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**Vapor Phase Condensation for Photovoltaic CdTe Films**

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Thin films of CdTe were obtained by vapor phase condensation, namely by open vacuum evaporation, using different technological factors, in particular, different thickness (different time of deposition  $t$ )  $d = (540 - 2835)$  nm, deposition temperature  $T_v = 200^\circ\text{C}$  and evaporator temperature  $T_e (500 - 600)^\circ\text{C}$ . The films were deposited on silicon substrates. The morphology of thin film condensates is determined on the basis of ASM and SEM studies analysis. Were received dependences of average roughness and root mean square roughness from the material of substrate and film thickness. It was established that the growth of surface nanostructures is determined by Stranki-Krastanov mechanism.

**Keywords:** cadmium telluride, thin films, nanostructures, growth processes.

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## Introduction

Cadmium Telluride (CdTe) is recognized as a very promising material for thin-film solar cells. CdTe is a semiconductor of groups II-VI with a band gap  $E_g = 1.5$  eV, and is widely used for photovoltaic converters of solar energy. It has also a high absorption coefficient  $> 5 \times 10^5 \text{ cm}^{-1}$ , which means that 99 % of photons with energy greater than the band gap width ( $E_g$ ) can be absorbed within 2  $\mu\text{m}$  of CdTe film [1-2].

The solar cells on the basis of CdTe take up from the middle of the last century. In 1956 J. Lohorsky theoretically verified the application of InP, GaAs, and CdTe in solar cells as semiconductors with a higher efficiency of photoelectric converting than CdS, CdSe, AlSb and Si [3]. The effectiveness of such laboratory samples of solar cell with p-n-junction on monocrystalline CdTe, first produced in 1959, was only 2 % [4] and barely 20 years later it slightly exceeded 7 %, and subsequently even is 10 % [5, 6].

Technological difficulties to create a perfect p-n-junction with a thin front layer and significant losses due to surface recombination were main reasons for the low efficiency of such devices. Therefore, further efforts were made to find an appropriate heterojunction, first of which was a junction of p-Cu<sub>2</sub>Te/n-CdTe with photovoltaic efficiency  $\sim 7$  % and which, due to the diffusion of copper, was too unstable [7]. Were investigated the possibility of other materials using as hetero-junction partners for p-CdTe: ITO, In<sub>2</sub>O<sub>3</sub>, ZnO

(materials with n-type conductivity and a comparable band gap to CdTe), which performed the role of "window", through which radiation reaches a photovoltaic active absorbing cadmium telluride layer [8].

In the first years of 21<sup>st</sup> century is managed to improve the technology of obtaining and producing of thin films solar cells based on CdTe, which can compete with silicon analogues. In industry, the efficiency of thin-film CdTe-modules is 10 – 11 % with perspective of increase in the near future by some percent [9]. In laboratory, the efficiency of experimental samples of CdTe thin-film solar cells is 16 - 17 %, and its theoretical limit is 28 – 30 % [10-11]. The costs of modules during last seven years decreased three times and overcome \$ 1 US / W, and the efficiency increased to 22.1 %. The major producers of solar cells are focused on reducing the cost of solar panels. Worth to note, that CdTe thin films have become much cheaper compared to modules on silicon plates.

Consequently, the semiconductor solar energy on the basis of CdTe thin-film is one of the most promising directions on the way of solving energy problems. Today, the main problem is influence of technological factors to obtaining the most optimal parameters of resulting thin films.

## I. Experiment Methodology

For obtaining of semiconductor films and nanostructured materials there are a large number of methods: molecular-beam epitaxy (MBE), metalloorganic vapor phase epitaxy (MOVPE), pulsed laser deposition (PLD), magnetron sputtering (physical vapor deposition - PVD), vapor-phase deposition ("hot wall" method for epitaxial growth, deposition in open vacuum, gas-dynamical stream of steam) and others [12].

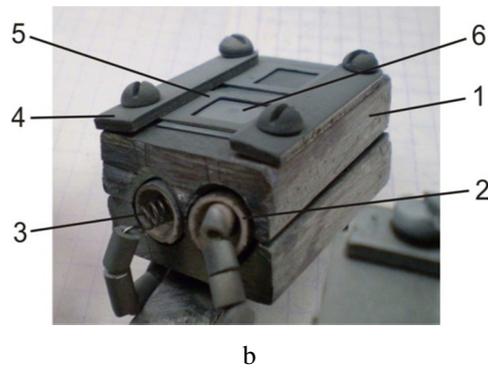
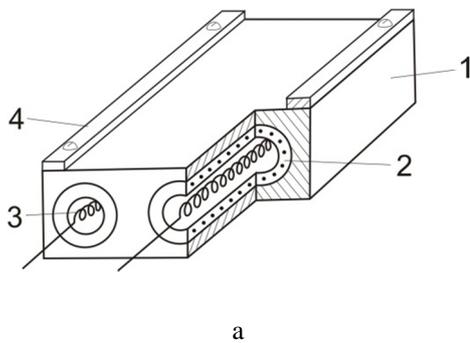
Cadmium Telluride synthesis was carried in vacuum quartz ampoules by mechanical mixtures of initial components. Additionally, in contradistinction to synthesis conditions of IV-VI compounds, ampoules were grafitized by acetone pyrolysis. The temperature mode of synthesis consisted of several stages of heating and withstanding, and namely, the synthesis temperature was 1120°C. Received ingots were ground up in planetary ball mills Pulverisette 6.

To obtain of the CdTe thin film condensates of different thickness by preset deposition temperature was used vacuum heater, which has a special design for films deposition. It consists five microheaters (Fig. 1, a, b) in form of the copper blocks of size 40×20×8 mm<sup>3</sup> [13]. In frame of the copper blocks 1 are drilled holes for ceramic tubes 2, which serve as an electrical insulator between the body of block and heating element 3. The lower block has a pad with holders 4 for the material of substrate 6. To reduce the surface heat losses of the

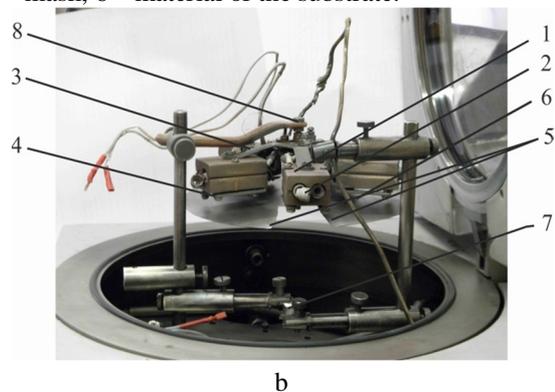
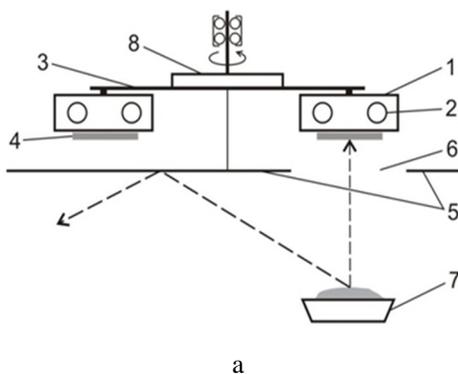
substrates and provide the necessary condensate layout, tantalum screens 5 with a thickness of 0.3 mm were constructed. All microheaters were calibrated to the same temperature by selecting the resistance of a Nichrome wire of 0.3 mm in diameter. The temperatures of microheaters are measured by thermocouples, placed close to the substrates. The system of microheaters is attached diagonally to the rotating cantilever, and the heating elements are connected in parallel (Fig. 2). The obtaining of vapor phase semiconductor condensates is carried out on the next way (Fig. 2) [13]. The evaporator 7 is filled with an investigated substance (pre-synthesized CdTe compound). In advance prepared substrates 4 (for example, glass, silicon, talk) are placed on surface microheater 1. The substrate was pre-purified by chemical etching. After the shutter is blocked, five microheaters 1 with substrates 4 and evaporator with synthesized composite are heated to preset temperature.

One of the microheaters places under the hole 6 in the shutter over the evaporator and provides vapor deposition on the substrate within a fixed time. Then the flow of vapor from evaporator is blocked by shutter, the next microheater with substrate is rotated, the shutter opens, and the deposition is carried out with another time. The process repeats five times for each microheater with a substrate, accordingly.

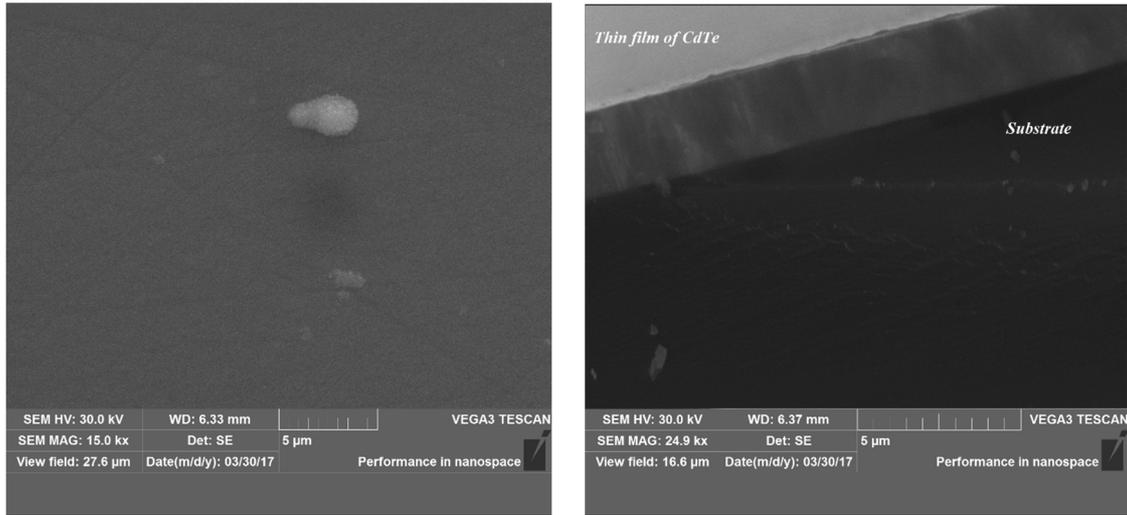
CdTe thin film nanostructures were deposited by vapor-phase condensation method on silicon substrates under the same process parameters (different samples



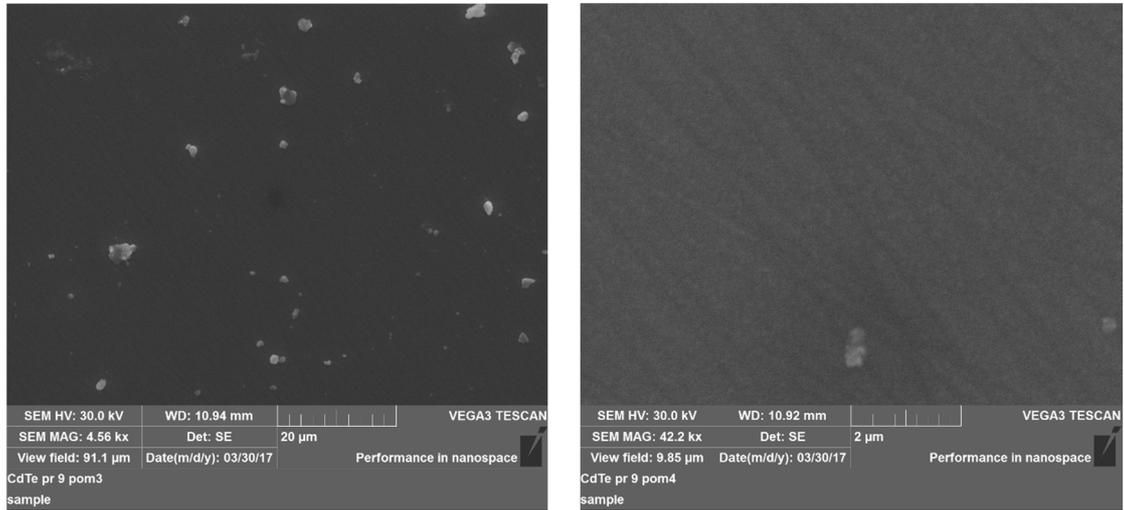
**Fig. 1.** Constructive scheme (a) and the image of the vacuum micro-stove (b): 1 – copper block, 2 – ceramic tube, 3 – spiral of the heater, 4 – substrate holders, 5 – mask, 6 – material of the substrate.



**Fig. 2.** Scheme (a) and image (b) of the device for films and two-layer structures deposition: 1 – system of microheaters, 2 – heaters, 3 – radial brackets, 4 – substrate for steam deposition, 5 – shutter, 6 – asymmetric hole, 7 – evaporator, 8 – mechanical system for microheaters rotating.



**Fig. 3.** SEM- image morphology and 5 µm cross-section image of CdTe thin films (sample 6).



**Fig. 4.** SEM- image morphology of CdTe thin films (sample 9).

**Table 1**

Technological factors of cadmium telluride films deposition on silicon substrates

Sample number	Substrate temperature $T_s, ^\circ\text{C}$	Evaporation temperature $T_e, ^\circ\text{C}$	Deposition time $t, \text{sec.}$	Thickness $d, \text{nm}$	Deposition velocity $V, \text{nm/sec.}$
6	200	550	300	2835	7.65
9	200	550	120	540	4.50

thickness) in single technological cycle. Deposition occurs on silicon substrates. The evaporation temperature of pre-synthesized cadmium telluride was  $T_E = 550^\circ\text{C}$ . This temperature was chosen in account of CdTe evaporate features, in particular, Cadmium Telluride in the range  $(500 - 600)^\circ\text{C}$  evaporates congruently with more than 98 % of the CdTe molecules in vapor [1]. The deposition temperature on the substrate was  $T_d = 200^\circ\text{C}$ . The thickness of condensate was determined by time of deposition in the range of (120 - 300) sec. within (540 - 2835) nm (Table 1), using the Bruker Dektak XT profilometer [14].

The morphology of the films was pre-determined by the Nexus 412 hardness meter, which makes it possible to determine the presence of phases of various materials

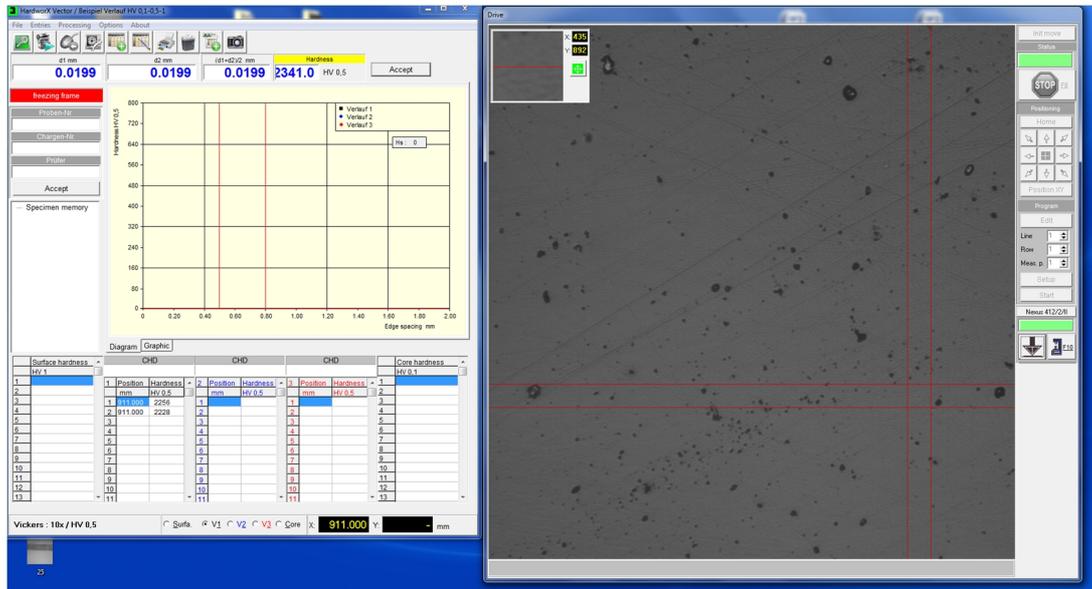
in the base material and to investigate the defect structure. It makes the possibility to determine of the presence of phases of various materials in the base material and to investigate the defect structure. It were received using hardener surface the images of CdTe samples (Fig. 5-6) obtained on silicon substrate with high resolution (camera zoom of 10x, 40x). The scanning was carried out along the X-Y axes, the measuring range on the samples takes 120x120 microns, the analysis was provided with 20x20 microns step. Results were processed using special software HardworX.

The obtained surface morphology of the thin-film structures were investigated by atomic force microscopy (CSM Instruments Swiss made) in the periodic contact mode. Measurements were made in the central part of the

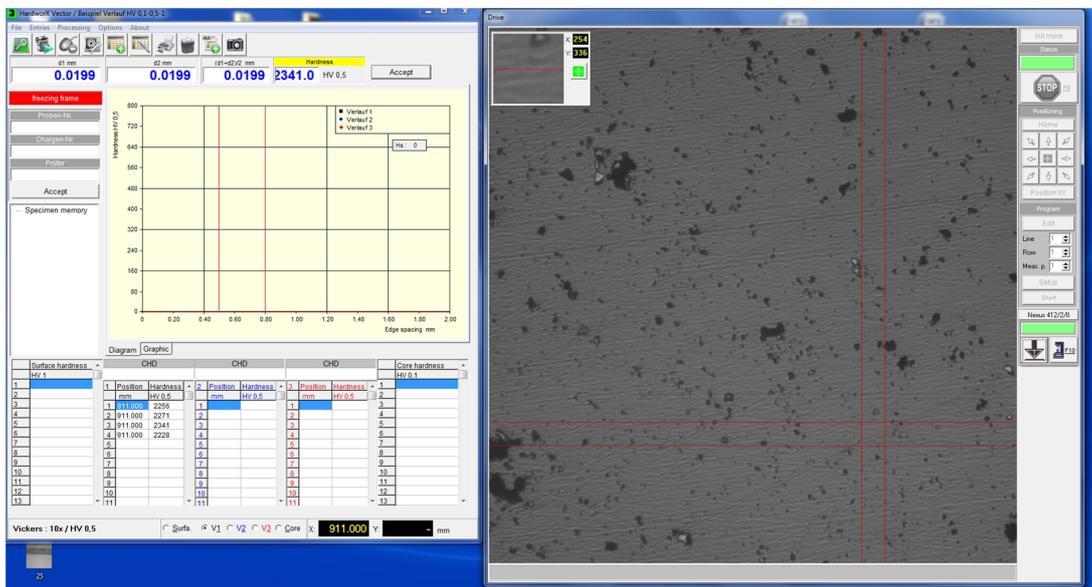
**Table 2**

The basic morphological parameters of CdTe thin films deposited in vacuum by vapor-phase condensation on silicon substrates. Sample numbers and technological parameters of deposition correspond to the data in Table 1

Sample number	Thickness d, nm	Average normal size $h_c$ , nm	Maximum normal size $h_{max}$ , nm	Average roughness $R_a$ , nm	Root mean square roughness $R_q$ , nm
6	2835	24.98	36.17	7.10	8.99
9	540	23.19	31.05	5.62	6.98



**Fig. 5.** Surface image of CdTe/Si thin films on hardener Nexus 412A (sample 6, 10x camera zoom).



**Fig. 6.** Surface image of CdTe/Si thin films on a hardener Nexus 412A (sample 9, 10x camera zoom).

samples using serial silicon probes CSM with a nominal radius of rounding up to 10 nm. According to results of ASM analysis, in addition to surface morphology and profilograms in the software package Gwyddion, the normal sizes of nanocrystals, average roughness and root mean square roughness were determined.

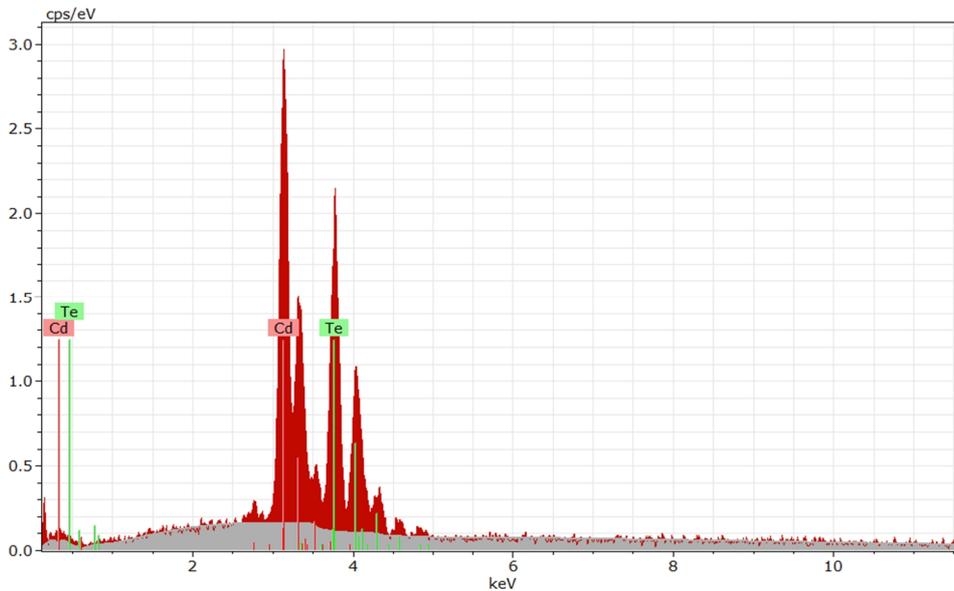
## II. Results and discuss

The influence of technological parameters on deposition process is main specify of formation and growth of vapor phase condensates. It may be due to significant supercooling and steam oversaturation

**Table 3**

The phase analysis data for CdTe/Si thin films (sample 6)

Element	AN	Series	Net	[wt.%]	[norm. wt.%]	[norm. at.%]	[norm. wt.%]	Error in wt.% (3 Sigma)
Cd	48	L-series	11711	41.4825	46.2809	49.4427	46.2809	4.1703
Te	52	L-series	8803	48.1494	53.7190	50.5572	53.7190	4.5827
			Sum:	89.6319	100	100		



**Fig. 7.** The EDS spectrum of CdTe/Si thin films (sample 6).

compared to crystallization conditions of bulk crystals and the numerous physical and technological parameters that make influence to their kinetics formation. In particular, the following parameters can be controlled [15]:

- evaporation temperature  $T_e$  at constant temperature  $T_s$  of substrates and time of deposition  $\tau$ ;
- deposition temperature at constant evaporation temperature  $T_e$  and time of deposition  $\tau$ ;
- deposition time  $\tau$  at constant temperatures of both the substrate  $T_s$  and evaporator  $T_e$ .

Some results of SEM analysis of the CdTe films deposited on silicon substrates are shown in Fig. 3-4. It can be observed that all thin-film condensates are characterized by homogeneous tightly ordered structure, without the presence of distinct macroscopic grains. Here it's mention layered growth of thin films [16], which is of Stranki-Krastanov mechanism of growth typical [17].

The basic morphological parameters of deposited CdTe thin films in vacuum by vapor-phase condensation on silicon substrates are presented in Table 2, where sample numbers and technological parameters of deposition correspond to the data in Table 1.

We observed the uniformly distributed nanoobjects on the surface of deposited films. The experimental factor that affects the change of nanoobjects morphology is deposition time  $\tau$ , which varied with constant values of evaporation and deposition temperatures. As can be seen at Fig. 1, the shape and size of these nanoobjects is

changable. The normal sizes of surface nanoparticles increase with increasing of film thickness (deposition time). Therefore, nanoparticles in normal direction increased from 21 - 25 nm for a film thickness of 540 nm to 22 - 28 nm for film of 2835 nm thickness. At the same time there is observed a sharpening of nanoobjects vertices. For small thicknesses, they have a visible domed shape.

As the increase of deposition time (thickness of the film) causes a slight normal growth of nanoobjects and rounded vertices transforms into more sharped peaks, one can argue about the implementation of Stranki-Krastanov mechanism of growth – at first is layer growth of CdTe on Si-substrate realized, with the subsequent formation of separate uniformly distributed nanoobjects on condensed film.

The Stranky-Krastanov mechanism is realized with some inconsistency between film and substrate lattice parameter ( $a_{Si} \sim 5,430 \text{ \AA}$ ,  $a_{CdTe} \sim 6,481 \text{ \AA}$ ). Therefore, the presence of this mechanism by CdTe vapor-phase condensation is evident both on amorphous glass and silicon substrates.

From the cross-section of the film (Fig. 3) can be noted that inside of investigated samples structure are formed implicitly visible columnar nanofibers. The larger is the diameter of nanofiber, the better film absorbs light rays. The obtained results can be applied for cadmium telluride thin films use in photoelectric converters.

The element or chemical analysis was provided on

Table 4

The phase analysis data for CdTe/Si thin films (sample 9)

Element	AN	series	Net	[wt.%]	[norm. wt.%]	[norm. at.%]	[norm. wt.%]	Error in wt.% (3 Sigma)
Si	14	K-series	4204	21.3176	28.6496	63.2031	28.6496	3.2516
Cd	48	L-series	4701	24.3974	32.7886	18.0725	32.7886	2.6828
Te	52	L-series	3967	28.6930	38.5617	18.7243	38.5617	3.0086
			Sum:	74.4081	100	100		

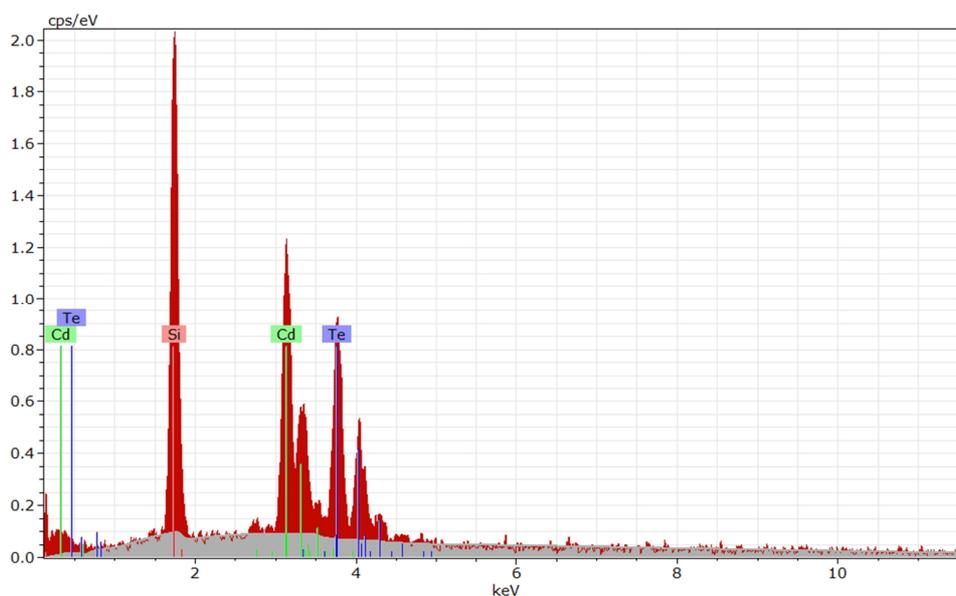


Fig. 8. The EDS spectrum of CdTe/Si thin films (sample 9).

the base of Energy-dispersive X-ray spectroscopy (EDX) in SEM method. The EDX spectrum for sample 6 and 9 are shown in Fig. 7-8.

For the samples 6 and 9 (CdTe)/Si the chemical composition analysis provided on SEM (Bruker Quantax) used the method of energy dispersive X-ray spectroscopy (EDS). The assayed EDS analysis was carried out in the low vacuum mode. In particular, the atomic weight percent consist Cd (49.44 %) and Te (50.56 %) for the sample 6.

For the sample 9 the atomic weight percent of Cd (18.07 %), Te (18.72 %), and Si (63.2) as basic element of the substrate was obviously observed in the spectrum. We can determine the condition for the deposition of stoichiometric CdTe semiconductor films using the vapor phase condensation method from sequential experiments result.

## Conclusions

1. It was investigated that method of free vapor-phase condensation in vacuum in a single cycle at preset temperatures of the substrates and the evaporator provides CdTe condensates of different thicknesses.

2. The analysis of SEM results of the CdTe/Si thin-film nanostructures obtained by free vapor-phase condensation for different technological deposition factors was carried out.

3. Were established the regularities of nanostructures normal size change on the surface of condensates, the most probable their normal sizes, as well as the average roughness and root mean square roughness magnitude from the temperature and time of vapor deposition on the substrate and the evaporation temperature.

4. It is shown that prevails Stranki-Krastanov mechanism of nanoobjects growth.

5. The relevance and perspectives of CdTe thin-film condensates applying as solar cells for photovoltaic converters is theoretically substantiated.

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## Технологія осадження відкритим випаровуванням у вакуумі фотоелектричних плівок CdTe

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Методом осадження із парової фази, а саме шляхом відкритого випаровування у вакуумі отримано тонкі плівки CdTe, використовуючи різні технологічні фактори, зокрема, різну товщину (задається часом осадження  $t$ )  $d = (540 - 2835)$  нм, температуру осадження  $T_d = 200^\circ\text{C}$  та температуру випарника  $T_e$  ( $500 - 600$ ) $^\circ\text{C}$ . Плівки осаджували на кремнієві підкладки. Морфологія тонкопліткових конденсатів визначається на основі аналізу ASM та SEM досліджень. Були отримані залежності середньої шорсткості та середньоквадратичного відхилення від матеріалу підкладки та товщини плівки. Встановлено, що ріст поверхневих наноструктур визначається механізмом Странкі-Крастанова.

**Ключові слова:** телурид кадмію, тонкі плівки, наноструктури, процеси росту.