Mikhail TIVANOV[1], Irina KAPUTSKAYA[1], Aleksy PATRYN[2], Anis SAAD[3], Ludmila SURVILO[4], Evgenij OSTRETSOV[4]

Belarusian State University, Belarus (1), Koszalin University of Technology, Poland (2), Al-Balqa Applied University, Jordan (3), SE "Center of LED and Optoelectronic Technologies of National Academy of Sciences of Belarus", Belarus (4)

doi:10.15199/48.2016.09.23

Determination of CdS_xSe_{1-x} thick films optical properties from reflection spectra

***Abstract**. A method for determining the band gap value and the refractive index near the absorption edge from reflection spectra was tested for CdS_xSe_{1-x} films prepared using the screen-printing and sintering technique.*

***Streszczenie**: Przeanalizowano metodę wyznaczenia szerokości przerwy energetycznej i współczynnika załamania z pomiarów widma współczynnika odbicie warstw CdS_xSe_{1-x} otrzymanych metodami sitodruku i konsolidacji termicznej (sintering technique). (**Wyznaczanie parametrów optycznych grubych warstw CdS_xSe_{1-x} z analizy widma odbicia**).*

Keywords: semiconductors, CdS_xSe_{1-x} thick films, refractive index, reflection spectra.
Słowa kluczowe: półprzewodniki, warstwy CdS_xSe_{1-x}, współczynnik załamania, widmo odbicia.

Introduction

The development of optoelectronics stimulates research of the photoelectric and optical properties of semiconductor films used in different optoelectronic devices [1-4]. The refractive index and the band gap value are some of the most important optical parameters of semiconductor films [5-6].
A method to determine the band gap value and the refractive index near the absorption edge of the thick films of semiconductor materials from optical reflection spectra, measured at different angles of incidence of the optical radiation, is theoretically justified and experimentally implemented in the present study.
Verification of this method for CdS_xSe_{1-x} films of solid solution prepared using the screen-printing and sintering technique was done in the present work [7-9]. The direct band gap semiconductors like CdS, CdSe and their solid solutions are excellent materials for the development of optoelectronic and photovoltaic devices due to their high absorption coefficients and appropriate band gap [9-11]. A simple screen-printing method can be suitable for the production of low-cost large-area photosensitive devices [7-9].

Theory

Let d be the thickness of the semiconductor film with a surface roughness smaller than the wavelength of the incident radiation, located on a transparent or opaque substrate. Denote n the refractive index of the semiconductor material, the refractive index of air take equal unity. Let I_0 be the intensity of the incident radiation on the film surface. The incident beam is refracted and reflected on the interface of the media.

Consider the reflection and refraction of light beam incident at a certain angle the surface of the semiconductor film. The calculation procedure proposed by V. Kumar et al. for near-normal angle of incidence [12] is taken for the basis.

Calculation of the intensity of the reflected radiation is considered here by taking into account the directly reflected beam from the surface of the film and the beam which goes out of the film after a double pass through it. The radiation leaving the film after multiple reflections is neglected. Denote r_1, r_2 and r_3 the reflection coefficients at front, inner and rear front faces of the film respectively, ϕ_0 angle of incidence and ϕ angle of refraction.

Accounting the Snell law, geometrical path length of the light inside the film between its surfaces is

(1) $$t = \frac{d}{\cos\phi} = \frac{d}{\sqrt{1-\left(\sin\phi_0/n\right)^2}}.$$

Mathematical manipulation (see details in [12]) gives for the intensity of the reflected radiation i.e.

(2) $$I = I_1 + I_2 e^{-2\alpha t} + I_3 e^{-4\alpha t},$$

where $I_1 = I_0 r_1^2$, $I_2 = 2I_0 r_1(1-r_1) r_2 (1-r_3)\cos(2\frac{2\pi}{\lambda}t)$, $I_3 = I_0(1-r_1)^2 r_2^2 (1-r_3)^2$, α is the absorption coefficient, λ is wavelength of the incident radiation.

The calculation of reflection coefficients r_1, r_2 and r_3 was based on the use of the Fresnel formulas for the intensities of the reflected and refracted at the interface of two media waves polarized in the plane of the beam incidence and in the plane perpendicular to it. The calculation shows that these factors can be assumed to be constant at angles of incidence of waves not exceeding π/4.

For the films having a thickness substantially larger than the wavelength of the radiation ($d >> \lambda$), the expression (2) takes the form [12]

(3) $$I = I_1 + I_2 e^{-2\alpha t}.$$

The intensity of the reflected light has a minimum value when $\alpha \to \infty$, and a maximum value when $\alpha = 0$ i.e.

(4) $$I_{min} = I_1, \; I_{max} = I_1 + I_2,$$

Substituting in (3), and finding the logarithm, resulting in

(5) $$2\alpha t = \frac{2\alpha d}{\sqrt{1-\left(\sin\varphi_0/n\right)^2}} = \ln\left(\frac{I_{max}-I_{min}}{I-I_{min}}\right) = \ln\left(\frac{R_{max}-R_{min}}{R-R_{min}}\right),$$

where R is the reflectance, $R = I/I_0$.

For a direct band gap material, as well known, the absorption coefficient

(6) $$\alpha h\nu = A(h\nu - E_g)^{1/2},$$

where $h\nu$ is the photon energy of the incident radiation, E_g is the semiconductor band gap, $A = const$. Then

(7) $$\left(h\nu\cdot\ln\left(\frac{R_{max}-R_{min}}{R-R_{min}}\right)\right)^2=\frac{(2dA)^2}{1-(\sin\varphi_0/n)^2}(h\nu-E_g)\cdot$$

At a certain angle of incidence ϕ_0, the function $\left(h\nu\cdot\ln\left(\frac{R_{max}-R_{min}}{R-R_{min}}\right)\right)^2$ almost linearly depends on $h\nu$. Extrapolation of the line to the intersection with the x-axis will determine the band gap energy E_g, as it was suggested by Kumar et al. [12].

After determining E_g, it is possible to get the refractive index n near the absorption edge. Transform the expression (5) to the form

(8) $$\frac{(2\alpha dn)^2}{\ln^2\left(\frac{R_{max}-R_{min}}{R_{\lambda_g}-R_{min}}\right)}=n^2-\sin^2\phi_0\cdot$$

where R_{λ_g} is the radiation reflectance corresponding to the film absorption edge wavelength $\lambda_g=hc/E_g$.

After sampling the reflection coefficients $R(\lambda)$ for the radiation wavelength of λ_g at different angles of incidence, it is possible to determine the refractive index corresponding to the absorption edge. For this it is necessary to approximate the dependency of $\ln^{-2}\left(\frac{R_{max}-R_{min}}{R_{\lambda_g}-R_{min}}\right)$ on $\sin^2\phi_0$ by the linear function $y=kx+b$ and to evaluate the parameters k and b from the graph. Then the square of the refractive index can be calculated as $n^2=-\frac{b}{k}$.

Experimental

The films of CdS_xSe_{1-x} solid solutions with different S/Se ratios (x = 0.2, 0.4, 0.5) were prepared using the screen-printing and sintering method. The thickness of the obtained films was 15-20 µm. The method of producing CdS_xSe_{1-x} films is described in detail in the work [13].

The spectral dependences of reflectance $R(\lambda)=I/I_0$ were carried out using a spectrophotometer Proscan MC 122. Measurements were carried out for incident angles between 20º to 45º in the spectral range from 300 nm to 1000 nm with a resolution of 3 nm.

Results and discussion

The reflection spectrum for the film of $CdS_{0,2}Se_{0,8}$ solid solution obtained at an incident angle of 20º to the normal (in the inset) and energy band gap determination in accordance with the formula (7) are shown in Fig. 1 as a typical example for the investigated CdS_xSe_{1-x} films. The measured spectra of CdS_xSe_{1-x} films for x = 0.2, 0.4 and 0.5 and for other incident angles between 20º to 45º have a similar form.

As follows from the reflection spectrum in Fig. 1, the maximum and minimum reflection coefficients are R_{max}=1.31% and R_{min}=0.40%. Band gap determination was made by plotting $\left(h\nu\cdot\ln\left(\frac{R_{max}-R_{min}}{R-R_{min}}\right)\right)^2$ versus the photon energy $h\nu$ using the obtained values of R_{max} and R_{min}; then extrapolating a straight line to intersect the x-axis resulting in the band gap value of E_g = 1.61 eV for $CdS_{0,2}Se_{0,8}$.

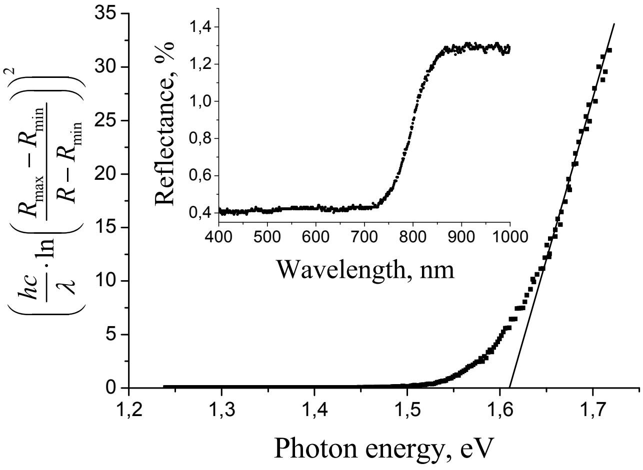

Fig. 1. Energy band gap determination for $CdS_{0,2}Se_{0,8}$ film and the corresponding source reflection spectrum (in the inset) obtained at an incident angle of 20º to the normal

To determine the refractive index n, reflection spectra were measured at various incident angles and dependence of $\ln^{-2}\left(\frac{R_{max}-R_{min}}{R_{\lambda_g}-R_{min}}\right)$ versus $\sin^2\phi_0$ was plotted (Fig. 2). Then the obtained dependency was approximated by the linear function $y=kx+b$ and the refractive index was calculated as $n=\sqrt{-\frac{b}{k}}$.

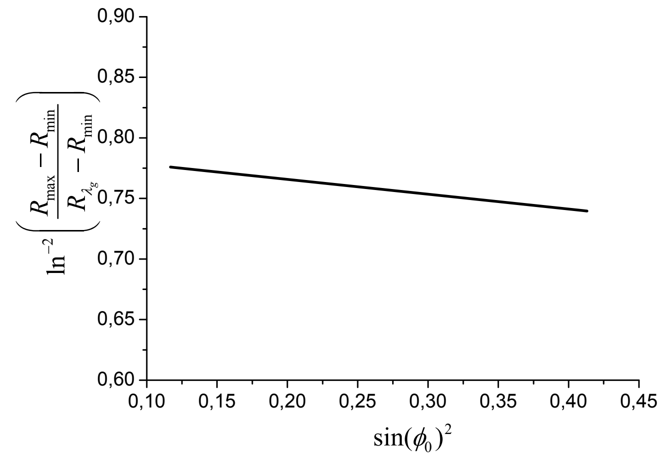

Fig. 2. Dependence of $\ln^{-2}\left(\frac{R_{max}-R_{min}}{R_{\lambda_g}-R_{min}}\right)$ versus $\sin^2\phi_0$ for $CdS_{0,2}Se_{0,8}$ film

The band gap and the refractive index near the absorption edge were determined for CdS_xSe_{1-x} films (x = 0.2, 0.4, 0.5) from the reflectance spectra according to the described procedure. The obtained results are presented in Table 1.

Table 1. Experimental and calculation results

The incident angle, °	R, % / E_g, eV	Material		
		$CdS_{0.5}Se_{0.5}$	$CdS_{0.4}Se_{0.6}$	$CdS_{0.2}Se_{0.8}$
20	R_{max}, %	1.42	1.40	1.31
	R_{min}, %	0.25	0.28	0.40
	E_g, eV	**1.92**	**1.84**	**1.61**
25	R_{max}, %	1.33	1.30	1.25
	R_{min}, %	0.27	0.28	0.43
	E_g, eV	**1.92**	**1.83**	**1.59**
30	R_{max}, %	1.25	1.26	1.21
	R_{min}, %	0.27	0.30	0.47
	E_g, eV	**1.91**	**1.84**	**1.61**
35	R_{max}, %	1.23	1.21	1.20
	R_{min}, %	0.31	0.32	0.54
	Eg, eV	**1.92**	**1.85**	**1.60**
40	R_{max}, %	1.23	1.19	1.25
	R_{min}, %	0.35	0.37	0.6
	Eg, eV	**1.90**	**1.85**	**1.60**
The refractive index *n*		**2.4**	**2.5**	**2.6**

It was found that the value of the band gap increases with the increase of the S concentration of the system CdS_xSe_{1-x}. It is also known from literature [e.g. 9, 14, 15] that the band gap of solid solutions of CdS_xSe_{1-x} varies over a range between 1.7 eV for pure CdSe and 2.4 eV for pure CdS. However, the values of the band gap obtained in the present work are slightly lower than the accepted values. For example, in comparison with E_g values estimated by K. Premaratne et al. [14] for films with the same S to Se ratio. The decrease in E_g values correlate to the shift of photosensitivity of the screen-printed films to long wavelength spectral region compared to the photosensitivity of vacuum deposited samples [13, 16]. One of the possible explanations is that the imperfection of the studied films contributing to the sub-band gap absorbance (probably due to the presence of the band tail states) [17, 18].

It is evident from Tab. 1 that the refractive index near the absorption edge increases with the increase of the Se concentration of the system CdS_xSe_{1-x}. The same dependence was obtained by M.P. Lisitsa et al. [19]. The numerical values are in good agreement with the data of reference [19].

Conclusion

The proposed method takes into account the incident angle of radiation, thus it differs from the known method of determining the band gap value of semiconductor films from reflectance measurements described in [12]. This allows one to reduce hardware requirements for the experiment (in [12] it is supposed to measure the reflection spectra at an angle of incidence equal to the normal), and to calculate the band gap energy and also the refractive index near the absorption edge.

Verification of this method was performed to determine the optical properties of the films of CdS_xSe_{1-x} solid solutions obtained by screen printing and sintering technique.

Authors: *Mikhail Tivanov, Belarusian State University, Nezavisimosti av. 4, 220030 Minsk, Belarus; Irina Kaputskaya, Belarusian State University, Nezavisimosti av. 4, 220030 Minsk, Belarus; Aleksy Patryn, Koszalin University of Technology, Sniadeckich str. 2, 75-453 Koszalin, Poland, E-mail: patryn@ie.tu.koszalin.pl; Anis Saad, Al-Balqa Applied University, PO Box 4545, Amman 11953, Jordan; Ludmila Survilo, SE "Center of LED and Optoelectronic Technologies of National Academy of Sciences of Belarus", Logoiski trakt str. 22, 220090 Minsk, Belarus; Evgenij Ostretsov, SE "Center of LED and Optoelectronic Technologies of National Academy of Sciences of Belarus", Logoiski trakt str. 22, 220090 Minsk, Belarus.*

REFERENCES

[1] Heavens O.S., Optical Properties of Thin Solid Films (Dover Publications Inc., New York, 1991)
[2] Shur M.S., Rumyantsev S.L., Gaska R., Semiconductor thin films and thin film devices for electrotextiles, *International Journal of High Speed Electronics and Systems*. Vol.12 Iss.02 (2002), 371-390
[3] Mellikov E., Hiie J., Altosaar M., Powder materials and technologies for solar cells, *International Journal of Materials and Product Technology*. Vol.28 Iss.3-4 (2007), 291-311
[4] Liang Li, Hao Lu, Zongyin Yang, Limin Tong, Yoshio Bando, Golberg D., Bandgap-graded CdS_xSe_{1-x} nanowires for high-performance field-effect transistors and solar cells, *Advanced Materials*. Vol.25 Iss.8 (2013), 1109-1113
[5] Lopez N., Reichertz L.A., Yu K.M., Campman K., Walukiewicz W., Engineering the electronic band structure for multiband solar cells, *Physical Review Letters*. Vol.106 Iss.2-14 (2011), 028701-1-4
[6] Ravindra N.M., Ganapathy P., Choi Ji., Energy gap–refractive index relations in semiconductors – An overview, *Infrared Physics & Technology*. Vol.50 (2007), 21-29
[7] Nakayama N., Matsumoto H., Nakano A., Ikegami S., Uda H., Yamashita T., Screen printed thin film CdS/CdTe solar cell, *Japanese Journal of Applied Physics*. Vol.19 No.4 (1980), 703-712
[8] Shaheen S.E., Radspinner R., Peyghambarian N., Jabbour Gh.E., Fabrication of bulk heterojunction plastic solar cells by screen printing, *Applied Physics Letters*. Vol.79 No.18 (2001), 2996-2998
[9] Kumar V., Sharma T.P., Structural and optical properties of sintered CdS_xSe_{1-x} films, *Journal of Physics and Chemistry of Solids*. Vol.59 Iss.8 (1998), 1321-1325
[10] Lu C., Zhang L., Zhang Y., Liu S., Liu G., Electrodeposition of CdSe layers of various thickness to improve the photocatalytic performance of the CdS/CdSe bilayer structure, *Chalcogenide Letters*. Vol.11 No.9 (2014), 425-431
[11] Kose S., Atay F., Bilgin V., Akyuz I., Ketenci E., Optical characterization and determination of carrier density of ultrasonically sprayed CdS:Cu films, *Applied Surface Science*. Vol.256 Iss.13 (2010), 4299-4303
[12] Kumar V., Sharma S.Kr., Sharma T.P., Singh V., Band gap determination in thick films from reflectance measurements, *Optical Materials*. Vol.12 (1999), 115-119
[13] Tivanov M., Ostretsov E., Drozdov N., Survilo L., Fedotov A., Trofimov Yu., Mazanik A., Optical and photoelectrical properties of CdS_xSe_{1-x} films produced by screen-printing technology, *Physica Status Solidi* (b). Vol.244 No.5 (2007), 1694-1699
[14] Premaratne K., Akuranthilaka S.N., Dharmadasa I.M., Samantilleka A.P., Electrodeposition using non-aqueous solutions at 170 °C and characterisation of CdS, $CdS_xSe_{(1-x)}$ and CdSe compounds for use in graded band gap solar cells, *Renewable Energy*. Vol.29 Iss.4 (2004), 549-557
[15] Murali K.R., Venkatachalama K., Electrical properties of sintered CdS_xSe_{1-x} films, *Chalcogenide Letters*. Vol.5 No.9 (2008), 181-186
[16] Saad A.M., Fedotov A.K., Mazanik A.V., Tarasik M.I., Yanchenko A.M., Posedko A.S., Survilo L.Y., Trofimov Yu.V., Kurilovich N.F., Modification of electrical properties of CdS_xSe_{1-x} films by hard irradiation and nanostructuring, *Thin Solid Films*. Vol.487 Iss.1-2 (2005), 202-204
[17] Takeuchi M., Sakagawa Yo., Nagasaka H., Photoconduction and photovoltaic effects in sputtered CdS films, *Thin Solid Films*. Vol.33 Iss.1 (1976), 89-98
[18] Hassanien A.S., Akl A.A., Effect of Se addition on optical and electrical properties of chalcogenide CdSSe thin films, *Superlattices and Microstructures*. Vol.89 (2016), 153-169
[19] Lisitsa M.P., Gudymenko L.F., Malinko V.N., Terekhova S.F., Dispersion of the refractive indices and birefringence of CdS_xSe_{1-x} single crystals, *Physica Status Solidi* (b). Vol.31 Iss.1 (1969), 389-399