

Properties of CdTe Films Prepared By DC Magnetron Sputtering

Kirichenko M.V., Zaitsev R.V., Dobrozhan A.I., Khrypunov G.S., Kharchenko M.M.

Materials for electronics and solar cells department

National technical university «KhPI»

Kharkiv, Ukraine

kirichenko.mv@gmail.com

Abstract – In order to create thin-film solar cells based on cadmium sulfide and telluride experimental studies of the process of cadmium telluride magnetron sputtering with direct current, and the impact of a magnetron sputtering mode on CdTe films crystalline structure were carried out. CdTe films for the base layers of thin film solar cells was obtained on flexible polyimide substrates by magnetron sputtering with direct current for the first time. It has found that increasing the magnetron discharge current up to 80 mA leads to increase in coherent scattering regions what is due to an increase in the thickness of the cadmium telluride films of the hexagonal modification having a columnar structure. A further increase in the discharge current leads to a decrease in the size of coherent scattering regions what caused by the thermodynamical output formation of low-angle boundaries. It has shown experimentally that the "chloride" processing of the obtained cadmium telluride layer leads to the transformation of the metastable hexagonal modification cadmium telluride in a stable cubic modification. At the same time, due to the eutectic recrystallization, increase in the sizes of coherent scattering regions by a decade and the microstrain level reduction in 1.5 times are observed.

Keywords – flexible solar cells based on cadmium sulfide and telluride, method of magnetron sputtering with direct current, "chloride" processing, hexagonal and cubic modification.

I. INTRODUCTION

Thin film solar cells (SC), based on cadmium sulfide and telluride, represent an alternative to the most widespread silicon crystalline photovoltaic converters in the capacity of autonomous sources of electric energy in terrestrial and space conditions. Modern high efficiency film SC based on CdS/CdTe are produced in the back configuration of the glass substrate through which solar radiation enters the base layer [1]. In terrestrial conditions, SC based on CdS/CdTe, in accordance with the optimum band gap of cadmium telluride, have the greatest efficiency - 29%. In space applications, due to the nature of the chemical bonds of CdTe such SC are the most resistant to radiation [2]. In addition, lower material and energy consumption of manufacturing process of film photovoltaic converters based on CdS/CdTe provides a lower cost compared to crystalline silicon photovoltaic converters. For example, in the conditions of industrial production, First Solar company which manufactures

photovoltaic converters based on CdS/CdTe said about reaching "grid parity" when the cost of electricity produced by photovoltaic converters equals the cost of electricity produced by conventional power sources [3]. It should be noted that conventional SC based on CdTe essentially concede to SC based on crystalline silicon in power density (value of electric power generated per unit weight of a SC).

Substitution of glass substrates, which are conventional for SC based on CdS/CdTe to a flexible substrate, allows the reduced power to increase by several orders of magnitude, and to surpass by this parameter not only silicon-based SC, but also SC based on A3B5. However, in addition, due to the lower thermal stability of the polyimide substrate it is necessary to reduce the deposition temperature of the cadmium telluride films below 400 °C what is impossible for methods of close-spaced sublimation [4,5] and vapor phase transport deposition [6, 7] which are conventionally used to produce high performance SC based on CdS/CdTe. When implementing these methods forming the base layer of cadmium telluride has carried out at a deposition temperature of 550 °C.

Low temperature techniques for production of cadmium telluride films that can be realized in mass production includes magnetron sputtering method [8, 9]. The main technological challenge of getting the semiconductor films by magnetron sputtering with direct current is a low rate of film growth. This is because during sputtering a low-conducting substrate accumulation of positive charge takes place, and this charge does not have time to drain off. This creates a counterfield inhibiting the argon ions which bombard the substrate what causes a decrease in the discharge current.

Therefore, obtaining of cadmium telluride films for base layers of flexible SC by magnetron sputtering with direct current is an urgent technological problem for which solution experimental studies of the process of cadmium telluride magnetron sputtering with direct current and of the impact of the magnetron sputtering modes on the crystalline structure of CdTe films was carried out.

II. EXPERIMENTAL TECHNIQUE

In the work, we have used deposition of cadmium telluride films by magnetron sputtering with direct current. We used an experimental vacuum plant VUP-5M with original magnetron

systems what important design feature was their cooling circuit which includes only a magnetic system. The target was made by cold pressing from cadmium telluride powder and with diameter - 76 mm, and thickness - 2 mm. Target cold pressing pressure was 100 MPa. The dwell time of the target at this pressure was 15 hours. After pressing the target its vacuum annealing has performed at a residual pressure of at least 10^{-4} mm Hg and a temperature of 80 °C. When depositing CdTe layers thermostable polyimide film manufactured by Upilex firm with thickness up to 10 microns has used in the capacity of a substrate. The flexible substrate has positioned in a movable substrate holder of VUP-5M vacuum chamber in close contact with the front surface of the thermocouple. Before the process of applying the cadmium telluride layers pumping in the working volume to a pressure of 10^{-5} Pa has carried out. Argon puffing in the capacity of a working gas has carried out using an automated puffing system SNO.

Taking of X-ray diffractograms for the cadmium telluride films was carried out by θ -2 θ scanning method with Bragg-Brentano focusing procedure using X-ray diffractometer DRON-4 with a step 0.01-0.02 degrees in K_{α} radiation of a cobalt anode ($\lambda_{CoK_{\alpha}} = 1.78897\text{\AA}$).

Under these conditions, the diffraction pattern has formed by the grains with reflecting planes parallel to the surface of samples (hkl) [10]. Identification of the phase composition of the samples was carry out by comparing the angles 2 θ of clearly defined peaks obtained when shooting, with filed reference data from JCPDS, which has obtained by means of an electronic database "PCPDFWIN" for the respective phases.

Processing of single peaks in X-ray diffractograms (smoothing, background separation, separation of the doublet $K_{\alpha 1}$ - $K_{\alpha 2}$) and calculation of the profile parameters of the diffraction lines (peak position, interplanar distance, integrated intensity of the peak, and integral width) were carry out using the computer program "New_Profile. Sizes of coherent scattering regions (L_c) and the micro strain level (ϵ) were determined with regard to the physical broadening of the diffraction maxima (β). The diffraction distribution β was estimate by calculation by approximation of the diffraction profiles with use of Gauss-Cauchy function [10].

To identify structural features of the cadmium telluride base layers the method of so-called "oblique" shooting was used. Where in the radiation of the cobalt anode by 2 θ -scanning there has detected and pointwisely registered the diffraction reflections from the planes of sphalerite and wurtzite modifications of cadmium telluride. That has not found when using the registration method set forth above, because the texture is available on the sample [11]. To do this, the sample was rotate relative to the initial position at an appropriate angle (the angle between the plane, w h i c h formed the most intense diffraction peak when focusing with regard to Bragg-Brentano, and the target plane).

III. RESULTS AND THEIR DISCUSSION.

In the course of studying the process of magnetron sputtering with direct current to produce cadmium telluride films, five technological modes have been implemented

(they differed by argon pressure (P_{arg}), the magnetron voltage (V), and substrate and the target heating mode. When conducting researches, the dependence of the discharge current of the magnetron (I) on the sputtering time (t) was measure. It has found that in the process of magnetron sputtering of a cadmium telluride target the change of discharge current has observed.

The carried out research of the magnetron sputtering process with direct current of the cadmium telluride target has shown that changing the magnetron sputtering current in the process of CdTe film deposition has related to target material surface heating. Experiments show that this can occur due to thermal radiation from the substrate surface. Indeed, it has experimentally demonstrated that with increasing of substrate temperature and, particularly, its heating time over the target surface, an increase of the initial discharge current of 1.2 mA to 75 mA has observed. The temperature of the target surface also increases with magnetron sputtering time due to the bombardment of the target by ions of the working gas. From our point of view, heating up of the target surface causes increase in the intensity of the thermal emission of secondary electrons from the target surface in the magnetron discharge zone and reducing the electric resistance of the target because of the thermal generation of the main charge carriers. Increase in the concentration of the secondary electrons increases the probability of ionization of the argon molecules what in turn causes increase in the intensity of the argon ion bombardment of the target surface and therefore the target sputtering rate. Generation of main carriers lowers the target resistivity and decreases the intensity of the accumulation of positive charge that leads to formation of the electric counterfield retarding accelerated argon ions, which bombard the target. Availability of a charge accumulation process is confirming by experimentally observed decrease in the discharge current. The experimentally observed stabilization of the discharge current irrespective of the technological process of magnetron sputtering indicates the occurrence of the heat balance mode in the target.

Based on the analysis of the process of magnetron sputtering cadmium telluride films with direct current we have selected deposition modes what provide intensive sputtering of a target. For this purpose, we pre-heated the substrate up to 410 - 420 °C. After reaching this temperature, the movable substrate holder has transferred to the mode above the target; as a result, the target has also heated for 5-8 minutes. A voltage was applying to the magnetron, and the process of deposition of cadmium telluride films has started. Upon that, the discharge current varied within the range of 40 mA to 100 mA for different samples by variation of the magnetron power ranging from 600 V to 650V, and of an argon partial pressure from 1 Pa to 0.8Pa. Thus, discharge current has almost not changed in the process of sputtering. The substrate temperature during the deposition was also virtually unchanged and was 300 °C. The duration of the films deposition process ranged from 15 to 25 minutes.

The increase in the average growth rate of the cadmium telluride films from 41nm/min to 367 nm/min with increasing discharge current from 40 mA to 100 mA

was established experimentally, so the selected modes of the magnetron operation do not fall in the saturation region what provides good process control and film deposition rate sufficient for mass production.

The crystalline structure of the cadmium telluride films has investigated using the method of X-ray diffraction. Figure 1 shows the X-ray diffractograms of samples 3 and 6. Analytical processing of the experimental X-ray diffractograms made it possible to determine the position of the diffraction peaks, their intensity and half-width (Table 1). In all X-ray diffractograms there are two distinguishable double peaks at angles 2θ 27.05° and 91.05° what may belong to both hexagonal and cubic CdTe modifications: a reflection (002) and (006) for wurtzite and reflection (111) and (333) for sphalerite, respectively. High intensity of these peaks indicates that the films have a preferred direction. This direction is [111] in the case of cadmium telluride sphalerite modification or [0001] in the case of CdTe wurtzite modification. As the X-ray diffractograms demonstrate peak reflections at the angles 2θ 49.89° and 78.98° what may belong to the wurtzite planes (103) and (105), it becomes evident that the studied cadmium telluride films have hexagonal modification. To determine whether there is a cadmium telluride of sphalerite modification in the test layers we have carried out "oblique" shooting. We have calculated the angles between planes (111) and (620) for the cubic modification (002), and (105) and (002) for the (515) hexagonal modification.

TABLE I. TECHNOLOGICAL MODES FOR PRODUCTION OF CdTe FILMS

Sample	I, mA	Peak position, degree	(hkl)	Interplanar distance, Å	Intensity, pulses/s	Half-width, degree
CdTe3	40	27.52	(002)	3.760	419	0.15
		49.89	(103)	2.121	23	0.30
		78.98	(105)	1.407	20	0.59
		91.07	(006)	1.253	10	0.24
CdTe4	60	27.49	(002)	3.764	1787	0.14
		91.03	(006)	1.254	24	0.33
CdTe6	80	27.48	(002)	3.770	944	0.18
		50.14	(103)	2.110	52	0.54
		78.89	(105)	1.410	8	1.07
		91.01	(006)	1.254	93	0.26
CdTe7	100	27.53	(002)	3.759	2750	0.14
		78.95	(105)	1.407	17	0.98
		91.05	(006)	1.254	117	0.27

Calculations demonstrate that the angle between the planes (111) and (620) of a cubic phase is about 43.08°, the angle between the planes (002) and (105), and (002) and (215) of the hexagonal phase - 20.7° and 78.46°, respectively.

Based on the calculations, X-ray surveys were conducted to determine the phase composition of the produced films at the angles 2θ of 72-85° by rotating the sample at an angle

of 20.7°. Selection of the sample rotation angle value was caused by the fact that the angle between the direction of [001] and [105] of the hexagonal modification is 20.68°, and the angles between the directions [331] and [422] to direction [111] are 22 to 19.47°. Therefore, if to turn to the specified angle the reflection of [105] for the hexagonal modification and the reflections [331] and [422] for the cubic modification should occur. Results of oblique shooting are shown in Figure 2.

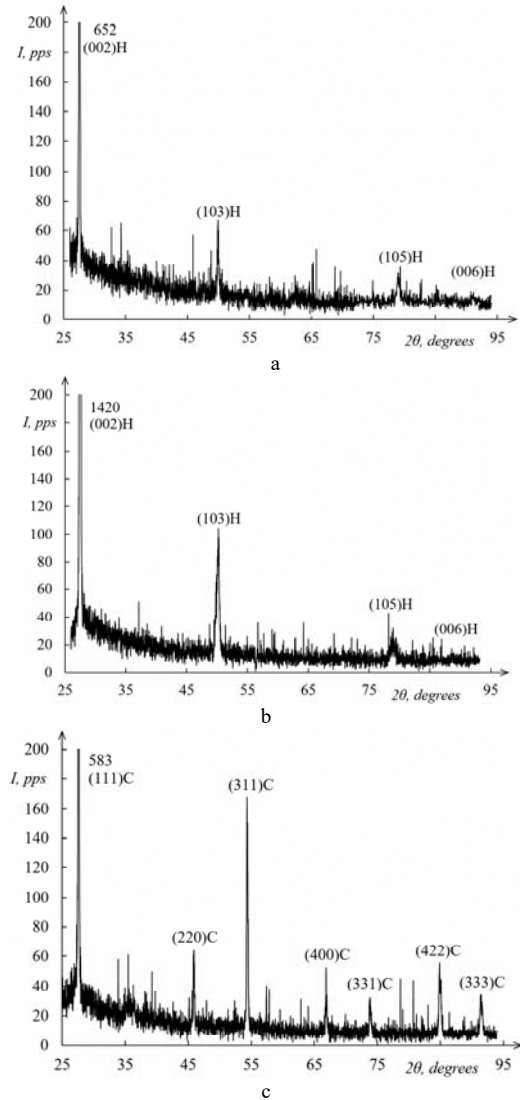


Fig. 1. X-ray diffractograms of CdTe films. a) - I = 40 mA, b) - I = 80 mA, c) - I = 80 mA after the "chloride" processing.

For the films studied, in the area of 2θ 72-85° only the diffraction peak (105) of the hexagonal phase is observed and diffraction peaks (331) and (422) of the cubic modification cannot be detected. Thus, it can be concluded that in this case, the tested films are forms of hexagonal CdTe modification and further calculations were carried out for this phase. Proceeding from the positions of diffraction peaks calculations of the interplanar distances (Table 1) were carried out. Data analysis shows that at the start with increasing the discharge current from 40 mA to 80 mA, an

increase of interplanar distances for all identified planes is observing. A further increase in the discharge current from 80 mA to 100 mA reduces the interplanar distances. By the physical broadening of the diffraction peaks by approximation of their profiles using the Gauss-Cauchy function there were investigated the effect of the magnetron sputtering modes on the size of coherent scattering regions (CSR) and microstrain level (Table 2) for grains oriented in the direction (002). It was to be find that by increasing the sputtering current from 40 mA to 80 mA, an increase in CSR size from 52 nm to 132 nm is observe. From our perspective, this is primarily due to the increase in the cadmium telluride film thickness from 1.0 micron to 5.2 microns with an increase in film growth rate, which is caused by the growth of the sputtering current. Increasing the CSR size with increasing the film thickness is a natural physical process. Traditionally, in the course of cadmium telluride film deposition on a no oriented substrate initially fine crystalline defect layer has formed in which grains have random crystallographic orientation. Then, as the film thickness, growth due to different rates of growth of grains with different crystallographic orientation a columnar structure has formed with grains oriented in the crystallographic directions, which are characterize by the maximum growth rate [12]. Upon that, grain growth with another crystallographic orientation has suppressed.

the intensity of the corresponding diffraction peaks (see table 3) and the presence of multiple peaks (004). For a columnar structure with increasing thickness a grain size is also grows, and the boundaries between them have high angle values. In addition, inside grains the degree of development of low angle boundaries also decreases due to the decrease in number of defects what leads to an increase in CSR size.

TABLE II. RESULTS OF CALCULATION OF COHERENT SCATTERING REGIONS SIZES (L_i) AND THE MICROSTRAIN LEVEL (E)

Sample	Cauchy approximation		Gaussian approximation		Average value	
	$L_i, \text{Å}$	$\varepsilon, \text{relative units}$	$L_i, \text{Å}$	$\varepsilon, \text{relative units}$	$L_i, \text{Å}$	$\varepsilon, \text{relative units}$
CdTe3	55	$7 \cdot 10^{-2}$	48	$8.5 \cdot 10^{-2}$	52	$7.8 \cdot 10^{-2}$
CdTe4	120	$5 \cdot 10^{-2}$	95	$5.3 \cdot 10^{-2}$	108	$5.2 \cdot 10^{-2}$
CdTe6	165	$4 \cdot 10^{-2}$	98	$7 \cdot 10^{-2}$	132	$5.5 \cdot 10^{-2}$
CdTe7	105	$5 \cdot 10^{-3}$	87	$5.5 \cdot 10^{-3}$	96	$5.3 \cdot 10^{-2}$

Further growth of the sputtering current from 80 mA to 100 mA reduces CSR sizes from 132 nm to 96 nm, in spite of the continued growth of the film thickness of cadmium telluride to 5.5 microns. This indicates an increase of defects number in the growing layers with increasing the sputtering current. In our view, the experimentally identified increase of film growth rate from 208 nm/min to 367 nm/min reduces the mobility of atoms deposited on the substrate what in turn increases the number of point structural defects. The defect density growth leads to an increase in free energy to such an extent that there becomes thermodynamically favorable the formation in the growing layer of low angle boundaries, which are the drain point structural defects.

Research of microstrain level shows that with the growth of the sputtering current from 40 mA to 60 mA, there is a decrease in the level of microstrains, and then the level of microstrain practically unchanged.

Thus, from the standpoint of obtaining cadmium telluride films with a minimum number of structural defects, optimal discharge current is 80 mA.

For the cadmium telluride film received in these modes there was carried out "chloride" processing which is convenient for the formation of basic layers of cadmium telluride for high-efficiency film photovoltaic converters on their basis. [13] To perform the "chloride" processing, cadmium chloride layers deposited on the surface of cadmium telluride films by vacuum evaporation without heating the substrate. Then annealing in air at 430 °C for 25 minutes was carry out [14].

According to the literature [15] at this temperature, base layers of cadmium telluride recrystallize without phase separation due to the presence of low-temperature eutectic in CdTe-CdCl₂ system.

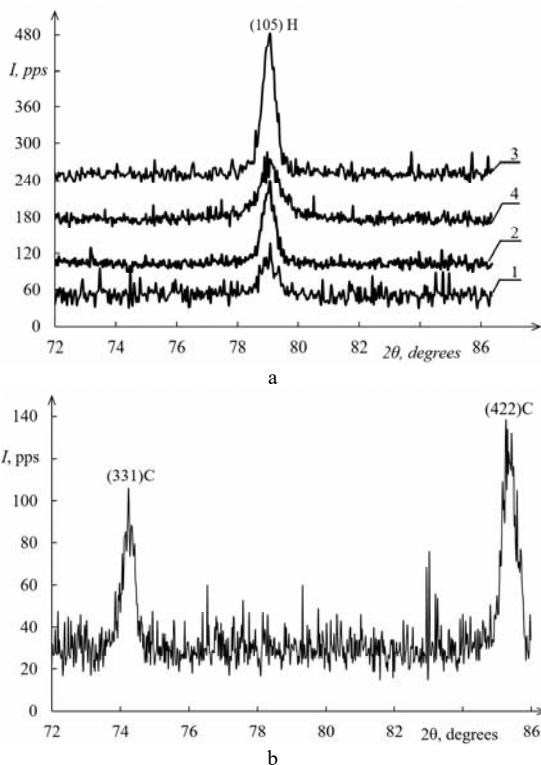


Fig. 2. X-ray patterns for basic CdTe layers during the "oblique" shooting. a) 1-I = 40 mA, 2-I = 60 mA, 3 - I = 80 mA, 4 - I = 100 mA, b) I = 80 mA, after the "chloride" processing

For hexagonal modification of cadmium telluride, maximum growth rate belongs to crystallographic direction (002). According to the results of structural studies, the obtained cadmium telluride films are oriented in this crystallographic direction, as evidenced by the high values of

The diffractograms of the cadmium telluride film after the "chloride" processing shows the peaks belonging to the cubic modification CdTe (Fig. 2, Table 3).

TABLE III. RESULTS OF PROCESSING THE DIFFRACTION PATTERN OF CdTe6 SAMPLE AFTER "CHLORIDE" PROCESSING.

Peak position, degree	Index hkl	Interplanar distance, Å	Peak intensity, pulse/s	Half-width, degree
27.59	(111)	3.751	402	0.15
45.88	(220)	2.295	34	0.19
54.35	(311)	1.959	128	0.15
66.89	(400)	1.623	20	0.23
73.83	(331)	1.489	18	0.22
84.90	(422)	1.325	76	0.25
91.44	(511)	1.249	40	0.32

Only peaks (331) and (422) of cubic modification are observed on the diffraction pattern obtained by the method of "oblique" shooting angle within the range of 2θ from 72.5° to 87.5° at 20.5° turn of the sample, and the peak (105) of hexagonal modification is not detected there. Thus, after the "chloride" processing a cadmium telluride film contains the hexagonal phase. After "chloride" processing there is also observed reduction of peak width (111) and (333) as compared with the peaks (002) and (006) of hexagonal phase in the samples before the "chloride" processing (compare tables 1 and 3). Calculations of CSR sizes and the level of microstrain showed an increase of CSR to 230 nm and a decrease in the level of microstrain up to $3 \cdot 10^{-2}$.

IV. CONCLUSIONS

For the first time, the cadmium telluride films of hexagonal modification by thickness of 1-5 μm have been produced on flexible polyimide substrates by magnetron sputtering with direct current due to heating the target surface to intensify the thermal emission of the secondary electrons in the magnetron discharge zone and to reduce the electrical resistance of the target as a result of thermal generation of main charge carriers; that allows the films to be used as a base layer in film photovoltaic converters.

It has found that upon increasing the magnetron discharge current to 80 mA the rise of CSR sizes has observed what has caused by an increase in the thickness of the cadmium telluride films having a columnar structure. Further growth of the discharge current leads to a decrease in CSR sizes due to thermodynamically favorable formation of low-angle boundaries what is the physical mechanism compensating the increase in number of radiation point defects upon intensification of the magnetron sputtering process.

It is show that a decrease in the level of microstrains is observe with an increase in the discharge current to 60 mA, and a further increase has no significant effect.

It is show experimentally that the "chloride" processing of cadmium telluride layers carried out by deposition of cadmium chloride films followed by annealing in air at 430°C for 25 minutes leads to the transformation of the metastable hexagonal modification cadmium telluride in a stable cubic modification. At the same time due to the eutectic recrystallization, CSR size growth by an order of magnitude is observed and decrease of a microstrain level in 1.5 times.

REFERENCES

- [1] Hädrich M., Heisler C., Reislöhner U., Kraft C., Metzner H. Back contact formation in thin cadmium telluride solar cells // *Thin Solid Films*. – 2011. – Vol. 519. – № 21. – P. 7156-7159.
- [2] Han J., Spanheimer C., Haindl G., Fu G., Krishnakumar V., Schaffner J., Fan C., Zhao K., Klein A., Jaegermann
- [3] W. Optimized chemical bath deposited CdS layers for the improvement of CdTe solar cells // *Solar Energy Materials and Solar Cells*. – 2011. – Vol. 95. – № 3. – P. 816-820.
- [4] FirstSolar [Official website]. – URL: www.firstsolar.com. Accessed: 5.11.2015.
- [5] Romeo N., Bosio A., Tedeschi R., Romeo A., Canevari V. Highly efficient and stable CdTe/CdS thin film solar cell // *Solar Energy Materials and Solar Cells*. – 1999. – Vol. 58. – № 1-4. – P. 209-218.
- [6] Britt J. Ferekides C. Thin-film CdS/CdTe solar cell with 15.8% efficiency // *Applied Physics Letters*. – 1993. – Vol. 62. – № 22. – P. 2851-2852.
- [7] Birkmire R.W., Elser E. Polycrystalline thin film solar cells // *Journal of Materials Research*. – 1997. – Vol. 27. – P. 625-653.
- [8] Kestner J.M., mcElvain S., Kelly S., Ohno T.R., Woods L.M., Wolden C.A. An experimental and modeling analysis of vapor transport deposition of cadmium telluride // *Solar Energy Materials and Solar Cells*. – 2004. – Vol. 83. – № 2. – P. 55-65.
- [9] Gupta A., Parikh V., Compaan A.D. High efficiency ultra-thin CdTe solar cells // *Solar Energy Materials and Solar Cells*. – 2006. – Vol. 90. – № 6. – P. 2263-2271.
- [10] Vasilyev D.M. Diffraction methods for structural studies. - M.: Metallurgy, 1977. - 310 p.
- [11] Hripunov G.S. Structural mechanisms for optimization of photovoltaic properties of CdS / CdTe film heterosystems // *Physics and Technology for Semiconductors 2005*. - V. 39, №10.-P.1266-1270.
- [12] Romeo A., Terheggen M., Abou-Ras D., Batzner D.L., Haug F.-J., Kalin M., Rudmann D., Tiwari A.N. Development of Thin Film Cu(In, Ga)Se₂ and CdTe solar cell // *Progress in Photovoltaics: Research and Applications*. – 2004. – Vol. 12. – № 2-3. – P. 93-111. Palatnik L. C. Mechanisms of formation and structure of condensed films - Moscow: Nauka, 1971. - 318 p.
- [13] Price K.J. Effect of CdCl₂ treatment on the interior of CdTe crystals// *Proceeding MaterialsResearch Society Symposium-San Francisco (USA)*.- 2001. - P. H1.6.1-H1.6.12 .
- [14] McCandless B.E. Thermochemical and kinetic aspects of cadmium telluride solar cell processing // *Proceedings of the MRS Spring Meeting*. – 2001. – San Francisco (USA). – P.1.6.1.
- [15] McCandless B.E. Thermochemical and kinetic aspects of cadmium telluride solar cell processing // *Proceedings of the MRS Spring Meeting*. – 2001. – San Francisco (USA). – P.1.6.1.