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Effect of Annealing on the Optical Properties and the Refractive Index Dispersion of CdS Nanometer Films

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The paper describes the optical properties of CdS ultrathin (~ 50 nm) films fabricated by the chemical surface deposition on transparent glass substrates. The influence of the atmosphere (Ar_2, $CdCl_2$, and air) of thermal annealing on the spectral dependences of the reflection $R(\lambda)$ and absorption $\alpha(\lambda)$ coefficients of CdS films was investigated. The extinction coefficient $k(\lambda)$, refractive index $n(\lambda)$, real $\varepsilon_1(\lambda)$ and imaginary $\varepsilon_2(\lambda)$ parts of the optical dielectric constant of the films annealed in different atmospheres were calculated using the experimental characteristics. The coefficients of Sellmeier equation to describe the $n(\lambda)$ dependence in the visible and near infrared spectrum were determined.

Keywords: Semiconductor films, CdS, Annealing, Optical properties, Dispersion of the refractive index.

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1. INTRODUCTION

Only during last three years (2009-2011) there was a three-fold increase (from 22,9 to 67,4 GW) [1] in the total power of mounted solar stations over the world. At present, thin-film solar cells (SC) are considered to be the main and cheap alternative to standard elements based on monocrystalline plates [2]. The largest in the world electric power station based on thin-film SC and 16-th (52 MW) in the list of the biggest stations based on solar batteries "Waldpolenz Solar Park" (Leipzig, Germany) is realized based on CdS/CdTe heterojunctions [3]. Nowadays the maximum efficiency of the best CdS/CdTe film SC is equal to 16,7% [4] and this value is far from theoretical 28-30%. Further increase in their effectiveness requires usage of new approaches; in particular, more effective mechanisms of light absorption are necessary.

Experimental investigations of organic [5-6] and inorganic [7-8] SC have shown that productivity of thin-film elements can be considerably improved due to the metal nanoparticles deposited on the upper part of photoactive layer. Improvement in the operating efficiency of such elements is connected with the increase in the optical absorption by a thin-film layer [9]. This more efficient optical absorption is conditioned by scattering on metal nanoparticles [10] and its amplification under the conditions of exciting of surface plasmon-polaritons in the active layer [11, 12]. Thus, total absorbed power by photoactive layer in CdS/CdTe SC which contains metal nanoparticles can be sufficiently increased.

Localized surface plasmon-polaritons exist under the conditions $\varepsilon_m(\omega)\,\varepsilon_d(\omega) < 0$, $\varepsilon_m(\omega) + \varepsilon_d(\omega) < 0$, where $\varepsilon_m(\omega)$, $\varepsilon_d(\omega)$ are the dielectric constants of metal and dielectric, respectively [13]. Thus, for the fulfillment of the initiation conditions of surface plasmons it is necessary to know optical characteristics of the environments on whose boundaries they appear. The aim of the present work is to determine the dependence of the extinction coefficient $k(\lambda)$, refraction coefficient $n(\lambda)$, real $\varepsilon_1(\lambda)$ and imaginary $\varepsilon_2(\lambda)$ parts of the optical dielectric constant of CdS films and possibilities of their change by the annealing in different atmospheres.

2. EXPERIMENTAL TECHNIQUE

CdS films were obtained by the method of chemical surface deposition (CSD) [14] from $CdCl_2$ aqueous solution on the pre-prepared surface of an optically uniform glass plate.

Using the scanning electron microscope REM-106I ("Selmi", Sumy), the surface morphology and elemental composition of the films were investigated. Thicknesses of CdS films were determined by ellipsometer LEF-3M. He-Ne laser ($\lambda = 633$ nm) was used as the light source. Optical absorption and reflection spectra of CdS films in the visible and near-infrared region of the spectrum were investigated using spectrophotometer Shimandzu UV-3600.

Thermal annealing of the films was carried out at 673 K during 60 minutes in atmospheres of Ar_2, $CdCl_2$, and air. The conditions, which were applied, satisfy the requirements of further usage of CdS films as a "window" of solar element based on heterojunctions with CdTe, Cu(In, Ga)(Se, S)$_2$ films [15, 16].

3. PROPERTIES OF CdS FILMS

During chemical deposition, transparent glass substrates were covered by the films of light-green color which is typical for semiconductor compound of CdS. Results of the X-ray microanalysis confirmed the stoichiometric composition of the films. They agree with our previous results [14], where crystallinity of the films is studied by the X-ray diffractometry methods.

Thickness of the films before and after annealing remained constant and was equal to 47,5 ± 7,5 nm. The extinction $k = 0$-$0{,}15$ and the refraction $n = 2{,}35$-$2{,}47$ coefficients of the films before annealing were defined by the ellipsometry method at $\lambda = 633$ nm.

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3.1 Absorption and reflection of the films

The reflection $R(\lambda)$ and absorption $\alpha(\lambda)$ spectra of CdS films before and after annealing are represented in Fig. 1.

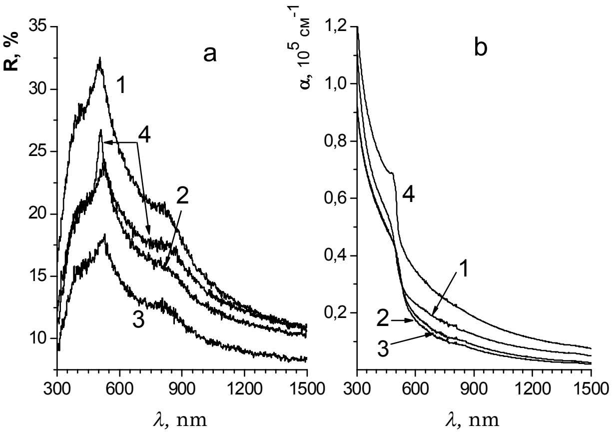

Fig. 1 – Reflection (a) and absorption (b) spectra of CdS films: unannealed (1) and annealed at 673 K during 60 min on air (2), in Ar (3), with deposited $CdCl_2$ film (4)

For films at radiation wavelengths larger than $\lambda \sim$ ~ 490-530 nm (energies less than E_g of the material), a considerable decrease in the reflection and absorption coefficients, typical for the transmission band of semiconductors, takes place. In the range of wavelengths $\lambda \sim$ 800-850 nm, which correspond to the photosensitivity region of CdTe, Cu(In, Ga)(S, Se)$_2$, reflection and absorption atypically slightly increase, and then they decrease almost to zero. Such tendency remains to the wavelength of $\lambda \sim 1500$ nm. In the transparent region $\lambda > 490$-530 nm (photon energies less than 2,53 eV) all films have high transmission coefficient which approaches 80-95%. Results of the experimental data analysis show that optical transmission of the films increases due to annealing: by 5% in air, by 3% in Ar, and decreases with $CdCl_2$ by 3% from the transmission coefficient of unannealed films. Distinction in the transmission coefficients of the films annealed at different atmospheres can be conditioned by different crystalline and phase structure of these samples that we observed previously using the atomic-force and scanning microscopy [15].

3.2 Dispersion of the refractive index

The spectral dependences of the refraction $n(\lambda)$ and extinction $k(\lambda)$ coefficients were calculated by using the reflection and absorption spectra of CdS films. As known, these coefficients are connected by the Fresnel formula

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}, \qquad (1)$$

where $k = \alpha\lambda/4\pi$ is the extinction coefficient [17].

Hence, calculating k, one can obtain the refractive index of the material

$$n = \left(\frac{1+R}{1-R}\right) + \sqrt{\frac{4R}{(1-R)^2} - k^2}\ . \qquad (2)$$

From the values of the refraction and extinction coefficients, the real ε_1 and imaginary ε_2 parts of the optical dielectric constant ε of CdS films can be found

$$\varepsilon_1 = n^2 - k^2, \qquad (3)$$

$$\varepsilon_2 = 2nk, \qquad (4)$$

where $\varepsilon = \varepsilon_1 + \varepsilon_2 = (n + ik)^2$.

Calculation of the spectral dependences of the optical constants of CdS films, namely, refractive index $n(\lambda)$ and extinction coefficient $k(\lambda)$, real $\varepsilon_1(\lambda)$ and imaginary $\varepsilon_2(\lambda)$ parts of the optical dielectric constant ε, was performed by using the packages of applied mathematical programs. Spectral dependences of the corresponding coefficients are shown in Fig. 2 and Fig. 3.

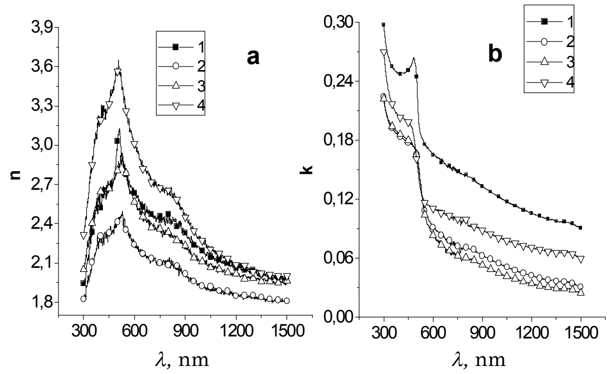

Fig. 2 – Spectral dependences of the refraction $n(\lambda)$ (a) and extinction $k(\lambda)$ (b) coefficients of CdS films: unannealed (1) and annealed at 673 K during 60 min on air (2), in Ar (3), with deposited $CdCl_2$ film (4)

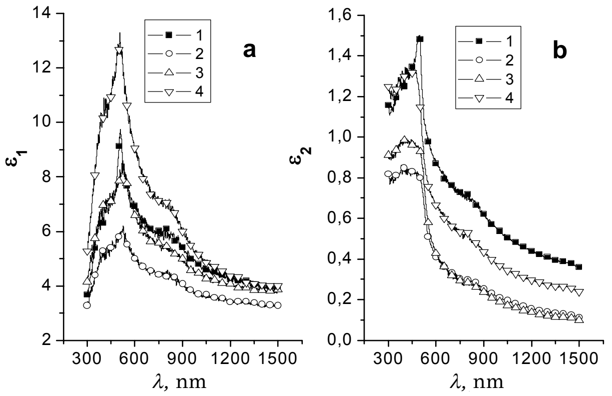

Fig. 3 – Spectral dependences of the real $\varepsilon_1(\lambda)$ (a) and imaginary $\varepsilon_2(\lambda)$ (b) parts of the optical dielectric constant of CdS films of the thickness of 50 nm: unannealed (1) and annealed at 673 K during 60 min on air (2), in Ar (3), with deposited $CdCl_2$ film (4)

As seen from Fig. 2, optical constants n and k in the transparent region of CdS ($\lambda > 490$ nm) decrease due to the increase in the radiation wavelength (decrease in the photon energy $h\nu$). The values of the refraction coefficient n, real ε_1 and imaginary ε_2 parts of the dielectric constant of CdS films calculated at the wavelength of $\lambda = 633$ nm, which corresponds to the wavelength of laser irradiation for ellipsometric measurements, are given in Table 1. For unannealed films, experimental value of the refractive index and calculated one practically coincide that confirms a right choice of the calculation method and precision of its realization.

Table 1 – Some optical characteristics of CdS films annealed in different atmospheres

№	Atmosphere of annealing	E_g, eV	Calculated values, $\lambda = 633$ nm			$B_i \cdot 10^{-5}$, nm^{-2}	λ_{01}, nm
			n	ε_1	ε_2		
1	unannealed	2,42	2,46	6,50	0,83	1,07	504
2	air	2,35	2,17	4,70	0,38	0,76	514
3	Ar_2	2,33	2,48	6,16	0,39	0,98	504
4	$CdCl_2$	2,41	2,89	8,34	0,64	1,06	514

For annealed films, values of n are changed in the range of 2,169-2,889, while values for monocrystalline material $n = 2{,}479$-$2{,}496$ ($\lambda = 610$ nm) are close to the values of initial films.

Dependences of the refraction coefficient on the wavelength can be approximated by Sellmeier formula

$$n^2(\lambda) = 1 + \sum_i \frac{B_i \lambda_{0i}^2 \lambda^2}{\lambda^2 - \lambda_{0i}^2}, \quad (5)$$

where $B_i = e^2 N_0/(\pi m c^2) f_i$; N_0 is the number of oscillators in the unit volume; f_i is the force of i-th oscillator; λ_{0i} is the resonant wavelength of i-th resonance [17]. In the region of intrinsic absorption, it is reasonable to consider only one resonance, i.e. $i = 1$, since influence of other oscillators is insignificant. This formula describes well obtained dependences $n(\lambda)$ for $\lambda > 700$ nm, square of the correlation coefficient $R^2 \geq 0{,}995$. Coefficients of Sellmeier formula are determined for all samples (see Table 1).

Spectral dependences of the real ε_1 and imaginary ε_2 parts of the optical dielectric constant ε are shown in Fig. 3. Behavior of these dependences is similar to that observed for the optical constants $k(\lambda)$ and $n(\lambda)$, i.e. their values monotonously decrease with the increase in the wavelength.

Imaginary part ε_2 of the dielectric constant ε was found to be one order of magnitude less than the real part ε_1. The values of ε_1 and ε_2 calculated at $\lambda = 633$ nm are given in Table 1. For this wavelength, the real and imaginary parts of the optical dielectric constant ε vary in the range of $\varepsilon_1 = 4{,}699$-$8{,}337$ and $\varepsilon_2 = 0{,}379$-$0{,}833$. These values correlate well enough with known data $\varepsilon_1 = 5{,}8$ and $\varepsilon_2 = 0{,}28$ for monocrystals.

4. CONCLUSIONS

It is established that due to the thermal annealing in different atmospheres (Ar_2, $CdCl_2$, and air, at 673 K during 60 min) of ultrathin (50 nm) CdS films deposited by the chemical surface deposition method, their optical characteristics can be varied in a relatively wide range: $n = 2{,}169$-$2{,}889$, $\varepsilon_1 = 4{,}699$-$8{,}337$, $\varepsilon_2 = 0{,}379$-$0{,}833$.

The validity of the performed calculations of $k(\lambda)$, $n(\lambda)$, $\varepsilon_1(\lambda)$, $\varepsilon_2(\lambda)$ dependences for annealed films using Fresnel formulas is confirmed by the agreement of the obtained results with the experimental ones determined ellipsometrically.

Dispersion of the refractive index of the studied films is described using Sellmeier formula. The corresponding coefficients are determined that gives the possibility to obtain a numerical value of n for any wavelength from the specified range.

The performed investigations give the possibility to establish the conditions of preparation of chemically deposited CdS films for their usage as a window and dielectric medium in solar elements with plasmon-polaritons effects.

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