change of the microstructure associated with recrystallization. The microstructure after heat treatment becomes more closely packed and the grain size equalizes. The results of X-ray diffraction analysis indicate that the obtained films have a preferred orientation before and after heat treatment.

Table 2. Values of the texture coefficient for CdTe films of different composition

	C_i					
Cd/Te (analys.)	(111)	(220)	(311)	(400)	(331)	(422)
1.08	5.29	0.02	0.16	0.29	0.08	0.16
1.05	4.95	0.07	0.21	0.34	0.15	0.26
1.01	5.65	0.095	0.076	0.12	0.045	0.096
0.94	2.94	0.49	0.84	0.88	0.48	0.4
0.88	5.56	0.017	0.11	0.13	0.066	0.11
0.79	5.21	0.012	0.21	0.35	0.05	0.15

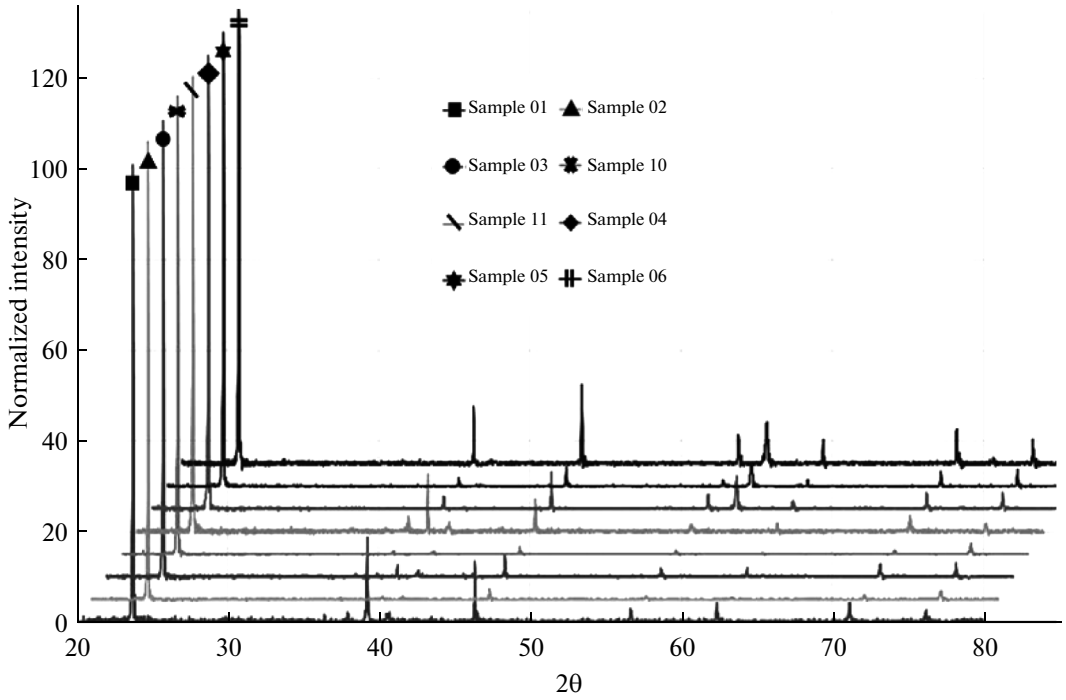

Fig. 5. X-ray spectra for CdTe films of different composition obtained after treatment of those obtained on (a) glass and (b) molybdenum substrates: (a) sample 01—Cd/Te 0.88, after treatment; sample 02—Cd/Te of 0.94, after treatment; sample 03—Cd/Te 1.08, after treatment; Sample 10—Cd/Te 1.01, after treatment; sample 11—Cd/Te 1.05, after treatment; (b) sample 04—Cd/Te 0.92, after treatment; sample 05—Cd/Te 0.92, before treatment; and sample 06—Cd/Te 1, after treatment.

ACKNOWLEDGMENTS

The work was carried out as part of an international project, grant no. M/CRDF-43/2013.

REFERENCES

1. Rios-Flores, A., et al., Procedure to obtain higher than 14% efficient thin film CdS/CdTe solar cells activated with HCF_2Cl gas, *Solar Energy,* 2011, vol. 86, no. 2, pp. 780–782. doi:10.1016/j.solener.2011.12.00.
2. US thin-film giant first solar achieves 21% efficiency in cadmium telluride solar cell. http://investor.firstsolar.com/
3. Lalitha, S., Sathyamoorthy, R., Senthilarasu, S., et al., Influence of $CdCl_2$ treatment on struktural and optical properties of vacuum evaporated CdTe thin films, *Solar Energy Mater. Solar Cells*, 2006, vol. 90, pp. 694–703.
4. Kranz, L. and Tiwari, A.N., Doping of polycrystalline CdTe for high-efficiency solar cells on flexible metal foil, *Nature Commun.*, 2013, vol. 4, p. 2306. DOI: 10.1038/ncomms3306. www.nature.com/naturecommunications
5. Ferekides, Ch., Marinskiy, D., Viswanathan, V., et al., High efficiency CSS CdTe solar cells, *Thin Solid Films*, 2000, vol. 361/362, pp. 520–526.
6. Razykov, T.M., Chemical molecular beam deposition of II–VI binary and ternary compound films in gas flow, *Appl. Surf. Sci.,* 1991, vol. 48/49, no. 1, pp. 89–92.
7. Razykov, T.M., Amin, N., Ergashev, B., et al., Effect of $CdCl_2$ treatment on physical properties of CdTe films with different compositions fabricated by chemical molecular beam deposition, *Appl. Solar Energy*, 2013,vol. 49, no. 1, p. 35.
8. Razykov, T.M., Kuchkarov, K.M., Ergashev, B.A., et al., The effect of complex thermal treatment on the electrophysical and morphological properties of CdTe films obtained by chemical molecular beam deposition, *Appl. Solar Energy,* 2010, vol. 46, no. 2, p. 111.
9. Razykov, T.M. and Kuchkarov, K.M., Influence of the growth rate on nanocrystallinity of II-VI films in CVD, *Solar Energy,* 2006, vol. 80, p. 182.
10. Salavei, A., Rimmaudo, I., Piccinelli, F., et al., Influence of CdTe thickness on structural and electrical properties of CdTe/CdSsolar cells, *Thin Solid Films*, 2013, vol. 535, pp. 257–260. http://dx.doi.org/10.1016/j.tsf.2012.11.121
11. Loginov, Y.Y., Durose, K., Al-Allak, H.M., et al., *Cryst. Growth*, 1996, vol. 161, p. 159.
12. Kendre, V., Evani, V., Ferekides, C.S., et al., CdTe films by Elemental Vapor, *Proc. 39th IEEE Photovoltaic Specialists Conf., PVSC–2013,* Tampa, FL, June 16–21, 2013, Code 103284.

Translated by S. Avodkova