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Optical Properties of Materials for Solar Energy Based on Cadmium Chalcogenides Thin Films

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The optical constants and thickness of cadmium chalcogenides (CdX, X= S, Se and Te) thin films prepared by quasi close-space sublimation (CdSe) and high-frequency magnetron sputtering method (CdTe and CdS) are determined. The optical constants and the band gap of the films under study have been determined. Optical properties (refractive index $n(\lambda)$, extinction coefficient $k(\lambda)$ and dielectric functions $\varepsilon(\lambda)$) of 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. The material optical parameter such as normalized integrated transmission, zero and high-frequency dielectric constant, density of state effective mass ratio was also calculated.

Keywords: thin films, solar energy, optical gap, optical functions, transmission, reflection index, dielectric functions.

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Introduction

Thin films of cadmium chalcogenides (CdX, X= S, Se and Te) representative of $A^{II}B^{VI}$ crystal group and shows semiconductor behavior. They are an important research field because of their wide application in various fields of optoelectronic devices.

The CdTe semiconductor compound has proven to be a leading compound for manufacturing cost-effective second-generation photovoltaic devices. CdTe based solar cells are attracting attention, since CdTe is characterized by a direct forbidden gap with an energy bandwidth of ~ 1.46 eV and a high absorbance (above 10^5 cm^{-1}) [1], which makes it an excellent light absorbing layer of solar cells.

For the formation of high-efficiency heterojunctions based on *p*-CdTe for a window layer of a solar battery, cadmium sulfide (CdS) is mainly used [2-4]. CdS is characterized by a high photoconductivity in the visible region. This is due to the fact that CdS is a direct-band gap semiconductor and, accordingly, is characterized by direct band–band optical transitions. The energy width of the band gap at room temperature is ~ 2.42 eV. The electrical properties of CdS are characterized by a resistivity value of about 106 Om·cm and the *n*-type conductivity.

CdS forms cubic and hexagonal phases, depending mainly on the choice of the method of synthesis and on the growth parameters [5-8]. In solar cells based on the CdS/CdTe heterojunction, the thickness of a CdS layer in most cases is about 150 - 300 nm [9]. Photogenerated charge carriers almost completely recombine inside the CdS film and do not generate photocurrent. Due to the absorption of light by the CdS film, no photocurrent appears in the structure. Therefore, it is desirable to use a CdS film with a thickness of less than 100 nm in order to fabricate high-efficiency CdTe-based solar cells [9-11].

Three crystalline forms of CdSe are known which follow the structures of: wurtzite (hexagonal), sphalerite (cubic) and rock-salt (cubic). The perspective of research this material is found in forming $CdS/CdSe_{1-x}Te_x$ heterojunction.

The aim of the present work is the investigation of the optical properties of CdX (X = S, Se and Te) thin films which are produced glass substrate by quasi close-space sublimation (CSS, for CdSe) and high-frequency

(HF) magnetron sputtering (13.6 MHz, for CdTe and CdS) method. In this paper we present results of investigation the refractive index *n*(λ), extinction coefficient *k*(λ) and dielectric functions ε(λ). Optical properties are determined from the measurements of transmittance spectra.

I. Experimental

CdX (X= S, Se and Te) thin films were obtained by CSS (CdSe) method [12-14] at pressure $1\cdot10^{-6}$ Torr and HF (CdTe and CdS) method using a VUP-5M vacuum station (Selmi, Ukraine) [11]. The source and substrate material temperature was 900 K and 700 K, respectively. The temperature was controlled using the PID-regulator of temperature PE-202 using a thermocouple of the type "K". The relative error of temperature didn't exceed 0.2 %. The substrates were ~14 mm in diameter were used for deposition CdX (X= S, Se and Te) thin films. Before the films deposition, the substrate surface was cleaned by boiling in a high purity CCl_4 solution during 0.5 h.

The spectral dependence of the optical transmittance (Shimadzu UV-3600) of the obtained samples in the visible and near infrared regions is studied at room temperature [11].

II. Results and discussion

Fig. 1 shows the transmission spectrum of a CdX (X = S, Se and Te) 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 minimums associated with interference effects, indicating the high structural perfection of thin films. A very rough surface will destroy the interference due to multiple reflections. For each a full transmission spectrum was calculated, and from this the normalized integrated transmission into the CdX (X= S, Se and Te) absorber was evaluated as follows:

$$\tilde{T} = \frac{1}{b-a}\int_a^b T\cdot dl \qquad (1)$$

where $\tilde{T}$ is the average fractional transmission over the range *a-b* specified (see Fig. 1).

The optical gap of materials is known as the minimum energy required by semiconductor material to excite a phonon. To determine the optical gap of the materials deposited, we used the Tauc coordinats. Plotting $(\alpha\cdot h\nu)^2$ versus *h*ν is possible to obtain the direct optical gap from extrapolation of the lineal portion of the plot to the energy axis (see Fig. 2). The optical gaps for the samples studied are 1.40, 1.68 and 2.39 eV for CdTe, CdSe and CdS, respectively. These results are good agreement with the value reported by other authors [1, 11-14].

The refractive index *n*(λ) and thickness *d* of a thin films can be easily evaluated from a transmission spectrum with interference effects using the envelope method [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.

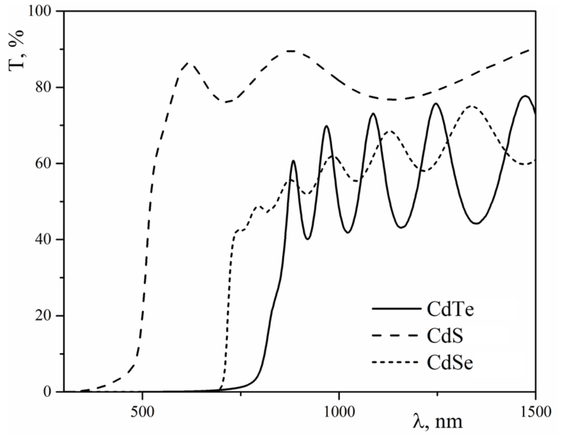


Fig. 1. Transmission spectra of CdX (X = S, Se i Te) thin film–substrate combination.

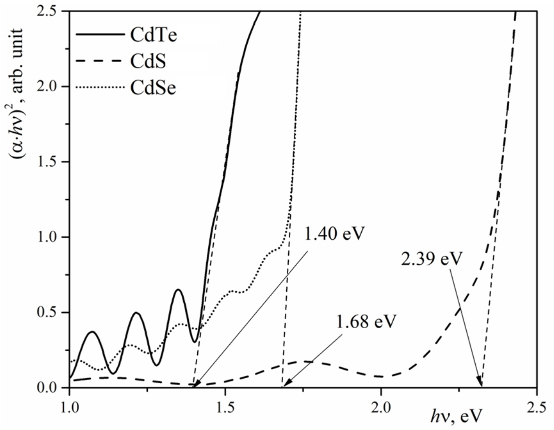


Fig. 2. The spectral dependence of optical absorption for the CdX (X = S, Se i Te) thin films.

Refractive index *n*(λ) of the CdX (X= S, Se and Te) thin films can be calculated using the following equation:

$$n = \sqrt{N + (N^2 - n_S^2)^{1/2}} \qquad (2)$$

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

where n_s is the refractive index of the substrate:

$$n_S = \frac{1}{T_S} + \sqrt{\frac{1}{T_S^2} - 1}, \qquad (3)$$

T_S is the transmittance of the substrate in the transparent zone. Hence following the Eq. (3) n_s= 1.64.

It should be emphasized that Eq. (2) is valid only within the interference zone. Outside this zone, the refractive index can be determined using an extrapolation of calculated data [15]. As is seen from Fig. 3 the refractive index of the thin films decreases with increasing wavelength. The dispersion of the refractive index is normal and it is well described by a single oscillator model. Also, we note that the behavior of the refractive index is good correlated with the other results

[17].

The extinction coefficient $k(\lambda)$ can be easily calculated from the following equation $k(\lambda) = \lambda\alpha(\lambda)/4\pi$ (see Fig. 4). It can be seen from Fig. 4 that the extinction coefficients also increase sharply near band gap absorption edges.

The following conditions are valid in a wavelength region near the self-absorption edge of CdX films: strong absorption in the film material, a completely transparent substrate, and $n^2 >> k^2$ (k- extinction coefficient).

The complex dielectric constant can be found as:

$$e = e_1 + i\cdot e_2 \quad (4)$$

where ε_2 and ε_1 are dielectric imaginary and real parts of the function, respectively. They are related to the extinction coefficient and refractive index by equations 5 and 6:

$$e_1 = n^2 - k^2 \quad (5)$$

$$e_2 = 2\cdot n\cdot k \quad (6)$$

Fig. 5 is shows dependence of dielectric functions (real and imagination) on wavelength of cadmium chalcogenides. For the value of n far greater than k, ε_1 is approximately equal to n^2, the dependence of ε_1 on λ can be examined using the relation [16]:

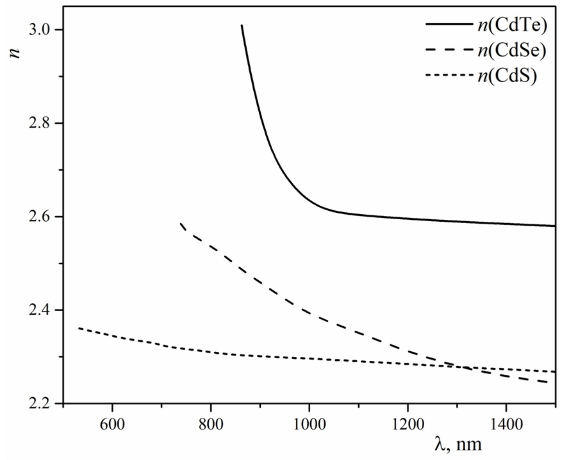


Fig. 3. Refractive index $n(\lambda)$ as a function of wavelength.

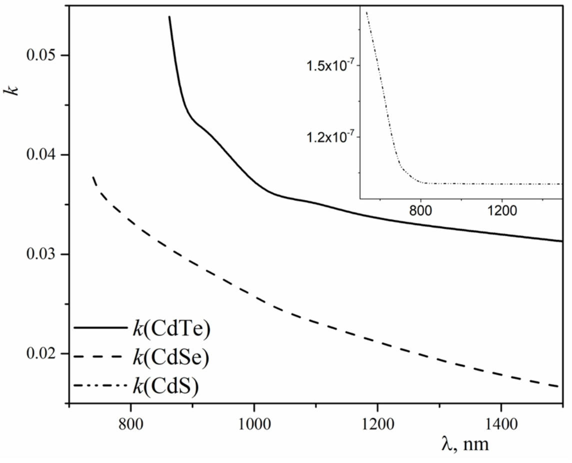
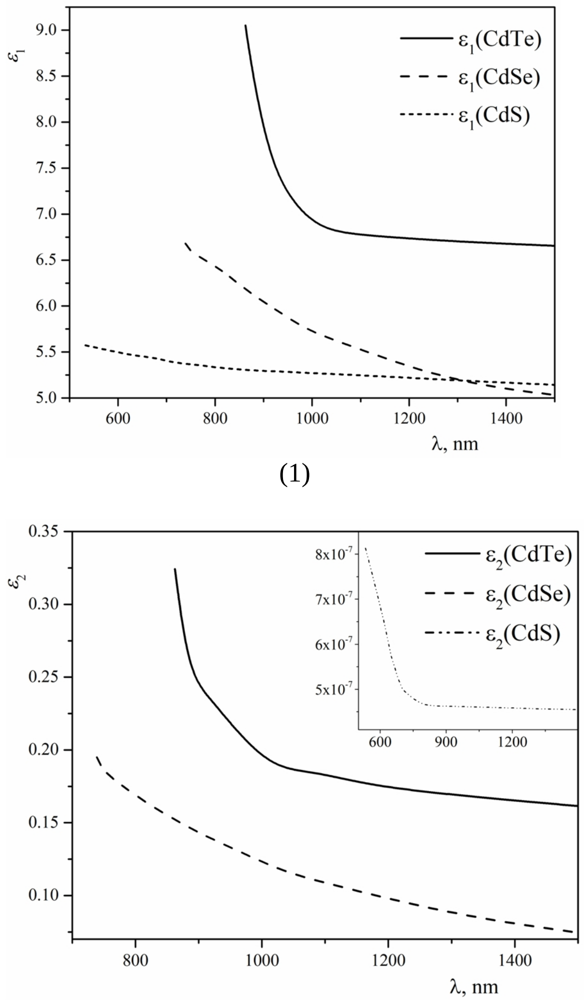


Fig. 4. Extinction coefficients $k(\lambda)$ as a function of wavelength.



(1)

(2)

Fig. 5. Optical dielectric real (1) and imaginary (2) part spectra for the CdX (X = S, Se i Te).

$$e_1 = n^2 = e_\infty - \left(\frac{e^2}{p\cdot c^2}\right)\left(\frac{N_c}{m^*}\right) l^2 \quad (7)$$

where c is the speed of light, m^* is the effective mass of the carrier, N_c is the carrier density, e is the electronic charge, and ε_∞ is the high-frequency dielectric constant. To obtain the high frequency dielectric constant ε_∞ we plot a graph n^2 as a function of λ^2 and extrapolated the linear part of the curve to $\lambda^2 = 0$. Taking into account that density of state is proportional to effective mass, we can calculation charge effective mass in conductivity band.

$$N_c = 2\cdot\left(\frac{2p\cdot m^*\cdot k\cdot T}{h^2}\right)^{3/2} \quad (8)$$

Using the single oscillator model in the form proposed by Wemple and Di Domenico (9) [15] can be obtained zero frequency dielectric constant ε_0.

$$n(hn)^2 - 1 \cong \frac{E_d\cdot E_0}{E_0^2 - (hn)^2} \quad (9)$$

were E_0 is the single oscillator energy, E_d is the dispersion energy and $h\nu$ is the photon energy. The value of the single oscillator energy is about twice the band gap

Table 1

Optical constants for the CdX (X = S, Se i Te)

Optical parameters	Symbol	CdTe	CdSe	CdS
Method of deposition	-	RF	CSS	RF
Substrate	-	Glass	Glass	Glass
Optical gap	E_g, eV	1.40	1.68	2.39
Normalized integrated transmission	$\tilde{T}$, %	48.71	55.84	62.41
Single oscillator strength	E_0, eV	2.07	4.26	6.97
Dispersion energy	E_d, eV	12.31	13.46	27.39
Ratio	E_0/E_g	1.48	2.54	2.92
High-frequency dielectric constant	ε_∞	7.18	5.29	5.38
Zero frequency dielectric constant	ε_0	6.95	4.16	4.93
Density of state effective mass ratio	$\left(\frac{N_c}{m^*}\right)$, $s^{-2}\cdot C^{-2}$	$7.09\cdot10^{45}$	$1.22\cdot10^{46}$	$1.21\cdot10^{46}$
Thickness	d, μm	1.39	1.875	0.38

energy. The values of these parameters are summarized in Table I. Both Wemple parameters can be obtained from the slope and the coincide with the y-axis of the plot, $(n^2-1)^{-1} = f(h\nu)^2$. From obtained parameters we can observe zero frequency dielectric constant using relation:

$$e_0 = n_0 = 1 + \frac{E_d}{E_0} \qquad (10)$$

The results optical parameters constants obtained from the analysis are listed in table 1. To determine the thickness of the films under investigation, we can use the following equation:

$$d = \frac{M \cdot l_1 \cdot l_2}{2 \cdot (n(l_1) \cdot l_2 - n(l_2) \cdot l_1)}, \qquad (11)$$

where λ_1 and λ_2 are wavelengths corresponding to neighboring extreme points in the transmission spectrum and 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 average thickness of the thin films is also listed in table 1.

The films thickness obtained from the transmission spectra are in good agreement with the thickness measured using stylus profilometer (Veeco, Dektak 8 model). The deviation between these two measurements is < 12 %.

Conclusions

CdX (X= S, Se and Te) thin films were deposited onto glass substrates by the quasi CSS (CdSe) and RF (CdTe and CdS) method. The increase of charge of chalcogens can reduce the band gap energy of CdX from 2.49 to 1.40 eV. The same results are observed in behavior of normalized integrated transmission. The optical constants of cadmium chalcogenides thin films (refractive index $n(\lambda)$, extinction coefficient $k(\lambda)$ and dielectric functions $\varepsilon(\lambda)$) are determined as functions of the wavelength using the envelope method. The smaller value of dispersion parameter for polycrystalline thin films than for single crystals is observed. The material optical parameter such as normalized integrated transmission, dispersion energy, single oscillator strength, zero and high-frequency dielectric constant, density of state effective mass ratio were also calculated.

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[1] N. Romeo, A. Bosio, R. Tedeschi, V. Canevari, Mater. Chem. Phys. 66(2), 201 (2000).
[2] B.M. Basola, B. McCandless , J. Photon. Energy. 4(1), 040996 (2014).
[3] N. Romeo, A. Bosio, V. Canevari, A. Podest`a, Sol. Energy 77(6), 795 (2014).
[4] N.R. Paudel, C. Xiao, Y. Yan, J. Mater. Sci.: Mater. Electron. 25(4),1991 (2014).
[5] S.V. Averin, P.I. Kuznetsov, V.A. Zhitov, N.V. Alkeev, V.M. Kotov, L.Y. Zakharov, N.B. Gladysheva, Tech. Phys. 57(11), 1514 (2012).
[6] R.N. Bhattacharya, M.A. Contreras, B. Egaas, R.N. Noufi, A. Kanevce, J.R. Sites, Appl. Phys. Lett. 89(25), 253503 (2006).
[7] I.O. ladeji, L. Chow, Thin Solid Films. 474(1-2), 77 (2005).
[8] W. Mahmood, J. Ali, I. Zahid, A. Thomas, A. Haq, Optik. 158, 1558 (2018).
[9] A. Bosio, N. Romeo, S. Mazzamuto, V. Canevari, Prog. Cryst. Growth Charact. Mater. 52(4), 247 (2006).
[10] B.E. McCandless, K.D. Dobson, Sol. Energy. 77(6), 839 (2004).
[11] R.Yu. Petrus, H.A. Ilchuk, A.I. Kashuba, I.V. Semkiv, E.O. Zmiiovska, Optics and Spectroscopy. 126(3), 220 (2019).
[12] G.A. Il’chuk, I.V. Kurilo, R.Y. Petrus, V.V. Kus’nezh, Inorg. Mater. 50(6), 559 (2014).
[13] G.A. Il’chuk, I.V. Kurilo, V.V. Kus’nezh, R.Y. Petrus, I.T. Kogut, T.N. Stan’ko, Inorg. Mater. 49(4), 329 (2013).
[14] H.A. Ilchuk, R.Y. Petrus, A.I. Kashuba, I.V. Semkiv, E.O. Zmiiovska, Nanosistemi, Nanomater. Nanotehnologii. 16(3), 519 (2018).
[15] H.A. Ilchuk, R.Yu. Petrus, A.I. Kashuba, I.V. Semkiv, E.O. Zmievskaya, Optics and spectroscopy 128(1), 50 (2020).
[16] S.H. Wemple, M. DiDomenico, Phys. Rev. B. 3, 1338 (1971).
[17] L.I. Nykyruy, R.S. Yavorskyi, Z.R. Zapukhlyak, G. Wisz, P. Potera, Optical Materials 92, 319 (2019).
[18] A.Y. Fasasi, B.D. Ngom , J.B. Kana-Kana, R. Bucher, M. Maaza, C. Theron, U. Buttner, Journal of Physics and Chemistry of Solids, 70(10), 1322 (2009).

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Оптичні властивості матеріалів для сонячної енергетики на основі тонких плівок халькогенідів кадмію

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Визначено оптичні константи та товщину тонких плівок халькогенідів кадмію (CdX, X = S, Se і Te) які були осаджені методом квазізамкненого простору та високочастотним магнетронним осадженням. Визначено оптичні константи та оптичну ширину забороненої зони досліджуваних плівок. Оптичні властивості (показник заломлення $n(\lambda)$, коефіцієнт екстинкції $k(\lambda)$ та діелектричні функції $\varepsilon(\lambda)$) тонких плівок та товщину d можна визначити із спектру пропускання. Дисперсію показника заломлення пояснювали за допомогою одноосциляційної моделі. З експериментально встановленої спектральної залежності показника заломлення було встановлено енергію одиночного осцилятора та енергію дисперсії. Також, були розраховані оптичні параметри досліджуваних матеріалів, такі як інтегральна величина пропускання, нульова та високочастотна діелектрична константа, співвідношення щільності станів носіїв заряду до їх ефективної маси в зоні провідності.

Ключові слова: тонкі плівки, сонячна енергетика, оптична ширина забороненої зони, оптичні функції, пропускання, коефіцієнт відбивання, діелектричні функції.