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Optical Properties of CdTe:In Thin Films Deposited by PVD Technique

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CdTe:In thin films on glass substrates were obtained by physical vapor deposition. Thin films were obtained with different thicknesses (by setting of different deposition time τ) at the constant temperature of substrate and temperature of evaporation. Identification of CdTe thin films was performed by the measurements of spectral distribution of optical transparency. Region of the fundamental absorption was observed in the transmission spectra. The films are characterized by high transparency in near infrared region and moderate transmission coefficient which varies from 52 % to 85 %. All of the films demonstrated very sharp absorption edge near 800 nm. Moreover, observed interference in optical transparency spectra is an indication of the uniform thickness of deposited films. The Swanepoel method is used to calculate maximum $T_M(\lambda)$ and minimum $T_m(\lambda)$ transmission curves by parabolic interpolation to experimentally determined positions of interference maxima and minima. Sharp increase of the refraction index at wavelengths < 1000 nm is due to decreased transmission near the fundamental absorption edge of thin films of indium-doped cadmium telluride. Main optical constants were determined, such as theoretical film thickness, refraction index, and absorption coefficient.

Keywords: Thin Films, PVD Technique, Solar Cells, Optical Properties, Swanepoel Method.

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1. INTRODUCTION

Energy is an irreplaceable resource which is closely connected with economic and social development. With fast development of technologies, electricity needs continue evermore to grow. That is why great effort in the recent years is directed to development of new and improving existing ways, methods, and technologies for the production of useful energy. Presently, oil, coal and natural gas remain the principal energy carriers in the world [1, 2]. A key characteristic of non-renewable resources is their limited quantity, since they are restored much slower than consumed. Their permanent use creates serious risk for further energy security.

One of the most promising solutions to the world energy and ecological problem is the use of solar energy thanks to numerous advantages. Solar energy is the most common and available resource among renewable energy sources. In the urgent challenges of climate change and the exhaustion of fossil fuel, solar photovoltaic devices are considered a clean and stable alternative [3, 4]. Photoelectric panels are presently the most commercialized technology of solar energy with significant global markets [5].

Modern photovoltaic industry is mainly based on silicon technologies (over 90%) due to high efficiency of solar devices manufactured from this semiconductor [6]. The main disadvantage of the use of Si in photovoltaic elements (PE) is low absorption due to indirect band gap. Therefore, the manufacture of photovoltaic systems from this semiconductor requires large quantity of material [7]. Thin film technologies minimize production costs by reducing the quantity of raw material.

Thin-film photovoltaic element technology based on CdTe is currently the leading thin-film technology of top ten world manufacturers. It is explained by the fact that CdTe is a strong and chemically stable material which can be manufactured by a wide spectrum of methods making it perfect for production [8]. CdTe solar cells underwent significant improvement in the last decade what led to increased efficiency of 21.5 % which later grew to 22.1 % [9].

CdTe has optimal band gap of 1.45 eV. According to Shockley–Queisser limit, it can achieve efficiency of 32 %, at open-circuit voltage over 1 V and short circuit current density over 30 mA/cm^2 [10]. CdTe crystallizes in the cubic zinc blende structure, with the lattice parameter 6.481 Å [11, 12].

The efficiency of solar cells is determined by such important parameters as open circuit voltage (V_{oc}), short circuit current density (J_{sc}), fill factor (FF). Short circuit current density depends on the quantity of photogenerated carriers, and the rate of their separation and recombination in the external circuit. However, after considering optical losses in the CdTe cells, all Jsc components are taken into account, and its efficiency is close to the practical limit [13]. Increase of FF and Voc values requires control and modification of cell parameters such as recombination rate, doping level of absorbing layer, and back contact. Significant changes of optical, electrical and mechanical properties of CdTe thin films are created by doping. Elements of Group I and V of the Periodic System act as acceptors, and those of Group III and VII are donors. Commonly, Al, Ga, In, I and Cl are used as donors, and Li, Cu, Ag, N, P, Sb and As as acceptors.

In the present work we used In as a dopant admixture to increase electrical conductivity of CdTe thin films for photovoltaic applications. The effect of In doping on optical properties and photoconductivity of CdTe thin films deposited by thermal evaporation was investigated.

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2. EXPERIMENTAL DETAILS

CdTe:In thin films were produced by physical vapour deposition method. The samples were deposited in a single technological cycle at pressure of 10^{-5} torr. The synthesis of indium-doped cadmium telluride for the mechanical mixture was performed in evacuated and soldered quartz ampoules. Additionally, unlike the synthesis of IV-VI compounds, ampoules were graphitized by acetone pyrolysis. Temperature regime of the synthesis consisted of several heating stages, with the maximum synthesis temperature of 1120 °C. Obtained ingots crushed in a ball mill. In concentration in samples was 10^{19} cm^{-3}. The evaporation temperature was 550 ºC, the substrate temperature 200 ºC, the film thickness was controlled by the deposition time from 60 to 420 s (Table 1).

Optical transmission spectra were measured in the wavelength range of 180 – 2100 nm using an Agilent Technologies Cary Series UV-VIS-NIR Spectrophotometer. Optical spectra were analyzed using the Swanepoel method.

Table 1 – Technological parameters of the deposition of CdTe:In thin films on a glass substrate

Sample No.	Substrate temperature T_S, ºC	Evaporation temperature T_E, ºC	Deposition time τ, sec	Film thickness, nm
1	200	550	60	540
2	200	550	120	1028
3	200	550	420	580

3. OPTICAL PROPERTIES OF CDTE:IN THIN FILMS

The Swanepoel method was used to calculate film thickness from optical properties. Presented by Swanepoel in 1983 [14], the method was used to calculate the thickness of amorphous silicon layer from optical transmission of the film. Rays of different wavelengths of the incident light interact with each other by multiple reflections inside the film. This results in a wave-like picture of film transmission in a wavelength range. The presence of interference pictures in optical transmission spectra is evidence of thickness uniformity of deposited films and of smooth surface [15].

Optical transmission spectra T of deposited In-doped CdTe thin films as a function of wavelength λ in the range of 300 – 2200 nm are shown in Fig. 1.

The CdTe:In spectra exhibit interference bands in the spectral region $\lambda > 800$ nm. Films are characterized by high transparency in near infrared region and moderate transmission coefficient. The maximum transmission coefficient is 93.02 % at 1379 nm for sample 2, with deposition time 60 s.

Optical constants such as refraction index, absorption coefficient, theoretical thickness of films and optical conductivity were investigated by the Swanepoel method. It is based on plotting enveloping interference maxima $T_M(\lambda)$ and minima $T_m(\lambda)$ of the transmission spectrum as shown in Fig. 2.

Film thickness and refraction indices of In-doped CdTe thin films were calculated by the Swanepoel method. For instance, if n_1 and n_2 are refraction indices calculated from two consecutive maxima or minima that correspond to wavelengths λ_1 and λ_2, then film thickness d is calculated by Equation 1 [16]:

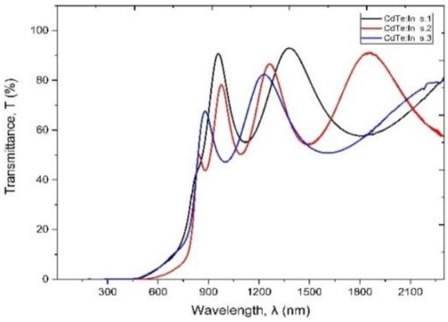

Fig. 1 – Transmission spectra of CdTe:In thin films

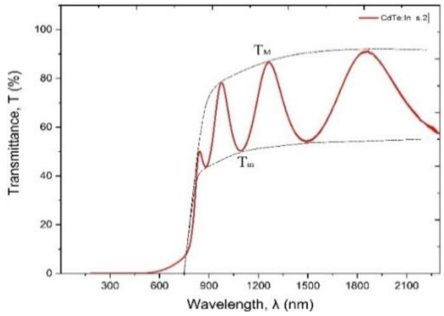

Fig. 2 – Optical transmission spectra of deposited CdTe:In thin films with defined T_M and T_m

$$d = \frac{\lambda_1 \lambda_2}{2(\lambda_1 n_2 - \lambda_2 n_1)}. \quad (1)$$

Application of the method of extrapolation of extrema for determination of optical parameters obtained from transmission spectra that are characterized by interference picture leads to some inaccuracies. The problem consists in accuracy of plotting the extrapolation between the interference extrema. This affects the practicality of this method in rapid calculation of the full set of optical parameters using only spectrophotometric measurements of T or R [17-19]. Frequently, obtained calculated results can be verified by comparing them with more accurate measurements of these parameters using ellipsometry.

Values of film thickness d calculated by Equation (1) for each sample are presented in Tables 2-4. Film thickness that was measured by a Bruker Dektak XT 2D Profilometer is presented in Table 1. Despite certain difficulties that the contactless profilometer has at the measurement at the substrate-film interface, obtained data are highly accurate (definition of 1 nm) for thickness and roughness. Thus film thickness obtained from oscillating transmission and reflection curves (Tables 2-4) is comparable to the profilometer data (Table 1). Although the error of determination of wavelengths of neighboring extrema is less than 1.5 nm (Maple software environment), the error for theoretical calculation of d_{theor} data includes also the absolute error of measuring T_M and T_m (no less than 1 %).

The thickness obtained by Equation (1) is very sensitive to errors in refraction index value. The refraction index is calculated by Equation (2):

$$n = [N + (N^2 - s^2)^{1/2}]^{1/2}, \quad (2)$$

where

$$N = \frac{2s(T_M - T_m)}{T_M T_m} + \frac{s^2+1}{2}. \quad (3)$$

Here s is the refraction index of the glass substrate, and T_M and T_m are the transmission maximum and corresponding minimum at certain wavelength λ.

The refraction index $n(\lambda)$ of CdTe:In thin films (sample 1) decreases with increasing wavelength in the range of 2.54–2.62 (Fig. 3). Sharp increase of the refraction index at wavelength < 1000 nm is due to decreased transmission near the fundamental absorption edge of indium-doped cadmium telluride thin films.

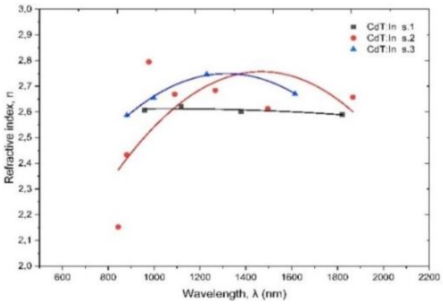

Fig. 3 – Dependence of refraction index n of CdTe:In thin films on wavelength

For insignificant dispersion of the refraction index that usually happens far from the absorption edge, the interference order m in the maxima of the transmission spectra for wavelength λ_1 is

$$m = \left(\frac{\lambda_2}{\lambda_1-\lambda_2}\right), \qquad (4)$$

where λ_1 and λ_2 are wavelengths of two adjacent transmission maxima ($\lambda_1 > \lambda_2$).

In the middle spectral absorption region where the interference rings are clearly revealed in the transmission spectra, the coefficient absorption α can be calculated as

$$\alpha = \frac{1}{d} ln \frac{(n-1)^3(n-s^2)}{E_m-(E_m^2-(n^2-1)^3(n^2-s^4))^{0.5}}, \qquad (5)$$

where

$$E_m = \left(\frac{8n^2 s}{T_m}\right) - (n^2-1)(n^2-s^2). \qquad (6)$$

The absorption coefficient of CdTe:In thin films is plotted in Fig. 4. The highest value of the absorption coefficient is $2.7 \cdot 10^3$ cm^{-1} for sample 3.

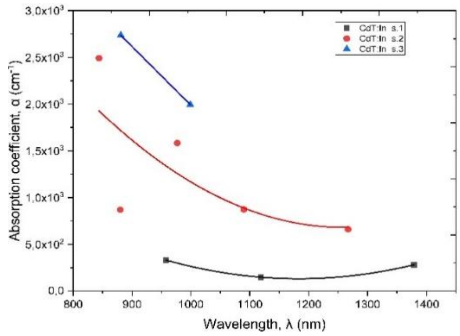

Fig. 4 – Absorption coefficient of CdTe:In thin films calculated by the Swanepoel method

Table 2 – Optical properties of CdTe:In thin films (sample 1) calculated by the Swanepoel method

λ, nm	T_M	T_m	n	d, nm	m	α, cm^{-1}	σ_{opt}, 10^{11}
2566	1.0033	0.6059	2.539				
1821	0.9594	0.5749	2.590				
1379	0.9302	0.5611	2.602	557.338	1	281.57	17.5
1119	0.9159	0.5505	2.622	542.883	1.5	148.05	9.3
958	0.9071	0.5513	2.607	599.116	2	330.85	20.6
				$\langle d \rangle$ =566.44			

Table 3 – Optical properties of CdTe:In thin films (sample 2) calculated by the Swanepoel method

λ, nm	T_M	T_m	n	d, nm	m	α, cm^{-1}	σ_{opt}, 10^{11}
1867	0.9135	0.5404	2.657				
1496	0.8837	0.5410	2.613				
1267	0.8660	0.5169	2.684	719.489	2	660.85	42.3
1090	0.8178	0.5026	2.669	711.884	3	872.86	55.6
977	0.7818	0.4626	2.795	673.487	3.5	1582.91	105.6
880	0.5808	0.4372	2.433	1582.802	4	869.47	50.5
844	0.5009	0.4249	2.152	1610.639	6	2491.89	128.0
				$\langle d \rangle$ =1059.66			

Table 4 – Optical properties of CdTe:In thin films (sample 3) calculated by the Swanepoel method

λ, nm	T_M	T_m	n	d, nm	m	α, cm^{-1}	σ_{opt}, 10^{11}
1615	0.8314	0.5076	2.670				
1230	0.8235	0.4874	2.746				
999	0.7319	0.4719	2.654	498.473	2	1994.08	126.3
881	0.6755	0.4599	2.587	710.917	2.5	2736.16	168.9
				$\langle d \rangle$ =604.69			

It should be noted that optical conductivity helps understand electronic structure material and is associated with the refraction index and the absorption coefficient [20]. Optical conductivity σ_{opt} can be determined from the calculated value of the absorption coefficient by the equation (7):

$$\sigma_{opt} = \alpha nc/4\pi \qquad (7)$$

where α is the absorption coefficient, c is the speed of light.

The change of optical conductivity σ_{opt} as a function of photon energy is plotted in Fig. 5. Optical conductivity of thin films increases with the photon energy. The values of optical conductivity are given in Tables 2-4.

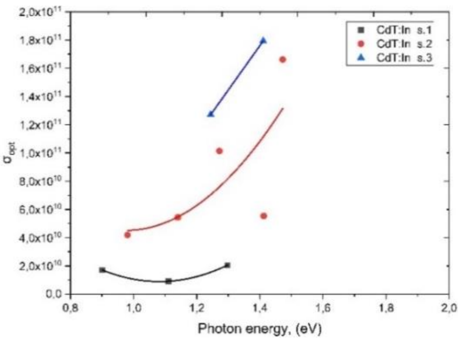

Fig. 7 – Dependence of optical conductivity of CdTe:In thin films on energy of photons

4. CONCLUSIONS

Optical parameters of indium doped CdTe thin films were investigated by spectrophotometric transmission measurements in the range of 300 – 2200 nm.

The films are characterized by high transparency in near infrared region and moderate transmission coefficient which varies from 52 % to 85 %. All films demonstrated very abrupt absorption edge near 800 nm. Interference picture that was observed in optical transparency spectra serves as an indication of the uniformity of the thickness of deposited films.

Optical characteristics of thin films (refraction index, film thickness, absorption coefficient, and optical conductivity) were calculated using the Swanepoel method. The highest achieved value of the absorption coefficient is $2.7 \cdot 10^3$ cm $^{-1}$.

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Оптичні властивості тонких плівок CdTe:In отриманих методом фізичного осадження у вакуумі

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Тонкі плівки CdTe:In отримувались методом фізичного вакуумного осадження на скляних підкладках. Тонкі плівки для дослідження отримували різної товщини (різний час нанесення τ) при однаковій температурі підкладки та однаковій температурі випарника. Спектральний розподіл оптичної прозорості здійснювався для ідентифікації тонких плівок CdTe. У спектрах пропускання спостерігалась область власного поглинання. Можна помітити, що плівки відрізняються високою прозорістю в ближній інфрачервоній області та середнім коефіцієнтом пропускання, який коливається від 52 % до 85 %. Усі плівки демонстрували дуже різкий край поглинання поблизу 800 нм. Крім того, спостережувана інтерференційна картина в спектрах оптичної прозорості є вказівкою на однорідність товщини осаджених плівок. Застосування методу Сванеполя полягає у обчисленні максимальної кривої пропускання $T_M(\lambda)$ і мінімальної $T_m(\lambda)$ за допомогою параболічної інтерполяції до експериментально визначених положень максимумів і мінімумів інтерференції. Різке збільшення показника заломлення при довжині хвилі < 1000 нм зумовлене зменшенням пропускання поблизу краю власного поглинання тонких плівок телуриду кадмію легованого індієм. Визначено основні оптичні константи, такі як теоретична товщина плівки, показник заломлення і коефіцієнт абсорбції.

Ключові слова: Тонкі плівки, Техніка ПВД, Соняні комірки, Оптичні параметри, Метод Свейнпола.