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The Vapour Thermal Synthesis of CdTe Films from Elementary Components

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The opportunities for synthesis of cadmium telluride (CdTe) semiconductor films by annealing of the cadmium (Cd) metallic films on glass substrates in the tellurium (Te) vapors were studied. The experiment of annealing-tellurisation (tellurium transfer to the plate with cadmium and expected CdTe synthesis) was preceded by theoretical analysis of partial pressures of the Te vapour above the Te_{sol}, the Cd above the Cd_{sol}, the Te above the $CdTe_{sol}$, the Cd above the $CdTe_{sol}$ for the case of congruent sublimation and by the choice of thermal annealing conditions from the results of conducted analysis.

With the use of the scanning electronic microscope the surface morphology of the initial Cd films and annealed films were investigated, and quantitative composition was determined from spectra of the characteristic X-ray radiation. Optical properties were investigated.

Key words: CdTe, II-VI compounds, thin films, vapor pressure.

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I. Films fabrication

The cadmium telluride (CdTe) is still one of the most promising semiconductor materials for photovoltaic applications [1, 2]. Necessity of decline in prices of solar cells and increase of their areas set the problem of subsequent search for effective methods of high-quality film fabrication. The fabrication of semiconductor films of cadmium telluride (CdTe) by annealing of the cadmium (Cd) metallic films in the tellurium (Te) vapor was the purpose of this research. Technological experiment was preceded by the theoretical analysis of vapor partial pressure for the tellurium above the solid tellurium, the cadmium above the solid cadmium [3], the tellurium above the solid CdTe [4], and calculated vapor pressure of the cadmium above solid CdTe for congruent sublimation conditions. Fig. 1 presents temperature dependence of vapor partial pressure for components.

The Cd films were deposited on optically uniform glass substrates (75×26×2 mm) by thermal vacuum deposition, $P = 5 \cdot 10^{-3}$ Pa. The substrates were pretreated by etching from 3 to 5 min in HF_2 aqueous solution. The glass substrates were heated to ~ 150 ÷ 200 ºC directly before the Cd deposition for better film adhesion. The high purity Cd was used for thin ≤ 1 μm uniform film deposition. The tellurisation (tellurium transfer to the plate with cadmium and expected CdTe synthesis) was conducted in a sealed quartz ampoule in an oven with two temperature areas: the Te sources and plates with Cd (deposition area). The ampoule was placed in the oven with the stationary thermal mode. The temperature gradient between the source $t_1 = 290 \div 320$ °C and deposition area $t_2 = 240 \div 260$ °C was in range $\Delta t = 40 \div 60$ °C. The average process of tellurisation lasted 6 hours.

The physical properties (surface morphology, quantitative composition, within accuracy to 2 %) of the initial Cd metallic films and films fabricated by tellurisation, were investigated by the electronic microscope (SEM-102-02, SELMI, Ukraine).

The optical transmission measurements have been done at room temperature with unpolarized light at normal incidence in the wavelength range from 300 to 1000 nm using MDR-23 spectrophotometer. The optical absorption coefficient α was calculated for each film using the equation

$$I_t = I_0 \exp(-at),$$

where t is the film thickness, I_t and I_o are the intensity of transmitted light and initial light, respectively. The absorption coefficient α is related to the incident photon energy hν as:

$$a \cdot hn = A\left(hn - E_g\right)^{n/2},$$

where A is a constant dependent on electron and hole effective mass and interband transition, Eg is the optical band gap, and n is equal to 1 for direct band gap material such as CdTe. The band gap Eg was determined for each film by plotting $(\alpha h\nu)^2$ vs hν and then extrapolating the straight line to the energy axis.

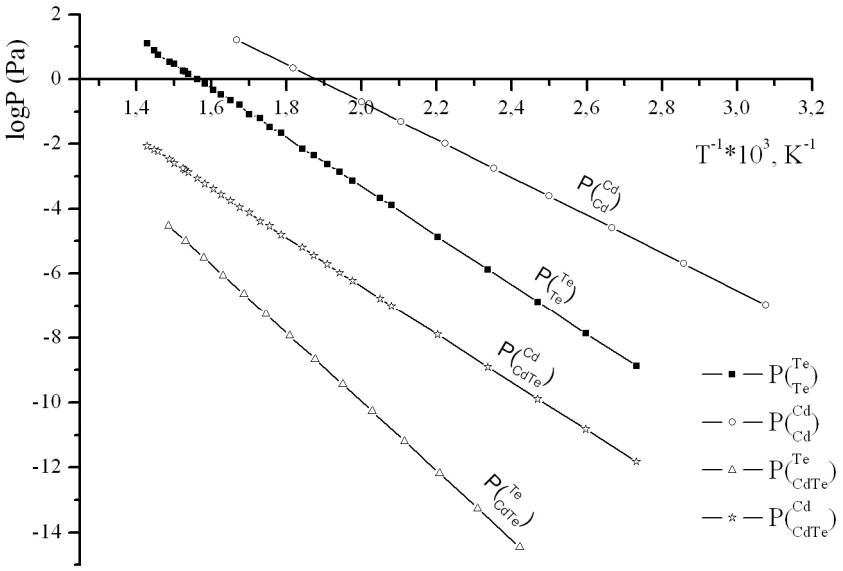

Fig. 1. Temperature dependence of components vapor partial pressure for tellurium above solid tellurium (P_{Te}^{Te}), cadmium above solid cadmium (P_{Cd}^{Cd}), tellurium above solid CdTe (P_{CdTe}^{Te}) congruent sublimation, and calculated vapor pressure of cadmium above solid CdTe (P_{CdTe}^{Cd}) for congruent sublimation.

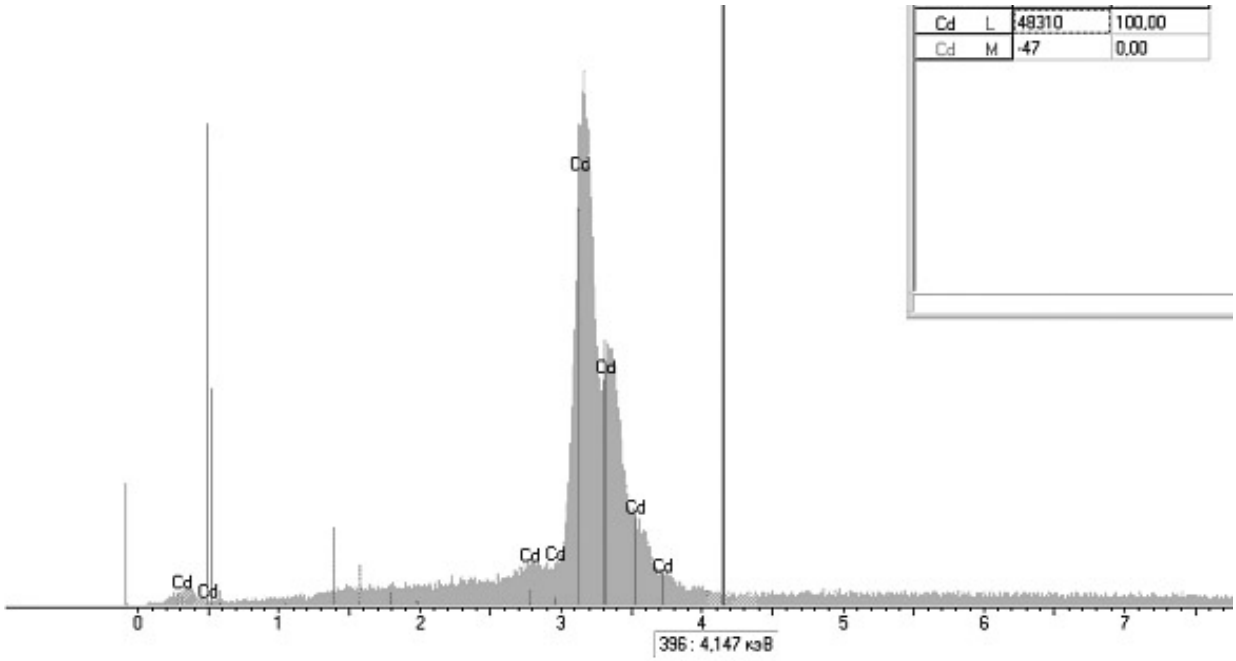

Fig. 2. The thermally deposited Cd film EDS spectrum. REMMA-102-02 microscope (SELMI, Ukraine).

II. Physical properties of fabricated films

The Cd film changed color from characteristic metallic to dark brown after annealing in tellurium vapour i.e. tellurisation. The transparence of tellurised Cd film increased in comparison to initial one. The transparence increase is conditioned by partial Cd film vaporization and film thickness decrease.

The Cd/glass sample EDS analysis showed absence of any impurities in the cadmium film, the oxygen in that number (see fig. 2). The film surface is uniformly packed by Cd granule as shown in fig. 3. The silicium from glass substrate absence in the case of microscope accelerating voltage 20 kV indicates that Cd film thickness is ≥ 1 μm. The specimen volume analyzed by EDS at 20 kV microscope accelerating voltage is 1×1×1 μm. The attempt to receive tellurised film surface SEM image failured. It is caused by tellurised film electrisation and substantial rapid growth of sheet resistance and it is not possible to receive SEM image in high vacuum mode. This circumstance gives indirect evidence that composition of tellurised film has changed in comparison

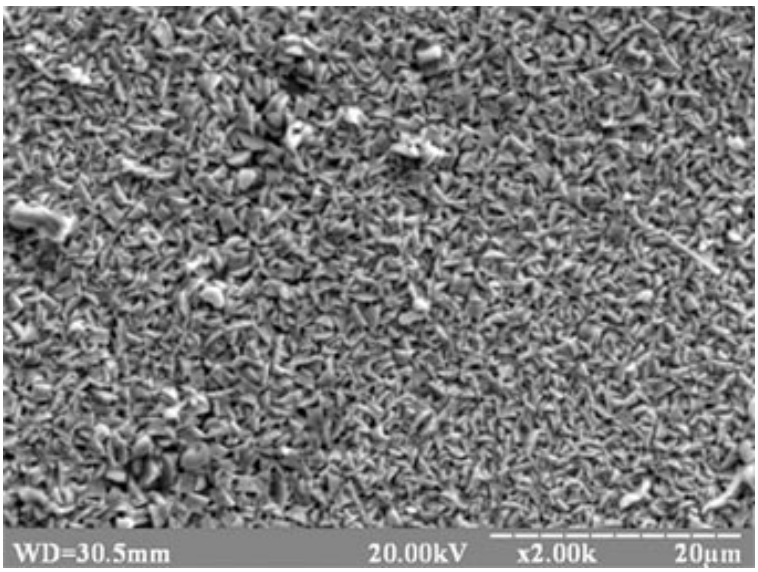

Fig. 3. The thermally deposited Cd film SEM image, 20 kV accelerating voltage, 2000 times magnification, received by means of REMMA-102-02 microscope (SELMI, Ukraine).

Table 1

Experiments result

	a		**b**		
Cd_{mas}	12,94	10,15	22,68	38,06	61,84
Te_{mas}	23,51	17,35	9,77	5,89	3,37
Cd	0,44	0,369	0,7	0,866	0,948
Te	0,56	0,631	0,3	0,134	0,052
	$Cd_{1-x}Te_{0,63\div0,56}$		**$Cd_{1-x}Te_{0,3\div0,052}$**		
source					
Cd	not find		44,20		0,433
Te	100		57,82		0,567

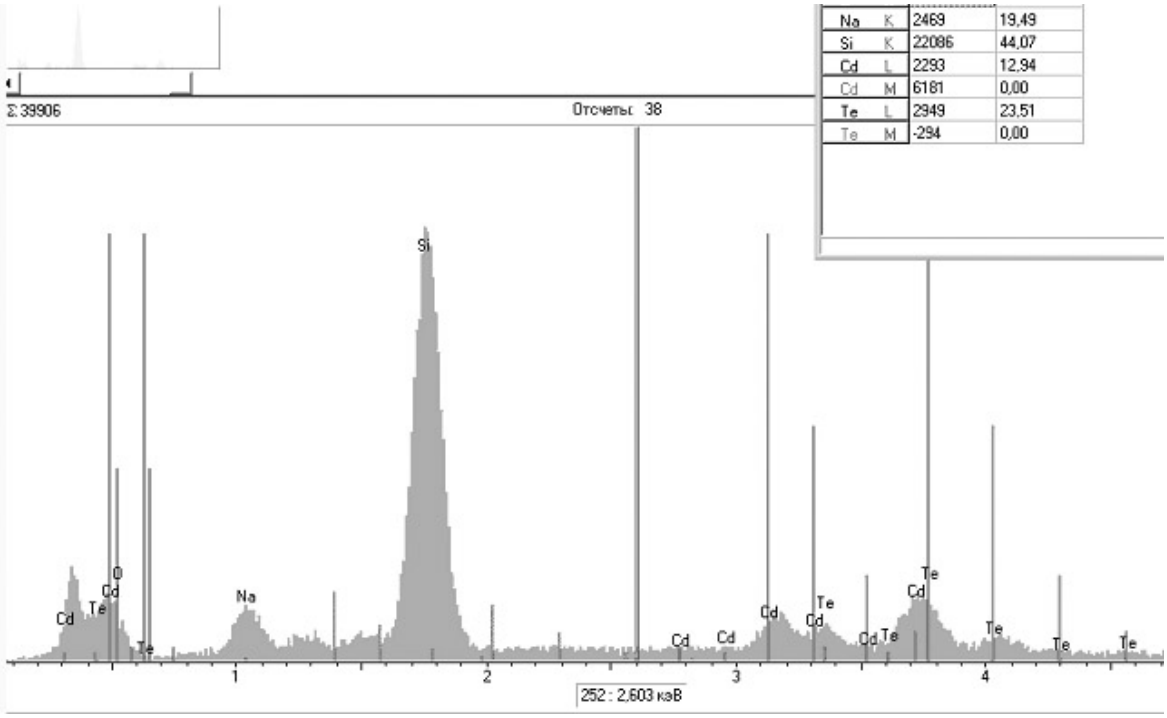

Fig. 4. The tellurised Cd film EDS spectrum.

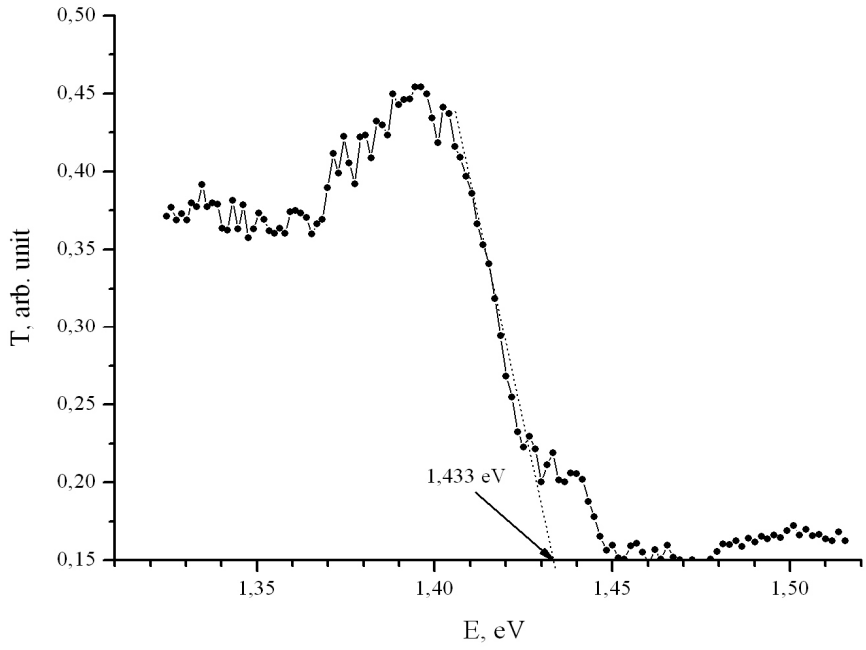

Fig. 5. The tellurised Cd film optical transparence in absorption edge region.

to initial one.

The tellurised sample EDS analysis was carried out in the low vacuum mode. It confirms the film composition change and film thickness decrease (fig. 4). In particular Cd (12,94 %) and Te (23,51 %) were determined in the film that confirms success of tellurisation. Si (44,07 %) and Na (19,49 %) as basic elements of the glass substrate were obviously observed in the spectrum. Decrease of film thickness is conditioned by the Cd partial evaporation in the process of tellurisation. Comparison of the Te and Cd amount shows the CdTe stoichiometry deviation. The Te partial pressure was too high for fabrication of stoichiometric CdTe semiconductor films. The temperature of the Te source determines the Te amount in fabricated CdTe film (see table 1). From sequential experiments result we can define the condition for deposition of stoichiometric CdTe semiconductor films. The Te source EDS analysis was carried out after tellurisation. The Cd reverse transport has not take place in first experiment (see table 1).

For identification of the CdTe compound in tellurisation film the spectral distribution of optical transparence was carried out. The region of fundamental absorption was observed in transparence spectra. Absorption coefficient in the fundamental absorption area for all CdTe samples was 10^5 cm^{-1} in order to magnitude. The transparence spectra of samples (Fig. 5.) clearly shows the existence of the CdTe compounds in all films. Spectral dependence of CdTe films absorption in the coordinates $(\alpha*h\nu)^2$ vs $h\nu$ demonstrate the presence of fundamental absorption edge, localized in the region 1,45 eV. The calculated band gaps of the films are in good agreement with the reported values of the monocrystalline CdTe [5] and correspond to the direct allowed band transition. We do not observe a straight-line behaviour on graphs of $(\alpha h\nu)^{2/3}$ vs $h\nu$ (direct forbidden), $(\alpha h\nu)^{1/2}$ vs $h\nu$ (indirect allowed) $(\alpha h\nu)^{1/3}$ vs $h\nu$ (indirect forbidden). These plots (not shown) reveal that the type of transition is neither direct forbidden nor indirect.

Conclusions

Physical and chemical grounds for the tellurisation method – new technology of CdTe film fabrication were established. The films composition stoichiometry deviation tailoring by tellurisation initial was demonstrated. The optical properties of fabricated CdTe semiconductor films correspond to bulk one and indicate possibility of photovoltaic application.

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Термічний паровий синтез плівок CdTe з елементарних сполук

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Вивчені можливості синтезу напівпровідникових плівок телуриду кадмію (CdTe) за допомогою відпалу в парах телуру (Te) плівок металічного кадмію (Cd) на скляних підкладках. Експерименту телуризайційного відпалу (телур переноситься на пластини з кадмієм і очікуваний синтез CdTe) передував теоретичний аналіз парціальних тисків пари Te над $Te_{твердий}$, Cd над $Cd_{твердий}$ Te над $CdTe_{твердий}$, Cd над $CdTe_{твердий}$ для випадку конгруентної сублімації і за допомогою вибору теплового режиму відпалу з аналізу результатів.

Використовуючи скануючий електронний мікроскоп SEM-102-02 (Селмі, Україна) досліджено морфології поверхонь вихідних плівок Cd і відпалених плівок; визначений кількісний склад зі спектрів характеристичного рентгенівського випромінювання.