

Nanostructured CdS thin films deposited by spray pyrolysis method

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Influence of solution pH on the structural and optical properties of CdS films deposited by conventional spray pyrolysis technique was studied. X-Ray Diffraction (XRD), Atomic Force Microscopy (AFM), Photoluminescence spectroscopy (PLS), and Spectroscopic Ellipsometry (SE) methods were used for the characterization of the deposited films. PL spectrum of the film deposited from the solution with pH = 10.2 shows broad-band

PL emission located at 460 nm (2.7 eV), which can be attributed to the quantum size effect at grain sizes of <10 nm. No shifts of ϵ_1 and ϵ_2 due to the quantum size effect are observed in dielectric function spectra, what can be caused by low concentration of nano-sized (<10 nm) CdS grains. The change in the film properties with the pH of the solution was analyzed in terms of variation of grain sizes of the polycrystalline films.

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1 Introduction Cadmium sulfide (CdS) thin films are widely used as universal window layers in thin film solar cells based on the different active-layer materials, such as cadmium telluride (CdTe) [1, 2], copper indium diselenide (CIS), and copper indium gallium diselenide (CIGS) [3, 4]. CdS has a band-gap of 2.42 eV which causes considerable absorption of sunlight in the short wavelength region. Extending transparency of a window material into a region above the energy gap of CdS may provide increased efficiency of solar cells. X. Wu [2] has reported the improvement of the conversion efficiency of CdTe solar cells when CdS film was deposited on CdTe by rf sputtering in the presence of oxygen at room temperature. According to the report [2], the prepared nanostructured CdS:O films had higher band-gap, as compared with bulk CdS, which improved the quantum efficiency of solar cells in the short wavelength region.

Structures and optical properties of CdS:O films deposited at different oxygen partial pressures by rf magnetron sputtering were examined in Ref. [5]. It was shown that CdS:O thin films obtained under partial oxygen pressure below 3% have crystal structure of bulk CdS, while above 3% show an amorphous structure. An increase in transparency of the CdS:O (5%) in short wavelength region was attributed to several factors including redistribution of the density of states in amorphous CdS, quantum size effect in nano-crystals of CdS, and contribution of amorphous CdO₂.

In this work the attempt of preparation of nanostructured CdS thin films by spray pyrolysis method was made. The preliminary results of structural and optical characterization of the films are given.

2 Experimental The CdS films were prepared by the spraying of aqueous mixture of cadmium acetate CdAc₂ (0.025 M) and thiourea (NH₂)₂CS (0.025 M) and ammonium acetate (NH₄) Ac onto heated up to 400 °C soda lime glass substrates. NH₄OH was added to the mixture to increase of pH of the solution. Three types of CdS films were deposited from different solutions with initial pH of 6.7; 9.5 and 10.2.

X-Ray diffraction (XRD) analyses of the films were carried out using Bruker D2 Phaser (Germany) diffractometer in θ -2 θ scan mode with Ni-filtered CuK α radiation ($\lambda = 1.54060 \text{ \AA}$) source.

The average grain sizes of the polycrystalline films were calculated by the Scherer equation,

$$D = \frac{\alpha\lambda}{\beta\cos\theta} \quad (1)$$

where D is the average grain size, α is constant (equal to 0,9), λ is the X-Ray wavelength (1.54060 \AA), β is full width at half maximum (FWHM) of the diffraction peaks. The

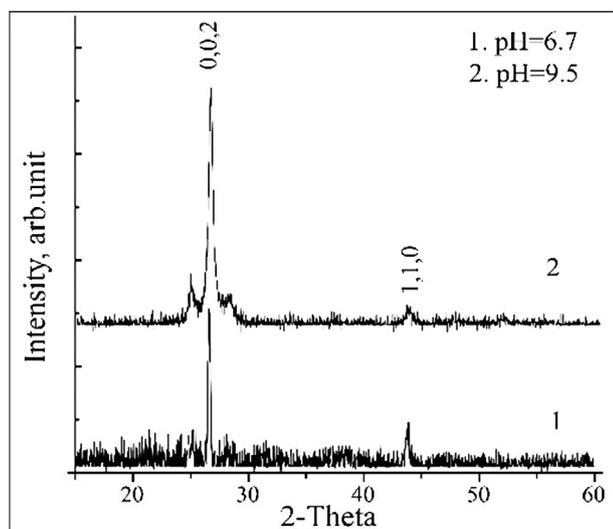


Figure 1 X-ray diffraction spectra of CdS thin films, deposited from solution with pH = 6.7 (curve 1) and pH = 9.5 (curve 2).

crystallinities were calculated from XRD patterns of the films using DIFFRAC.EVA.V2.1 PC program.

Topography analysis of the thin films was performed in Smart SPM 1000 AIST NT (Tokyo Instruments, Japan).

Photoluminescence (PL) measurements were performed using standard spectrometer LS-55 (Perkin-Elmer, USA).

The samples were excited by the 400 nm line of xenon lamp.

The spectroscopic ellipsometry measurements in 220–1700 nm spectral range were performed using Woollam M2000 (USA) rotating compensator instrument. Incident light angles were varied between 50° and 60° with 5° step. WVASE32 computer program was used for the ellipsometric data fitting procedure. Experimental data were fitted (employing the Levenberg–Marquardt algorithm) to optical model using parameterized model dielectric functions simultaneously for all the data points measured in UV/VIS ranges.

3 Results and discussions The thicknesses all of the studied films determined from the spectroscopic ellipsometry fit were around 130 nm.

The XRD patterns of the CdS sample deposited from the solution with pH = 6.7 and pH = 9.5 exhibit prominent broad peaks at 26.7° and 44° which can be attributed to hexagonal wurtzite structure (PDF 01-074-9663) with p63mc space group and lattice parameters $a = 4.136$,

Table 1 The crystallinities and average grain sizes of CdS films.

samples	crystallinity (%)	average grain size, (nm)
CdS (pH) = 6.7	28.7	20.4
CdS (pH) = 9.5	~11.5	10
CdS (pH) = 10.2	weak reflection	<10



Figure 2 Surface morphology of CdS thin films, deposited from solution with pH = 6.7 (a), pH = 9.5 (b), and pH = 10.2 (c).

$c = 6.716$ (Fig. 1). The films have highly oriented crystallites with a preferential orientation along the c -axis (002) perpendicular to the substrate plane. CdS films deposited from the solution with pH = 10.2 shows very weak reflection and has nearly amorphous structure.

The crystallinities (crystallization degree) and average grain sizes of the films derived from the XRD data are summarized in Table 1.

As it is seen from the Table 1, the structural properties of the CdS thin films strongly depends on deposition conditions. The crystallinities and average grain sizes of the films decrease with pH of the solution.

AFM measurements were performed to study of surface morphology of the CdS thin films deposited at different pH of the solution. Figure 2 illustrates the AFM images of the films deposited from the solution with pH = 6.7 (Fig. 2a), pH = 9.5 (Fig. 2b), and pH = 10.2 (Fig. 2c). Scanning area is $1.0 \times 1.0 \mu^2$. As it is seen from the Fig. 2, the AFM measurement results are in good agreement with XRD data. The grain sizes of the films decrease with pH of the solution. Surface roughness (RMS) are 8.62, 6.93, and 4.63 nm for the films with pH = 6.7, pH = 9.5, and pH = 10.2, respectively.

Photoluminescence measurements were used to study the optical properties of the deposited thin films (Fig. 3). PL spectrum of CdS film deposited from the solution with pH = 6.7 shows two bands at 520 and 600 nm caused by band to band and defect center transitions, respectively (Fig. 3, curve 1). Nearly the same bands contains the PL spectrum of CdS film deposited from the solution with pH = 9.5. But PL spectrum of the film deposited from the solution with pH = 10.2, except for these bands, shows also

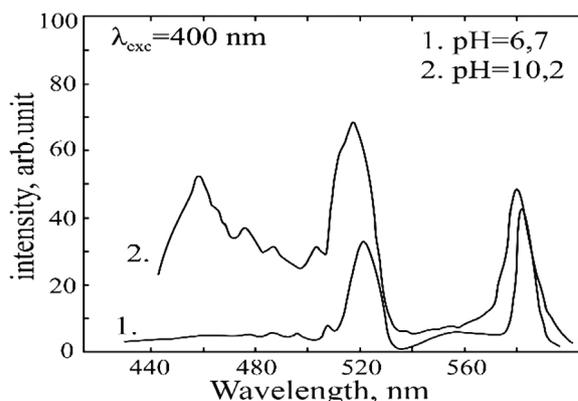


Figure 3 PL spectra of CdS thin films, deposited from solution with pH = 6.7 (curve 1) and pH = 10.2 (curve 2).

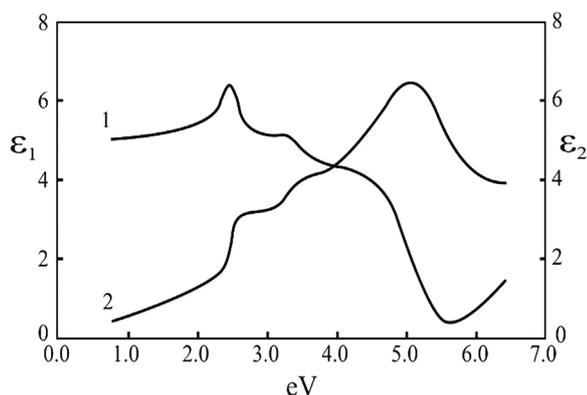


Figure 4 Real ε_1 (curve 1) and imaginary ε_2 (curve 2) parts of dielectric function of CdS film, deposited from solution with pH = 10.2.

broad band PL emission located at 460 nm (2.7 eV) (Fig. 3, curve 2). This emission seems to be caused by peak shift of the band-to band emission of nanostructured CdS films due to the quantum size effect.

Energy positions of emission peaks for nano-sized CdS can be determined from well-known equation [6, 7]

$$E_g = E_g^{(\text{bulk})} + E_b \left(\frac{\pi a_B}{R} \right)^2 \quad (2)$$

where E_g – band-gap of nano-crystal, E_g^{bulk} – band-gap of bulk crystal, E_b – exciton binding energy, a_B – exciton Bohr radius, R – grain size.

According to the equation (2), noticeable blue-shift of band edge of CdS films takes place at the grain sizes below 10 nm, but for the significant (up to 2.7 eV) shift about ~3 nm sized grains are required. The lack of detectable reflections in XRD spectra of CdS films, deposited from the solution with pH = 10.2 indicates the availability of some low-dimensional (<10 nm) centers in the films.

Spectroscopic ellipsometry measurements were performed to reveal the quantum size effect in nanostructured CdS films, deposited from the solution with pH = 10.2. The real ε_1 (curve 1) and imaginary ε_2 (curve 2) parts of dielectric function of the film are shown in Fig. 4.

Two transitions can be observed in these spectra: the first transition at about 2.4 eV is due to the absorption at the fundamental band gap of CdS and the second one above 4.5 eV represents the transitions along the $\Gamma \rightarrow A$ direction of the Brillouin zone of the hexagonal CdS lattice [8]. As opposed to luminescence spectra, no shifts of ε_1 and ε_2 due to the quantum size effect are observed in dielectric function spectra, and energy band gap at the critical points of the electronic band structure of CdS are not affected by the increased pH of the solution. The possible reason of this can be low concentration of nano-sized (<10 nm) grains, which are well manifested in luminescence spectra of the films, but not in dielectric function spectra, because density of state at these centers are negligible in comparison with the density of states at the fundamental band gap of bulk CdS.

4 Conclusions Grain sizes of CdS thin films deposited by spray pyrolysis method decrease with increase of pH of reaction solution. PL spectrum of the film deposited from the solution with pH = 10.2 shows broad band PL emission located at 460 nm (2.7 eV), which can be attributed to the quantum size effect at grain sizes of <10 nm. No shifts of ε_1 and ε_2 due to the quantum size effect are observed in dielectric function spectra, what can be caused by low concentration of nano-sized (<10 nm) CdS grains, and therefore, negligibility of density of state at these centers in comparison with the density of states at the fundamental band gap of bulk CdS.

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