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Optical properties of CdTe thin films obtained by the method of high-frequency magnetron sputtering

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The optical constants and thickness of CdTe thin films prepared by high-frequency magnetron sputtering method are determined. The synthesis procedure and the results of optical studies of CdTe thin films deposited on the surface of a glass/ITO substrate are given. The optical constants and the band gap of the films under study have been determined. Optical properties (refractive index $n(\lambda)$, absorption coefficient $\alpha(\lambda)$, and extinction coefficient $k(\lambda)$) of the thin films and thickness d can be determined from the transmission spectrum. The dispersion of the refractive index was explained using a single oscillator model. Single oscillator energy and dispersion energy are obtained from fitting. Optical parameters of the films were determined using the Cauchy, Sellmeier and Wemple models.

Keywords: thin films, absorption, dispersion, refractive index, transmission.

Определены оптические функции и толщина тонких пленок CdTe, полученных методом высокочастотного магнетронного распыления. Приведена методика синтеза и результаты оптических исследований тонких пленок CdTe нанесенных на поверхность стеклянной подложки/ITO. Оптические свойства (показатель преломления $n(\lambda)$, коэффициент поглощения $\alpha(\lambda)$ и коэффициент экстинкции $k(\lambda)$) тонких пленок и толщины d определены из спектра пропускания. Дисперсия показателя преломления объяснена с использованием одноосциляторной модели. Оптические параметры пленок анализируются с использованием моделей Коши, Селлмейера и Уэмпла.

Оптичні властивості тонких плівок CdTe отриманих методом магнетронного розпилення. *Р.Ю.Петрусь, Г.А.Ільчук, А.І.Кашуба, І.В.Семків, Е.О.Змійовська.*

Визначено оптичні константи та товщину тонких плівок CdTe, отриманих методом високочастотного магнетронного розпилення. Наведено методику синтезу та результати оптичних досліджень тонких плівок CdTe, нанесених на поверхню підкладки скло/ITO. Визначено оптичні константи та ширину забороненої зони плівок, що досліджувалися. Оптичні властивості (показник заломлення $n(\lambda)$, коефіцієнт поглинання $\alpha(\lambda)$ та коефіцієнт екстинкції $k(\lambda)$) тонких плівок та товщину d визначено із спектра пропускання. Дисперсія показника заломлення аналізується з використанням одноосциляторної моделі. Оптичні параметри плівок аналізуються за допомогою моделей Коші, Селмеєра та Вемпле.

1. Introduction

Cadmium telluride (CdTe) thin films are representatives of the $A^{II}B^{VI}$ crystal group and show semiconductor behavior. They are important research objects because of their wide application in various optoelectronic devices. CdTe based solar cells attract attention, since CdTe is characterized by a direct forbidden gap with an energy bandwidth of 1.46 eV and a high absorbance

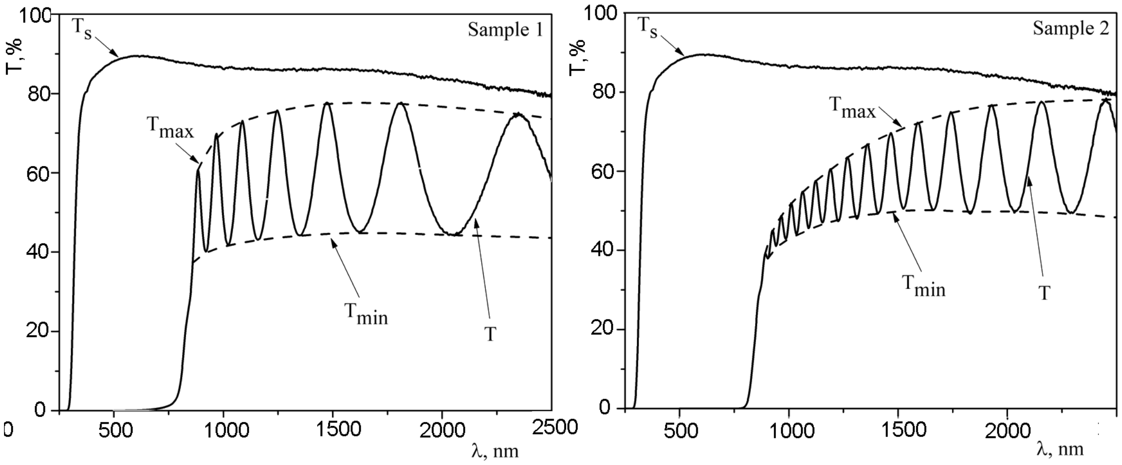

Fig. 1. Transmission spectra of CdTe thin film-substrate combination (T_s — clean glass substrate, envelope curves for interference maxima — T_{max} and minima — T_{min}).

(above 10^5 cm^{-1}) [1], which makes it an excellent light-absorbing layer of solar cells.

For preparation of thin films of CdTe (and other compounds of the $A^{II}B^{VI}$ group), different methods are used: physical vapor deposition, sputtering, spray pyrolysis, electrodeposition, close-space sublimation (CSS), etc. [2–10]. A high-frequency magnetron sputtering method is one of the most advantageous methods for obtaining uniform films [11, 12].

The aim of the present work is to investigate optical properties of CdTe thin films which are deposited on glass/ITO substrates by a high-frequency magnetron sputtering method. In this paper we present the results of studying the refractive index, absorption and extinction coefficients. Optical parameters and thickness are determined from the measurements of transmittance spectra.

2. Experimental

The CdTe films were deposited on glass/ITO substrates (NANOCS IT100-111-25, 100 Ω/sq) with a size of 16×8×1.1 mm^3 by the method of high-frequency (HF) magnetron sputtering (13.6 MHz) using a VUP-5M vacuum station (Selmi, Ukraine) [1]. A single crystal disc of 99.999 % purity with a thickness of 2 mm and a diameter of 40 mm was used as a target. The target-substrate distance was 60 mm. The deposition time was 0.5 h (sample 1) and 1.25 h (sample 2). The start and end of the process were controlled by means of a movable shutter.

Before the sputtering process, the chamber was evacuated. The gas pressure inside the chamber was $4 \cdot 10^{-4}$ Pa. This pressure is achievable using 5F4E polyphenyl ether diffusion fluid in a vapor oil vacuum pump that provides a low partial vapor pressure ($9 \cdot 10^{-7}$ Pa).

The sputtering was carried out at argon (Ar) pressure in the range of 1.0–1.3 Pa. The power of the HF magnetron was maintained at 100 W and the temperature of the substrate was 563 K. For heating the substrates, a 300 W high-temperature tungsten heater was used. A proportional integral derivative (PID) controller was used to control heating and cooling rates, as well as for ensuring the temperature conditions of deposition. The average deposition rate of films is in the range of 6.9 to 7.8 Å/s.

The spectral dependences of optical transmittance (Shimadzu UV-3600) of the samples were studied in the visible and near infrared regions at room temperature [13].

3. Results and discussion

Fig. 1 shows the transmission spectra of a clean glass substrate (T_S) and the CdTe thin films-substrate combinations. The transmission coefficient strongly depends on the film structure, which is determined by the preparation methods, film thickness and deposition conditions.

The transmission spectra of the thin films exhibit periodic peaks and minima associated with interference effects indicating a high structural perfection of the thin films. A very rough surface would destroy the interference due to multiple reflections.

The optical properties of a thin film (refractive index $n(\lambda)$, absorption coefficient $\alpha(\lambda)$, extinction coefficient $k(\lambda)$ and thickness d) can be easily evaluated from a transmission spectrum with interference effects

Table 1. Optical parameters of samples of the AIIBVI crystal group

Sample	Preparation method	Form	d, μm	E_g, eV	E_0, eV	E_d, eV	β, eV
CdTe	HF magnetron sputtering	Thin film	1.393	1.42	2.07	12.31	0.19
			3.200	1.44	1.97	11.76	0.18
CdSe [7]	CSS	Thin film	1.21	1.672	3.391	13.47	–
CdS [20]	Chemical deposition	Thin film	~340	2.41	4.097	5.12	0.0048
CdTe [17]		Crystal	–	–	4.13	25.7	0.40
CdSe [17]		Crystal	–	–	4.0	20.6	0.32
CdS [17]	–	Crystal	–	–	4.9	20.4	0.32
ZnTe [17]	–	Crystal	–	–	4.34	27.0	0.42
Cauchy parameters							
d, μm	Δd, μm	δ, %	α	β, μm^2	n_∞		
1.393	0.450	32.3	2.46	0.27	2.46		
3.200	0.553	17.3	2.46	0.28	2.46		
Sellmeier parameters							
d, μm	Δd, μm	δ, %	A	B, μm^2	n_∞		
1.393	0.450	32.3	5.03	0.22	2.46		
3.200	0.553	17.3	5.05	0.23	2.46		

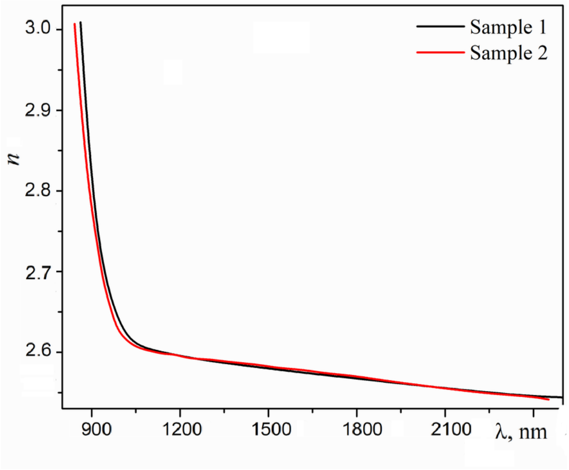

Fig. 2. Refractive index $n(\lambda)$ as a function of wavelength.

using the envelope method [6, 7, 14, 15]. This method is applicable in the case of a weakly absorbing thin film on an entirely transparent substrate that is much thicker than the thin film. These conditions are met in this work.

The envelope curves $T_{max}(\lambda)$ and $T_{min}(\lambda)$ can be obtained by means of parabolic extrapolation of experimentally determined points that coincide with the location of interference maxima and minima (see Fig. 1).

Refractive index $n(\lambda)$ of the CdTe thin films can be calculated using the following equation:

$$n = \sqrt{N + \left(N^2 - n_s^2\right)^{1/2}}, \qquad (1)$$

$$N = 2 \cdot n_s \frac{T_{\max} - T_{\min}}{T_{\max} \cdot T_{\min}} + \frac{2 \cdot n_s^2 + 1}{2}.$$

where n_s is the refractive index of the substrate:

$$n_s = \frac{1}{T_s} + \sqrt{\frac{1}{T_s^2} - 1}, \qquad (2)$$

T_s is the transmittance of the substrate in the transparent zone. The glass/ITO substrate transmittance shows a complex behavior. Hence, according to Eq. (2), the refractive index changes with wavelength.

It should be emphasized that Eq. (1) is valid only within the interference zone. Outside this zone, the refractive index can be determined using an extrapolation of calculated data [16]. As seen from Fig. 2, the refractive index of the thin films decreases with an increase of wavelength. The dispersion of the refractive index is normal and it is well described by the model of a single oscillator. In Fig. 3, the lines represent the fitting of the experimental points using the

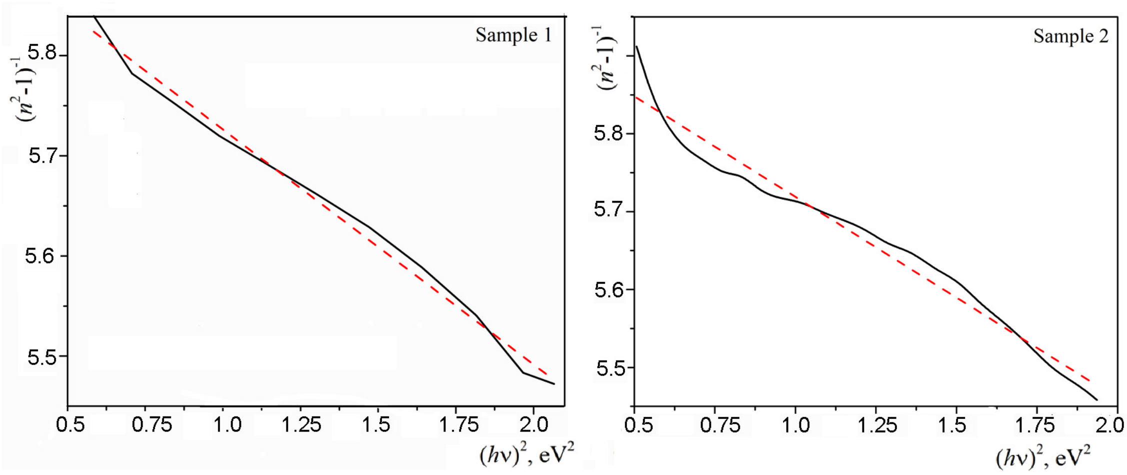

Fig. 3. Plot of refractive index factor $(n^2 - 1)^{-1} = f(h\nu)^2$ for CdTe thin film.

model of a single oscillator in the form proposed by Wemple and Di Domenico [17]:

$$n(h\nu)^2 - 1 \cong \frac{E_d \cdot E_0}{E_0^2 - (h\nu)^2}, \tag{3}$$

were E_0 is the energy of a single oscillator, E_d is the dispersion energy, and $h\nu$ is the photon energy. Both Wemple's parameters can be obtained from the slope of the plot and its coincidence with the y-axis, $(n^2 - 1)^{-1} = f(h\nu)^2$.

The values of these parameters are summarized in Table 1. The energy of the single oscillator is about twice the band gap energy $E_0 \approx 1.46 \cdot E_g$ (sample 1) and $E_0 \approx 1.37 \cdot E_g$ (sample 2). For single crystals of the $A^{II}B^{VI}$ group the dispersion parameter is near 20 eV, while for our polycrystalline thin films we found a smaller value. The parameter E_d which is a measure of the energy of interband optical transitions obeys the simple empirical relationship:

$$E_d = \beta N_c Z_a N_e, \tag{4}$$

N_c is the coordination number of a cation nearest neighbor to the anion, Z_a is the formal chemical valence of the anion, N_e is the effective number of valence electrons per anion. In our cause, $N_c = 4$, $Z_a = 2$ and $N_e = 8$. Using Eq. (4) we obtained a "covalent" values $\beta \approx 0.19$ eV (sample 1) and $\beta \approx 0.18$ eV (sample 2).

The dispersion spectrum of the refractive index was fitted using the Cauchy formula [18]:

$$n = \alpha + \frac{\beta}{\lambda^2}, \tag{5}$$

where α and β are the Cauchy parameters. For $\lambda \to \infty$, the value of the α parameters becomes immediately as n_∞. The values of the fit parameters are presented in Table 1.

Another model used in the study of the refractive index dispersion is Sellmeier's model [19]; it gives:

$$n^2 = 1 + \frac{A \cdot \lambda^2}{\lambda^2 - B}, \tag{6}$$

where A and B are the Sellmeier parameters. Under these conditions: $n_\infty \approx (1 + A)^{1/2}$, and the calculated values are given in Table 1. Comparison of these values with the α value gives a good agreement.

To determine the thickness of the films under investigation, we can use the following equation:

$$d = \frac{M \cdot \lambda_1 \cdot \lambda_2}{2 \cdot (n(\lambda_1) \cdot \lambda_2 - n(\lambda_2) \cdot \lambda_1)}, \tag{7}$$

where λ_1 and λ_2 are wavelengths corresponding to neighboring extreme points in the transmission spectrum; $M = 1$ for two neighboring extrema of one type (max-max, min-min) and $M = 0.5$ for two neighboring extrema of opposite types (max-min, min-max). The thicknesses of the CdTe thin films are calculated by Eq. (7) and given in Table 1.

Absorption coefficient $\alpha(\lambda)$ for the CdTe thin films can be calculated using the following equation:

$$\alpha(\lambda) = \frac{1}{d}\ln\left\{\frac{[n-1] \cdot [n - n_s] \cdot [(T_{\max}/T_{\min})^{1/2} + 1]}{[n+1] \cdot [n + n_s] \cdot [(T_{\max}/T_{\min})^{1/2} - 1]}\right\}. \tag{8}$$

Table 2. Comparisons of optical parameters of CdTe thin films at room temperatures.

λ, nm	*n*						*k*				
	sample 1	sample 2	[21]	[22]	[23]	[15]	Sample 1	Sample 2	[22]	[23]	[15]
925	2.72	2.74	2.89	2.87	2.81	~3.53	0.042	0.024	0.041	0.0026	~0.022
1008	2.62	2.63	2.84	2.83	2.76	~3.52	0.037	0.018	0.036	0.00045	~0.02
1100	2.61	2.61	2.81	2.81	2.74	~3.49	0.035	0.015	0.033	0.000071	~0.02

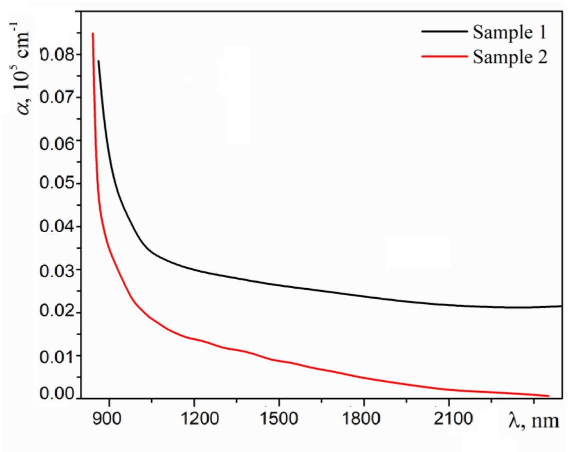

Fig. 4. The absorption coefficients α(λ) of the CdTe thin films.

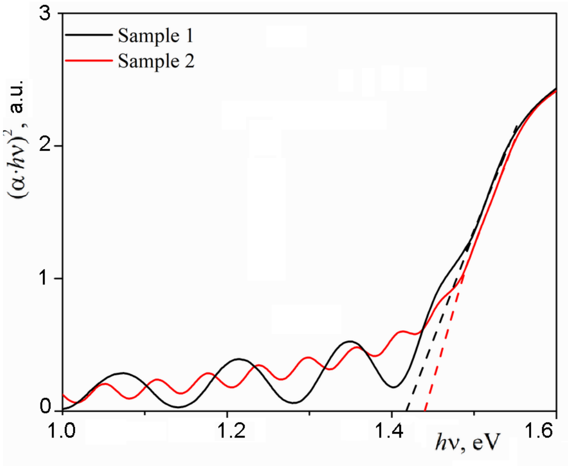

Fig. 5. The spectral dependences of optical absorption for CdTe thin films.

Fig. 4 shows absorption coefficient α for the material of the CdTe thin films as a function of the wavelength. A sharp increase in the absorption coefficients is observed in the short wavelength region near the band gap absorption edges of the CdTe thin films.

By plotting $(\alpha \cdot h\nu)^2$ versus $h\nu$ it is possible to obtain a direct optical gap from extrapolation of the lineal portion of the plot to the energy axis (see Fig. 5). The optical gaps for the samples studied are 1.42 and 1.44 eV for samples 1 and 2, respectively. These results are in good agreement with the value reported by other authors [1, 2, 9, 10, 15].

The extinction coefficient $k(\lambda)$ can be easily calculated from the following equation: $k(\lambda) = \lambda\alpha(\lambda)/4\pi$ (see Fig. 6). It can be seen from Fig. 6 that the extinction coefficients also increase sharply near band gap absorption edges. The envelope method can be used only in the limits of the transparency region of a thin film. The following conditions are valid in a wavelength region near the self-absorption edge of CdTe thin films: strong absorption in the film material, a completely transparent substrate, and $n^2 > k^2$.

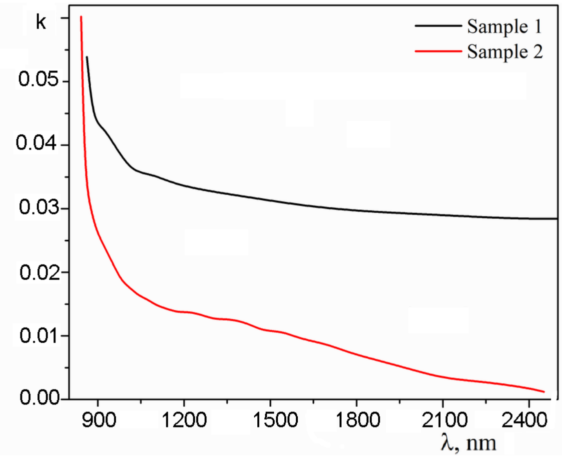

Fig. 6. Extinction coefficients $k(\lambda)$ of CdTe thin films.

The optical parameters ($n(\lambda)$ and $k(\lambda)$) for the CdTe samples are listed for comparison in Table 2. We can observe that the discrepancy with the experimental data is insignificant (except [15]). The disparity of results in our work with [15] can be explained using different methods for producing thin films. In [15], authors presented spectral dependences of absorption coefficients α(λ). Their behavior shows changes near 10^{-3} cm^{-1}, whereas we obtained the value near 10^5 cm^{-1}.

4. Conclusion

Thin films of CdTe were deposited onto glass/ITO substrates by the HF magnetron sputtering method. The optical constants of the CdTe thin films (refractive index $n(\lambda)$, absorption coefficient $\alpha(\lambda)$, and extinction coefficient $k(\lambda)$ are determined as functions of the wavelength using the envelope method. The dispersion of the refractive index is normal and was successfully fitted with the Cauchy, Sellmeier and Wemple formulas, and good agreement between the models is observed. For polycrystalline thin films, the dispersion parameter turned out to be less than for single crystals. The fundamental absorption edge was found in the optical absorption spectrum of the CdTe sample.

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