

Study of the Structural and Optical Properties of Dy Doped CdS Thin Films Deposited by Close-spaced Vacuum Sublimation

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In this work we deposited CdS:Dy thin films using a close-spaced vacuum sublimation method at different temperatures (T_s) of the glass substrate. The XRD analysis reveals that the obtained films only correspond to a single wurtzite phase. The microstress level in Dy doped CdS films decreases compared with undoped films. The results of the pole density calculations show that at $T_s = (573-673)$ K the [002] crystallographic direction corresponds to the main axial growth texture. The intrinsic defects in the investigated films were studied based on the low temperature photoluminescence measurements. It was shown that the CdS:Dy thin films are sufficiently stoichiometric. Analysis of the free exciton reflection spectra indicates that the polarization of the bands corresponds to the optical c -axis perpendicular to the substrate surface. The optical transmittance of CdS:Dy thin films in the range of transparency (600-800 nm) at room temperature exceeded 80 %. Based on the obtained results, it is concluded that the CdS:Dy thin films are excellent crystalline and optical quality and may be increase the efficiency their photovoltaic applications.

Keywords: Semiconductor thin films, Structural properties, Low-temperature photoluminescence, Intrinsic defects.

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1. INTRODUCTION

CdS films relate to direct semiconductors with a bandgap about of 2.50 eV at room temperature and have n-type conductivity. Now these films are widely studied because they are suitable for engineering of a number of optoelectronic devices such as photo sensors, piezoelectric devices, photoconducting cells, and non-linear optical devices, etc [1-5]. Besides, the CdS thin films are used in solar energy photovoltaic conversion, in particular, as window layers in the top of tandem high efficiency solar cells [6-8].

In order to use effectively semiconductor thin films in micro- and optoelectronics, it is necessary to improve their optical, structural, and electronic properties. In the case of CdS thin films having an anisotropic crystal structure, it is necessary to obtain both high optical quality and highly-structured films. The fulfillment of these two conditions will greatly improve the efficiency of using these films in various optical applications. One of the effective methods for improving the electronic properties of semiconductor materials is their doping with various impurity atoms. Usually the doping with donor or acceptor impurities is used [7-9].

It should be noted that the rare earth (RE) elements play an important role among impurity atoms [10-11]. They may be considered as effective gettering agent for residual impurities in semiconductor materials [11]. In the case of II-VI semiconductors triply charged RE ions replace doubly charged cations [10]. Therefore, they may form complex centers with residual impurities that are electrically inactive. Thus, doping II-VI semiconductor materials with RE atoms allows improving their optical quality and electronic properties.

Earlier [12], it was shown that a close-spaced vacuum sublimation (CSV) method enables to deposit the stoichiometric films of binary II-VI semiconductors with the controllable physical properties using a glass as substrate. The CSV is a simple and inexpensive technique. In addition, it makes is possible to optimize the defects structure and, accordingly, the electronic properties of the films by monitoring the growth parameters such as the temperature of the substrate and the evaporator temperature.

The aim of this work is to study structural and optical properties of Dy-doped CdS thin films in order to obtain data about the effect of the impurity on the crystal and defect structure of the investigated materials and to improve their optical quality.

2. EXPERIMENTAL DETAILS

The cleaned glass substrates were used for depositing CdS polycrystalline films. In this case the evaporator temperature was $T_e = 1173$ K, the substrate temperature T_s was varied from 573 K to 773 K. The stoichiometric powder of CdS doped with Dy as the initial material was used. CSV technique is described in detail in [13]. XRD studies were carried out with a DRON 4-07 diffractometer using K_α Co radiation source. Structural parameters, namely, the average grain size in the layers, phase analysis, texture, pole density, coherent scattering domain (CSD) size, microdeformation level (ϵ) were estimated using the methods described in [13].

Steady state PL measurements were carried out using an MAYA2000-pro spectrometer (Ocean Optics) with a variable temperature liquid-helium cryostat.

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The PL spectra were excited by an LED with $\lambda = 395$ nm and the power of 20 mW. Besides, exciton PL and reflection spectra were measured by an SDL-1 grating spectrometer. An LGN-404 argon laser was used for excitation by the 488.8 nm line. The spectral resolution of the system was of the order of (0.1–0.2) meV.

3. RESULTS AND DISCUSSION

3.1 XRD-spectra of CdS:Dy Films

The results of X-ray measurements of CdS:Dy films deposited under different growth conditions are presented in Fig. 1. The observed peaks are associated with the (002), (101), (102), (103), (004), (104), (105) planes of the wurtzite phase. The peaks caused by other phases were not observed. The most intense peak corresponds to the (002) plane. So, this indicates that the optical c -axis is perpendicular to this plane, which coincides with the substrate surface. It was found that for undoped CdS films, obtained at the same growth conditions as CdS:Dy ones, the dominant peak corresponds in mainly to the (103) plane. Thus, doping CdS films with Dy allowed us to produce such films with a clearly expressed texture and a stable wurtzite phase. It is known that CdS films obtained by the chemical bath method have a cubic metastable structure, which is converted into a stable hexagonal phase by annealing the films [12].

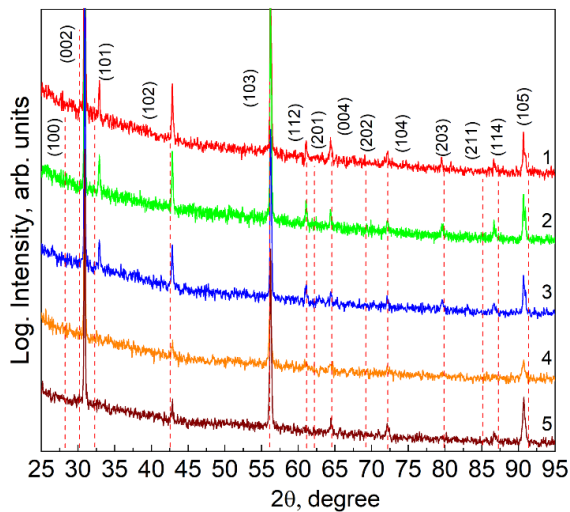


Fig. 1 – X-ray patterns of CdS:Dy films deposited at the different substrate temperatures T_s , K: 573 (1); 623 (2); 673 (3); 723 (4) and 773, respectively

The film texture is characterized by the pole density $P_{(hkl)}$ which determines the volume fraction of the crystal grains having a certain crystal direction [14]. The results of the pole density calculations for the investigated CdS:Dy films are shown in Fig. 2. They indicate that the value $P_{(hkl)}$ is smaller than one for [101], [112] and [102] crystallographic directions and weakly depends on T_s up to 673 K. In the case of [102]-crystal direction the value $P_{(102)}$ is equal to about 0.6 up to 673 K and then decreases to 0.3 for $T_s = 773$ K. For the [002] and [004] crystal directions, which are equivalent and coincide with the optical c -axis, the pole density is

greater than one, which is characteristic for wurtzite-type films [7]. It should be noted that the value $P_{(002)(004)}$ is monotonically changing from 3.4 to 2.5 for the films obtained at $T_s = 573$ K and $T_s = 673$ K, respectively. This indicates that the crystallites are preferably oriented with the (002) planes parallel to the substrate. For the films grown at $T_s = 723$ K the value

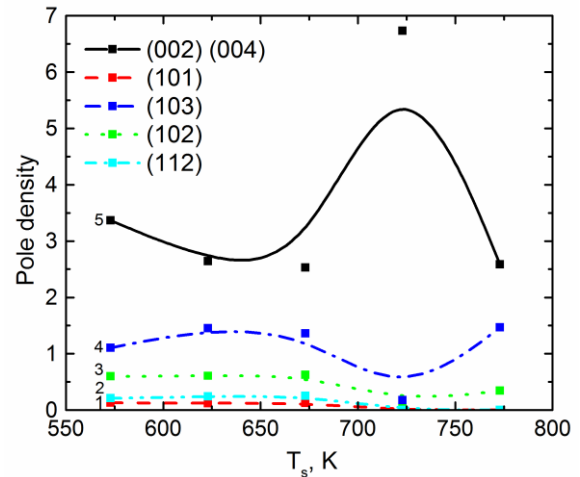


Fig. 2 – Pole density $P_{(hkl)}$ as function of substrate temperature. Curves 1–5 correspond to the crystallographic planes (101), (112), (102), (103) and (002)(004), respectively

$P_{(002)(004)}$ greatly increases and equals about 7.0. At the same time, the values of the pole density for any direction are smaller than 1. This indicates that these films are strongly structured in the direction along the optical c -axis. It should be noted that the value $P_{(103)}$ is greater than one, with the exception of the films obtained at $T_s = 723$ K. This means that the CdS:Dy thin films have two-component texture. The latter direction corresponds to the direction slightly inclined to the optical c -axis.

The value ε for CdS:Dy films was determined from the studies of the physical broadening of (002) and (103) diffraction peaks [15]. The obtained results indicate that these values in the [002] direction parallel to the c -axis are smaller than in the [103] direction, inclined to this axis. According to the obtained results of the morphology studies of the films, they have the preferred orientation of their optical c -axis perpendicular to the substrate surface. Thus, such orientation of the films obviously contributes to the improvement of their optical and crystalline quality. The value ε also depends on the substrate temperature and is maximal at $T_s = 723$ K. As noted above, the optical axis of the films obtained at this temperature is strongly oriented perpendicular to the substrate surface. Therefore, in this case, we should expect a decrease in the value of ε . An increase in this value may be due to the doping of CdS films with dysprosium. The results of the EDS spectra analysis of the investigated thin films show that the concentration of Dy for the films obtained at $T_s = (573–673)$ K is lower than 0.1 Mol. %. At the same time, for the films obtained at $T_s = 723$ K this value corresponds to about 0.4 Mol. %.

The microstress level for CdS:Dy films ($\varepsilon_{(002)} = (0.73–$

$0.92) \cdot 10^{-3}$) is lower in comparison with the undoped CdS films ($\epsilon_{(103)} = (1.12-1.55) \cdot 10^{-3}$), which indicates a high crystal quality of the investigated thin films. As a result of increasing the substrate temperature, the CSD size for the [002] direction initially increases from 62.2 nm ($T_s = 573$ K) to 72 nm ($T_s = 623$ K), and then decreases to 55.7 nm ($T_s = 773$ K). A similar dependence is also characteristic of the [103] direction.

3.2 Photoluminescence Spectra of CdS:Dy Films

The low-temperature PL measurements, which is a very sensitive and nondestructive technique, let us determine the nature and energy levels of both intrinsic and impurity defects, as well as the optical quality of the polycrystalline CdS:Dy films. This is very important, since these parameters determine the efficiency of various applications of semiconductors.

Fig. 3 shows PL spectra of the CdS polycrystalline films doped with Dy at 4.5 K for the samples obtained at different T_s . As can be seen from Fig. 3, the most intense PL bands cover the spectral region from 2.25 eV to 2.50 eV. This emission is known as the green (G) PL bands which are associated with the radiative recombination of free electrons and acceptor centers, as well as the optical transitions associated with the recombination of donor-acceptor pairs [11]. In this case, the energy levels of the donor and acceptor centers are 30 meV and 169 meV, respectively. The donor centers may be caused by interstitial Cd (Cd_i) which may be created in the investigated films, since the concentration of Cd atoms is higher than the concentration of S atoms. According to EDS measurements, the ratio of the concentration of Cd and S atoms equals to 1.37.

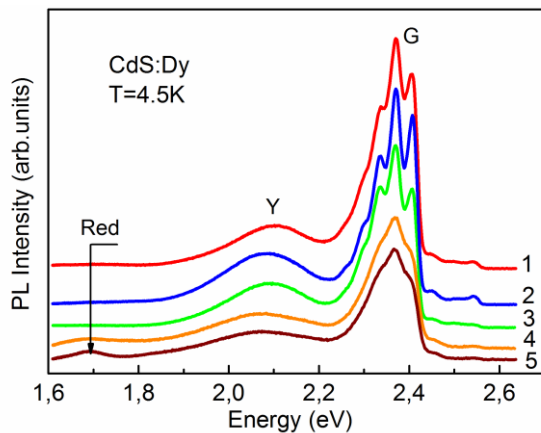


Fig. 3 – PL spectra of CdS:Dy films grown under different substrate temperatures. Curves 1-5 correspond to T_s , K: 573, 623, 673, 723 and 773 K, respectively

The broad nonstructured band located at 2.083 eV is known as the yellow (Y) PL band and is originated from the formation of the V_{Cd} – and Cd_i – centers [12]. An increase in the Cd_i concentration leads to an increase in the yellow PL and a decrease in the green PL. This emission is also observed in Cd-rich and in Cd-treated crystals [16]. Thus, we can conclude that the concentration of the Cd_i – centers in the investigated films is small.

As can be seen from Fig. 3, for the samples 4 and 5 a

PL band at 1.70 eV is observed which is known as red (R) emission and is usually associated with V_s defects [12]. This band may also be associated with optical transitions from the V_s donor center to the V_{Cd} acceptor associated with the surface defects. Since the intensity of this band is low, this indicates that the density of surface Cd vacancies for the investigated films is low. Thus, this fact confirms the high optical quality of the films. Since for the CdS:Dy films the intensity of R band is considerably lower than the intensity of G band, this also indicates that the CdS:Dy films are sufficiently stoichiometric.

The emission of low intensity observed in short-wavelength spectral region is caused by exciton recombination [17]. In Fig. 4 this part of PL spectra, measured with an SDL-2 spectrometer with a high spectral resolution, is represented. As can be seen from Fig. 4, sharp lines are observed at 2.5484 eV and 2.5364 eV which are associated with the donor and acceptor bound excitons (D^0X - and A^0X -lines, respectively) [17]. In the case of sample 4, the exciton PL spectrum is strongly broadened, which is caused by an increase in the microstress level in this sample. For sample 5, the exciton emission is not observed, which indicates a deterioration in the optical and crystalline quality of films obtained under such technological conditions.

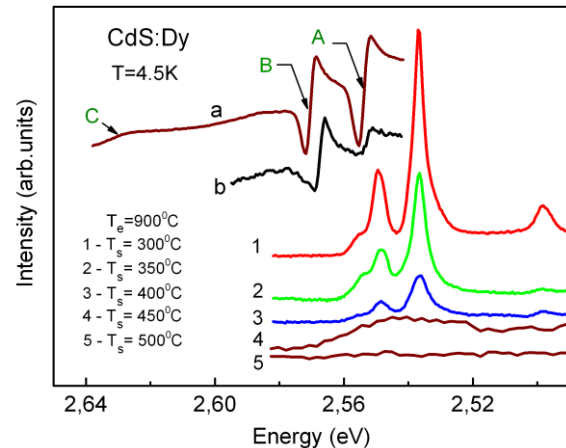


Fig. 4 – PL spectra associated with the excitonic emission and the excitonic reflection spectra. Curves 1-5 correspond to the CdS:Dy films grown under the following substrate temperatures: T_s , K: 573, 623, 673, 723 and 773, respectively. Curves a and b correspond to the reflection spectra for the film ($T_s = 673$ K) and the bulk optically non-oriented CdS:Dy crystal, respectively

The optical studies of CdS:Dy films also observe the formation of free excitons in reflection spectra for samples 1-3 at 4.5 K. In Fig. 4 a typical reflection spectrum is shown for the sample 2 (curve a). The peaks designated A, B and C correspond to the formation of free excitons. The appearance of these peaks is caused by the low symmetry crystal field and spin-orbit splitting of the valence band [17]. It should be noted that polarization of the A exciton is perpendicular to the optical c-axis. At the same time the B and C excitons are observed for both polarizations ($E \perp c$ and $E \parallel c$). Fig. 4 also shows the exciton reflection spectrum for an optically non-oriented bulk CdS:Dy crystal (curve b). It is seen that in this case the intensity of the A exciton is noticeably lower than

that for the B exciton (sample 2). Since in the reflection spectra the intensity of the A and B excitons for the sample 2 is the same, this indicates that crystalline grains of CdS:Dy polycrystalline films were grown with the optical axes, preferably oriented perpendicular to the substrate surface. It should be noted that the result regarding the optical orientation of the CdS:Dy crystalline grains coincides with the data of the XRD spectrum and the calculated pole density. It should be noted that the width of the reflection lines, which is determined by the distance between the minimum and maximum of the dispersion curve in the reflection spectra for thin CdS:Dy films is close to the value for bulk CdS:Dy crystal (3.7 meV and 2.6 meV, respectively). The observation of free and bound excitons in the optical spectra indicates the excellent optical quality of these films.

4. CONCLUSIONS

In summary, it was shown that the films grown by CSVS technique at different substrate temperatures $T_s = (573-773)$ K correspond to only the single wurtzite phase. The investigated thin films have the preferred orientation of their optical c -axis perpendicular to the substrate surface. Such orientation of the films obviously contributes to the improvement of their optical and crystalline quality. The microstress level for CdS:Dy films is lower in comparison with the undoped CdS films, which indicates the high crystal quality of the CdS:Dy thin films. The results of the EDS spectra analysis of the investigated thin films show that the concentration of Dy for the films obtained at $T_s = (573-673)$ K is lower than 0.1 Mol. %. At the same time this value for the films obtained at $T_s = 723$ K is about 0.4 Mol. %. In the latter case the microstress level of the films increases.

The analysis of low-temperature PL spectra shows that CdS:Dy films contain the intrinsic defects such as Cd_i , which are the donor centers. Besides, the films obtained at $T_s \geq 723$ K contain also another donor type defects, namely V_s . It was shown that the concentration of the surface V_s defects is low. The main acceptor centers in the films is associated with Na(Li) residual impurities. Their concentration and the concentration of other residual impurities are significantly reduced compared with undoped CdS films that may be due to the "cleaning" effect as a result of the doping by dysprosium. The presence of narrow lines of bound and free excitons in the PL spectra, as well as free excitons in the reflection spectrum indicates a high optical quality of the investigated films grown at $T_s = (573-673)$ K. This results correlate with the decrease of the microstress level in CdS:Dy thin films in comparison with undoped CdS films. The optical transmittance of CdS:Dy thin films in the range of transparency (600–800 nm) at room temperature exceeded 80 %.

Our findings shows that the structural and optical properties of polycrystalline CdS films doped with Dy are considerably improved which will help to increase their efficiency for optoelectronic and photovoltaic applications.

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Дослідження структурних і оптичних властивостей плівок CdS легованих Dy, отриманих методом випаровування в квазізамкненому об'ємі

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В роботі досліджено плівки CdS:Dy, отримані методом вакуумного випаровування в квазізамкненому об'ємі при різних температурах скляних підкладок (T_s). Результати рентгенівського аналізу показали, що отримані плівки є однофазними та мають вюрцитну структуру. Для легованих Dy плівок спостерігався менший рівень мікродеформацій у порівнянні з нелегованими. Результати розрахунку полюсної густини показали, що при $T_s = (573-673)$ K напрям [002] відповідав головній аксіальній тектурі росту. Власні дефекти в досліджуваних плівках були вивчені з використанням методу низькотемпературної фотолюмінесценції. Було показано, що плівки CdS:Dy є досить стехіометричними. Аналіз вільних екситонів на спектрах відбивання світла від плівок свідчить, що поляризація екситону відповідає оптичній осі кристалічної ґратки c , перпендикулярній до поверхні підкладки. Оптичне пропускання плівок CdS:Dy в хвильовому діапазоні (600-800 нм) при кімнатній температурі перевищує 80 %. На основі отриманих результатів, було зроблено висновок, що плівки CdS:Dy мають покращені властивості (високу кристалічну та оптичну якість), що може підвищити ефективність фотоперетворювачів світла при їх використанні в фотовольтаїці.

Ключові слова: Напівпровідникові тонкі плівки, Структурні властивості, Низькотемпературна фотолумінесценція, Власні дефекти.

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