Determination of CdS$_x$Se$_{1-x}$ 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$_x$Se$_{1-x}$ films prepared using the screen-printing and sintering technique.

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].

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. The 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 faces of the film respectively, $\phi_0$ angle of incidence and $\phi$ angle of refraction.

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

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

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

$$I = I_1 + I_2e^{-2\alpha d} + I_3e^{-4\alpha d},$$

where $I_1 = I_0r_1^2$, $I_2 = 2I_0r_1(1 - r_1)r_2(1 - r_3)\cos(\frac{2\pi}{\lambda}d)$, $I_3 = I_0(1 - r_1)^2r_2^2(1 - r_3)^2$, $\alpha$ is the absorption coefficient, $\lambda$ is wavelength of the incident radiation.

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

$$I = I_1 + I_2e^{-2\alpha d}.$$

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

$$I_{\text{min}} = I_1, \ I_{\text{max}} = I_1 + I_2.$$ Substituting in (3), and finding the logarithm, resulting in

$$2\alpha d = \frac{2\alpha d}{\sqrt{1 - (\sin \phi_0/n)^2}} = \ln \left( \frac{I_{\text{max}} - I_{\text{min}}}{I_{\text{min}}} \right) = \ln \left( \frac{R_{\text{max}}}{R_{\text{min}}} \right),$$

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

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

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

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

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Słowa kluczowe: półprzewodniki, warstwy CdS$_x$Se$_{1-x}$, współczynnik załamania, widmo odbicia.
Experimental

The films of CdS$_x$Se$_{1-x}$ 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 $\mu$m. The method of producing CdS$_x$Se$_{1-x}$ 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 20° to 45° 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 20° 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$_x$Se$_{1-x}$ films. The measured spectra of CdS$_x$Se$_{1-x}$ films for $x = 0.2, 0.4$ and 0.5 and for other incident angles between 20° to 45° have a similar form.

As follows from the reflection spectrum in Fig. 1, the maximum and minimum reflection coefficients are $R_{\text{max}} = 1.31$% and $R_{\text{min}} = 0.40$%. Band gap determination was made by plotting $(h\nu \cdot \ln \left( \frac{R_{\text{max}} - R_{\text{min}}}{R - R_{\text{min}}} \right))^2$ versus the photon energy $h\nu$ using the obtained values of $R_{\text{max}}$ and $R_{\text{min}}$, 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 20° to the normal.

To determine the refractive index $n$, reflection spectra were measured at various incident angles and dependence of $\sin^2 \phi_0$ was plotted (Fig. 2).

Then the obtained dependency was approximated by the linear function $y = k x + b$ and the refractive index was calculated as $n = \sqrt{\frac{b}{k}}$.

Fig. 2. Dependence of $\sin^2 \phi_0$ versus $\ln^{-2} \left( \frac{R_{\text{max}} - R_{\text{min}}}{R_{\lambda g} - R_{\text{min}}} \right)$ for CdS$_{0.2}$Se$_{0.8}$ film.

The band gap and the refractive index near the absorption edge were determined for CdS$_x$Se$_{1-x}$ 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.
It was found that the value of the band gap increases with the increase of the S concentration of the system CdS$_x$Se$_{1-x}$. It is also known from literature [e.g. 9, 14, 15] that the band gap of solid solutions of CdS$_x$Se$_{1-x}$ 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$_x$Se$_{1-x}$. 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$_x$Se$_{1-x}$ solid solutions obtained by screen printing and sintering technique.

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### Table 1. Experimental and calculation results

<table>
<thead>
<tr>
<th>$\theta_0$, $^\circ$</th>
<th>$R_{\text{max}}$, %</th>
<th>$R_{\text{min}}$, %</th>
<th>$E_g$, eV</th>
<th>Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>1.42</td>
<td>1.40</td>
<td>1.31</td>
<td>CdS$<em>0.4$Se$</em>{0.6}$</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>0.28</td>
<td>0.40</td>
<td>CdS$<em>0.2$Se$</em>{0.8}$</td>
</tr>
<tr>
<td>35</td>
<td>1.92</td>
<td>1.84</td>
<td>1.61</td>
<td>CdS$<em>0.4$Se$</em>{0.6}$</td>
</tr>
<tr>
<td></td>
<td>1.33</td>
<td>1.30</td>
<td>1.25</td>
<td>CdS$<em>0.2$Se$</em>{0.8}$</td>
</tr>
<tr>
<td>40</td>
<td>1.25</td>
<td>1.26</td>
<td>1.21</td>
<td>CdS$<em>0.4$Se$</em>{0.6}$</td>
</tr>
<tr>
<td></td>
<td>0.27</td>
<td>0.30</td>
<td>0.47</td>
<td>CdS$<em>0.2$Se$</em>{0.8}$</td>
</tr>
</tbody>
</table>

The refractive index $n$ = 2.4, 2.5, 2.6.

### REFERENCES


[4] Liang Li, Hao Lu, Zongyin Yang, Limin Tong, Yoshio Bando, Golberg D., Bandgap-graded CdS$_x$Se$_{1-x}$ nanowires for high-performance field-effect transistors and solar cells, Advanced Materials. Vol.25 Iss.8 (2013), 1109-1113


