HORIZONS IN WORLD PHYSICS

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Horizons in World Physics. Volume 299 opens with a study on the analysis of photoluminescence spectra of II-VI-based thin films (pure II-VI semiconductor compounds – CdTe, ZnTe, CdSe, Cd1-xZnxTe ternary compound, CdS:Dy rare-earth element doped II-VI compound) at different substrate temperatures.

Next, the authors introduce a novel universal carrier-guided nanopore dielectrophoresis technology that can selective capture and detection of single nucleic acid molecules. In this approach, each target nucleic acid molecule is hybridized with a designed cationic carrier to impart a tunable synthetic dipole to the target.

This compilation also describes the numerical investigations of some of the possibilities for enhancing the amplified spontaneous emission, generated from a thulium-doped silica fiber at the 2µm wavelength region. The authors provide a fundamental description of the amplified spontaneous emission process and the progress toward the development of the numerical modelling of this phenomenon.

Abinitio calculations and high temperature series expansions are used to study the electronic and magnetic properties of Mn2X compounds. Polarized spin and spin-orbit coupling are included in the calculations within the framework of the antiferromagnetic state between two adjacent Mn and Mn atoms.
The authors go on to review the behavior of critical systems of the Ising universality class in strip geometry with variable symmetry-breaking boundary conditions and an internal grain boundary based on the Mikheev-Fisher theory. The foundations of the method and the concept of the grain boundary within it are elucidated.

Lastly, the structural and optical properties of thin smectic films is discussed by way of a combination of statistical mechanical theories, hydrodynamics of liquid crystal phases, and optical and calorimetric techniques. The authors examine the validity of theoretical descriptions of thin smectic films, both deposited on a solid surface or stretched over an opening.

Chapter 1 - In this chapter the analysis of photoluminescence (PL) spectra of II-VI-based thin films (pure II-VI semiconductor compounds - CdTe, ZnTe, CdSe, Cd$_{1-x}$Zn$_x$Te ternary compound, CdS:Dy rare-earth element doped II-VI compound) at different substrate temperatures is performed. In all cases of studied samples they are deposited onto non-oriented substrates using the close-spaced vacuum sublimation technique (CSVS) which makes a possibility to obtain films with optimal crystalline and optical quality. The study of the PL spectra of the investigated films makes it possible to determine their optimal growth conditions in order to obtain the films of good optical quality. The obtained results are in good agreement with the structural investigations, which the authors have carried out earlier using the X-ray diffraction technique. In all cases of investigated samples on PL-spectra there were observed lines that correspond to the residual impurities, which are typical for II-VI compounds (Li, Na, Cu, P). Moreover there were observed an additional lines which may be caused by the presence of point defects in crystalline structure, donor-acceptor pairs recombination processes, phonon replicas, etc.

Chapter 2 - Dielectrophoresis (DEP) is the motion of a polarizable particle in a nonuniform electric field due to an unbalanced electrostatic force on the induced dipolar in the particle. This technology has been extensively utilized for concentration, separation, sorting, and transport of bioparticles, from cancer cells and viruses. DEP also has broad
applications in medical detection; however, using DEP to selectively manipulate biomolecules at single molecule resolution remains a challenge due to the molecule’s weak dipoles induced in a non-uniform field. In this chapter, the authors introduce a novel universal carrier-guided nanopore dielectrophoresis technology that can selective capture and detect single nucleic acid molecules. In this approach, each target nucleic acid molecule is hybridized with a designed cationic carrier to impart a tunable synthetic dipole to the target. Meanwhile, the engineered nanopore acts as an ideal foul-free point source that generates an extremely high field gradient ($\Delta E \sim 10^7$ V·m$^{-1}$ per nanometer or $\sim 10^{16}$ V·m$^{-2}$) around the nanopore entrance. When the carrier-target binding complex moves into the nanopore field gradient, its strong synthetic dipole dramatically increases the dielectrophoretic response, and it is captured by a nanopore. The dielectrophoretic capture of the carrier–target dipolar complexes can be visualized as a transient blockade of ionic current in nanopore recording, whereas any non-target nucleic acids without hybridization with the carrier are repelled from the nanopore by electrophoresis. Thus, non-target nucleic acids cannot interfere with the detection of target. This single-molecule dielectrophoresis technology can be applied to detection of both DNAs and RNAs (e.g., microRNAs) of any length or with tertiary structures. Combined with an ultrasensitive nanopore single molecule identifier, the single-molecule DEP technology can simultaneously detect multiple targets and discriminate target nucleic acids fragments carrying single nucleotide polymorphisms (SNP). The authors expect that this selective, multiplex single-molecule DEP technology will have broad applications in real-time interference-free genetic analysis of complex clinical samples.

Chapter 3 - In this chapter, the authors describe the numerical investigations of some of the possibilities for enhancing the amplified spontaneous emission (ASE), generated from a thulium-doped silica fiber at 2µm wavelength region. The authors first review a fundamental description of the ASE process and the progress toward the development of the numerical modelling of this phenomenon. The developed model provides the ASE spectral power as functions of the fiber length and the pump power under single-pass forward (SPF) and double-pass bi-
directional (DPB) pumping schemes. The authors solve a set of rate and propagation equations to produce a broadband ASE source when pumped at the wavelengths 1570 nm and 793 nm and consider the effects of the cross-relaxation process. The authors have demonstrated by means of a numerical model that the broadband ASE source outperforms when using a DPB pumping scheme. The proposed broadband source offers high ASE power and broad spectral bandwidth which is suitable for applications such as optical coherence tomography and fiber optic gyroscopes.

Chapter 4 - The abinitio calculations and high temperature series expansions (HTSEs) have been used to study the both electronic and magnetic properties of Mn$_2$X (X = Sb, Au and Sn) compounds. The abinitio calculations, based on density functional theory approach and using full potential linear augmented plane wave method, are performed to investigate both electronic and magnetic properties of the Mn$_2$X (X = Sb, Au and Sn) compounds. Polarized spin and spin-orbit coupling are included in calculations within the framework of the antiferromagnetic state between two adjacent Mn and Mn atoms. In this work, the authors also magnetic moment considered to lie along (001) axes are c. The antiferro and ferromagnetic energies of Mn$_2$Sb, Mn$_2$Au and Mn$_2$Sn compounds have been obtained. The obtained data from abinitio calculations are used as input for the HTSEs calculations to compute other magnetic parameters. The exchange interactions between the magnetic atoms Mn-Mn in three compounds are given by using the mean field theory. The HTSEs of the magnetic susceptibility through Ising model is given up to tenth order series. The Curie temperature has been obtained from HTSEs of magnetic susceptibility series combined with the Padé approximant method for three compounds. The critical exponent $\gamma$ associated with the magnetic susceptibility has been deduced as well for Mn$_2$Sb, Mn$_2$Au and Mn$_2$Sn. The obtained results have been comparable with those obtained by experiment results.

Chapter 5 - This review of the behavior of critical systems of the Ising universality class in strip geometry with variable symmetry-breaking boundary conditions and an internal grain boundary is based on the
Mikheev-Fisher theory. The foundations of the method and the concept of the grain boundary within it are elucidated.

The idea of the free energy functional, based on the simultaneous use of two primary scaling densities for the Ising systems (both the order parameter and energy density) is expounded.

The article is followed by a consideration of the more involved problem of two boundaries confining the system with an internal grain boundary. A thorough exposition of the behavior of energy density and Casimir amplitude is provided.

Chapter 6 - The problem of predicting structural and dynamical behavior associated with thin smectic films, both deposited on a solid surface or stretched over an opening, when the temperature is slowly increased above the bulk transition temperature towards either the nematic or isotropic phases remains a very interesting one in the physics of condensed matter. A useful route in studies of structural and optical properties of thin smectic films is provided by a combination of statistical-mechanical theories, hydrodynamics of liquid crystal phases, and optical and calorimetric techniques. The authors believe that this chapter shows some useful routes not only for the further examining of the validity of theoretical description of thin smectic films, both deposited on a solid surface or stretched over an opening, but also for analyzing their structural, optical and dynamical properties.
Chapter 1

LUMINESCENCE STUDY OF II-VI-BASED THIN FILMS DEPOSITED BY CLOSE-SPACED VACUUM SUBLIMATION TECHNIQUE

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ABSTRACT

In this chapter the analysis of photoluminescence (PL) spectra of II-VI-based thin films (pure II-VI semiconductor compounds - CdTe, ZnTe,

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CdSe, Cd$_{1-x}$Zn$_x$Te ternary compound, CdS:Dy rare-earth element doped II-VI compound) at different substrate temperatures is performed. In all cases of studied samples they are deposited onto non-oriented substrates using the close-spaced vacuum sublimation technique (CSVS) which makes a possibility to obtain films with optimal crystalline and optical quality. The study of the PL spectra of the investigated films makes it possible to determine their optimal growth conditions in order to obtain the films of good optical quality. The obtained results are in good agreement with the structural investigations, which we have carried out earlier using the X-ray diffraction technique. In all cases of investigated samples on PL-spectra there were observed lines that correspond to the residual impurities, which are typical for II-VI compounds (Li, Na, Cu, P). Moreover there were observed an additional lines which may be caused by the presence of point defects in crystalline structure, donor-acceptor pairs recombination processes, phonon replicas, etc.

**Keywords**: photoluminescence, CdTe, ZnTe, CdSe, CdS:Dy, ternary compound

**INTRODUCTION**

Thin films of II–VI semiconductors are widely used in the design of a large number of high-performance electronic devices for modern optoelectronics. Furthermore, they are considered as the promising materials for nuclear radiation detectors, switching devices, light-emitting diodes (LEDs), etc. [1-2]. These semiconductors are also important for the production of polycrystalline thin-film solar photovoltaic cells where CdTe is used as an absorber layer [3]. In this case ZnTe can be used as back-contact material to improve the efficiency of $p$-CdTe solar cells [4-5]. It should be noted that semiconductor CdSe films with the energy of a direct band gap (BG) of about 1.75 eV at room temperature have $n$-type conductivity and high photosensitivity in the visible spectral range. Recently, CdTe, ZnTe and CdSe films have been intensively studied mainly because they can be used to develop a number of optoelectronic devices, namely photo-electrochemical solar cells, photo and gas detectors, high-performance thin film transistors, gamma-ray detectors, etc. [6–8].
addition, CdSe thin films can also be used as the absorber layers in the top of tandem solar cells and they are considered an important material for photovoltaic applications. This ability may be caused by a high absorption coefficient of CdSe films and their almost optimal BG energy for the coefficient of conversion of light absorption to electrical power.

Due to the high atomic number, high density and adjustable BG from 1.50 eV (CdTe) to 2.26 eV (ZnTe) [6] the single crystals of Cd$_{1-x}$Zn$_x$Te (CZT) ternary semiconductors are widely used for radiation detectors [9-12]. It should be noted that the presence of zinc atoms substantially increases the resistivity of CZT crystals and hence their performance as a detector [12]. Moreover, it can lead to a decrease in their crystalline quality due to lattice deformation [13-15]. Also, the non-uniformity of Zn distribution in the crystal is one of the key problems of their growth technologies [11-12, 16-17]. This is one of the reasons why for the most of CZT detectors the concentration of Zn atoms does not exceed 20% [11]. At the same time, the theoretical calculation shows the advantage of using CZT with concentration of Zn up to 80% [18]. The need in obtaining inexpensive and large-area uniform CZT layers for X-ray image detectors [19] leads to the use of thick films with the thickness of 30 mm [20-21] and more [19, 22-25] instead of bulk crystals.

In addition, CZT films are widely used in photovoltaic applications as a top absorber layer or as a contact layer in CIGS [26-28] and CdTe solar cells, respectively [29]. Moreover, the possibility of elaboration of graded BG solar cells based on CZT was also considered in Ref. [30].

One of the key problems of CZT films fabrication technology is the obtaining of high-quality layers with the pre-specified Zn concentration as well as its distribution even in the case of Zn-rich samples. Thus, the main objective is a comprehensive study of structural and optical properties of CZT thick films with different concentrations of Zn atoms and analysis their spatial distribution in order to obtain the thick films of high optical quality for the Zn concentrations of $x > 0.10$. 

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The electronic properties of semiconductor thin films can be also improved by the optimization of the technological conditions of their growth processing. Thus, CSVS technique application makes it possible to optimize the defects structure and, accordingly, the electronic properties of the films by observing their growth parameters such as substrate and evaporator temperatures. Besides, the CSVS is a simple and low-cost technique [31–33].

Another method for improving the physical properties of semiconductors is their doping by impurities [34-36]. It should be noted that rare-earth (RE) elements are characterized by specific features among impurity atoms. The most important of them is that RE elements can be considered as effective gettering agents for residual impurities in semiconductors [37–40]. Thus, in the semiconductor materials there is a “cleaning” effect that occurs due to the formation of the complex centers of RE elements with residual impurities, which becomes electrically non-active. In this case, the electronic properties of semiconductors are actually improved. Besides, RE elements may also form deep complex centers with participation of point intrinsic and impurity defects [41]. In case of III–V semiconductors they are isoelectronic impurities because the RE atoms are usually embedded in semiconductor materials in three-charge state. Therefore, till now, III-V semiconductors doped by RE are the most studied materials [39, 42–44]. It should be noted that three-charged RE ions in II–VI semiconductors are replaced two-charged cationic sites [45]. Thus, in this case the excessive free electrons are formed and they have a possibility to affect the electronic properties of II–VI semiconductor films. At present time, II–VI semiconductors, doped with RE elements, are not well-studied yet [46–49].

The measurements of low temperature photoluminescence (PL) spectra allow us to study the defect structure of according semiconductor materials [42, 50-51]. In this case the nature and energy levels of both the point intrinsic defects and the residual impurity atoms in these materials can be determined. It should be noted that the complex PL study of thin films allow us to determine the optical and crystalline quality of these semiconductor materials.
METHODS

The studied thin films, based on II-VI semiconductors, were deposited using close-spaced vacuum sublimation (CSVs) technique [1, 40, 43, 52-53]. A detailed description of the device for the deposition of II-VI thin films using this method is represented in Figure 1. The stoichiometric powder of materials is evaporated in an evaporator (1) with a molybdenum boat (2). In order to prevent vapor condensation the walls (4) were heated by the wall electric heater (3).

The vapor transport occurred in the cylindrical enclosed volume (5) at the temperature gradient between the evaporator and substrate (8). The substrate holder (6) with substrate electric heater (7) was pressed near the enclosed volume. The substrate was fixed at a distance of about 17 mm close to evaporator. The temperatures of evaporation and substrate were controlled using the thermal couples (9). The CSVs device is equipped with thermal shield (10) and is placed in vacuum chamber with the vacuum level of $P \sim 10^{-4}$ Pa.

Figure 1. Scheme of CSVs chamber: 1 - evaporator, 2 - molybdenum boat, 3 - walls heater, 4 - walls, 5 - enclosed volume, 6 - substrate holder, 7 - substrate heater, 8 - substrate, 9 - thermal couples, 10 - thermal shield [53].
The evaporator temperatures during the deposition of thin films of different semiconductors were the following: CdTe ($T_e = 873$ K), ZnTe ($T_e = 973$ K), CdSe ($T_e = 973$ K), CdS ($T_e = 1173$ K). The substrate temperatures $T_s$ were varied in the following ranges: CdTe ($T_s = 473$–$823$ K), ZnTe ($T_s = 573$–$873$ K), CdSe ($T_s = 473$–$873$ K), CdS ($T_s = 573$–$773$ K).

The CZT thick films were obtained by CSVS method analogously as in previous works [53-55]. Taking into account the ternary compound, the setup of films growth was equipped with two separated evaporators for CdTe and ZnTe materials.

The stoichiometric CdTe and ZnTe powders were placed independently into different evaporators without mixing. In order to obtain CZT films with different Zn concentration the mass ratio ($M_R$) between CdTe and ZnTe powders has been varied as the following values: 8, 4, 3 and 2 for CZT1, CZT2, CZT3 and CZT4 samples, respectively. The thick films of pure CdTe and ZnTe compounds were also obtained by CSVS method. The diameter of the samples was constant $d = 1.6$ cm. The substrate temperatures for both types of films were the same, namely, 673 K. At the same time the evaporator temperatures for CdTe and ZnTe were 893 and 973 K, respectively. The ultrasonically cleaned Mo-coated glass plates were used as substrates. In case of CdS:Dy films the stoichiometric powder of CdS doped by Dy as the initial material was used.

The PL spectra of CdTe, CdSe, ZnTe films had been measured using an SDL-1 grating spectrometer [33, 56-57]. An LGN-404 argon laser was used for excitation by the 488.8 nm line, together with an FEU-62 photomultiplier under the photon-counting mode. The excitation intensity was kept below 1.0 W/cm$^2$ to avoid sample thermal increase. The samples were mounted on the cold finger of a liquid-helium cryostat with variable-temperature ability. The accuracy of the measurements and temperature stabilization observed by the UTREKS system was kept at $\Delta T = \pm 0.01$ K. The exciting beam was modulated using a mechanical chopper and the luminescence signal was measured using a phase-sensitive lock-in detection system. The spectral resolution of the system was kept of the order of (1–2) cm$^{-1}$ (0.1–0.2 meV).
The PL measurements of CZT films were performed using a standard setup with a fully automated 1-m focal length monochromator. The excitation was provided by the wavelength of 457 nm (2.71 eV) CW diode pumped solid state laser. The diameter of the laser spot was close to 1 mm. The excitation intensity was reduced to 9 W/cm² using neutral glass filters. The PL spectra were dispersed using a blazed at 750 nm holographic grating of 1200 mm⁻¹, achieving the spectral dispersion of 0.8 nm/mm. The PL spectra were obtained by a thermal-and-electrically cooled, high efficiency extended-red multi-alkali cathode photomultiplier operating in the photon counting regime. The sample temperature might be varied from room temperature (300 K) down to 3.6 K using a closed cycle helium optical cryostat.

The PL measurements of CdS:Dy films were performed using an MAYA 2000-pro spectrometer (Ocean Optics) with a variable temperature liquid-helium cryostat. The temperature stabilization by the UTREKS system was similar to the previous samples. The PL spectra were excited by LED with λ = 385 nm and the power of 100 mW. Besides, the PL spectra were also measured with an SDL-1 grating spectrometer [58] using an LGN-404 argon laser for excitation by 488.8 nm line for the measurements of the excitonic emission.

**RESULTS**

**CdTe Films**

Figure 2 shows the PL spectra of the CdTe polycrystalline films at 4.5 K for the samples deposited at different substrate temperatures. Curves 1, 2, 3 and 4 correspond to the CdTe films obtained at T, which is equal to 473 K, 523 K, 623 K and 823 K, respectively. The I₁-line of the highest intensity in the PL spectra of CdTe films is observed at energy of 1.545 eV. Since the BG of CdTe at 4.5 K is 1.606 eV, this line can be caused by the emission with the participation of free electrons and the shallow acceptor level with the energy of about 60 meV. In this case, the
recombination of free electrons with the acceptor holes took place. According to Ref. [59] the acceptor level may be caused by the presence of Na or Li residual impurities in CdTe crystals.

![Graph showing PL spectra of CdTe thin films deposited by CSVVS technique](image)

**Figure 2.** Low-temperature \((T = 4.5 \text{ K})\) PL spectra of CdTe thin films deposited by CSVVS technique at the following technological conditions: \(T_e = 873 \text{ K}\); curves 1–4 for \(T_s = 473, 573, 623\) and 823 K, respectively [78].

These impurity atoms are typical residual impurities for II–VI compounds [60]. The low-intensity lines, observed on the long-wavelength range of the \(I_1\)-line correspond to the 1LO- and 2LO-phonon replicas of the observed line.

At the same time, these sharp lines may be caused by the recombination of the donor electrons and the acceptor holes with the energy of \(E_c = 0.010 \text{ eV}\) and \(E_v = 0.050 \text{ eV}\), respectively. In this case, the acceptor level corresponds to the single charged cadmium vacancies [33, 59]. Additional information about the nature of intrinsic defects and residual impurities may be obtained as a result of the PL spectra study in the excitonic region.

As it can be seen from Figure 2, the low-intensity line at 1.586 eV is observed on the short-wavelength range of the \(I_1\)-line. The energy position of this line demonstrates the appearance of the recombination of the excitons bound with acceptors, i.e., the \(A^0X\)-line [33, 59]. It confirms the ability to observe the excitonic line in the PL spectra and indicates a good
optical quality of CdTe films. Moreover, the presence of the A°X-line shows that these films have a p-type conductivity. Thus, we can expect that the concentration of the donor centers in CdTe films is negligible. The appearance of the A°X-line in the PL spectra of these films may be only due to the presence of the acceptor level with energy of $E_\alpha \approx 0.060$ eV which may be caused by the Na(Li) residual impurity. It should be noted, that the acceptor level with this energy was observed in CdTe crystals using the time-resolved photoelectric spectroscopy technique [61].

Analysis of the observed PL spectra also allowed us to observe a broad band in the energy region of (1.380–1.500) eV. On the one hand, this broad band may be caused by the recombination of the donor–acceptor pairs (DAP) with the participation of the acceptor complexes. On the other hand, the presence of the 1.470 eV emission band is caused by the extended defects typical to dislocations [62–64]. Therefore, the PL intensity in this spectral range can be used as a measure to evaluate the relative dislocation density. It should be noted, that the acceptor complex includes a double-charged cadmium vacancies ($V^2_{-Cd}$) and a single-ionized donors ($D^+$). The ionized donors can be the residual impurities of group III atoms, positioned on cationic sites [51], which also are present in pure cadmium telluride.

As it can be seen from Figure 2, the highest intensity of the broad band corresponds to the films obtained at $T_s = 473$ K. In the case of the films obtained at $T_s = 623$ K the intensity of broad band is negligible. This indicates that in the case of CdTe films obtained under the above-mentioned growth condition the dislocation density is small. This result is in accordance with the data obtained in Ref. [32], where the minima of the total dislocations density in CdTe films corresponds to the substrate temperature $T_s = 623$ K. It has been shown in Ref. [32] that the dislocations are mainly located on the boundaries of the coherent scattering domains (CSD). It can be seen from Figure 2 that the intensity of broad PL band of the CdTe films at $T_s = 823$ K is considerable. Therefore, the dislocation density in these films is larger than in the case of films grown at $T_s = 623$ K. In addition, the concentrations of stacking faults (SF) dislocations in thin films obtained at $T_i = 823$ K is four times more than for the CdTe films grown at $T_s = 623$ K [32].
ZnTe Films

Figure 3 shows the PL spectra of ZnTe films grown at different substrate temperatures. The narrow I_X-line at 2.384 eV, which is available in all spectra of the samples grown at different T_s, is associated with the recombination of free excitons [65]. The I_A1-line at 2.375 eV observed for the sample deposited at T_s = 573 K is caused by the radiative recombination of excitonic emission bound to neutral shallow acceptor (namely Cu, Li or Na) [52-53]. In this case the exciton binding energy value of the acceptor bound excitons reaches to 8.4 meV. The emission in the spectral range 2.250–2.330 eV is associated with the DAP recombination [53, 66]. The I_B-line at 2.330 eV corresponds to zero-phonon transition followed at a lower energy by its longitudinal-optical (LO) phonon replicas at 2.304 eV (1LO) and 2.278 eV (2LO).

It has been shown [65] that in this case the donor and acceptor ionization energies are 22 meV and 51 meV, respectively.

Figure 3. Low-temperature (T = 4.5 K) PL spectra of ZnTe thin films obtained by CSVS technique under the following deposition conditions: T_e = 973 K; curves 1–5 correspond to T_s = 573, 623, 673, 723 and 873 K, respectively [78].
It is considered that the former level corresponds to Cl$_{Te}$ donor [65], while the acceptor level can be associated with the presence of zinc vacancies V$_{Zn}$. Another sharp I$_{Cu}$-band at 2.245 eV is ascribed to free-to-band transitions with the participation of a Cu$_{Zn}$ acceptor level with the binding energy of $E_A = 149$ meV [52]. Here, the bound exciton (BE) energy of ZnTe at low temperature corresponds to 2.394 eV [53]. The low intensity of I$_{Y2}$-band at the energy 2.159 eV is also observed in the PL spectra of the ZnTe sample grown at $T_s = 573$ K. The energy position of this band is close to Y$_2$-band observed earlier by Naumov et al. in the case of the heteroepitaxial ZnTe layer at $E = 2.147$ eV [67].

This band is associated with the structural defects (dislocations), which may influence on the electronic properties of the ZnTe-based materials [68]. As a result, of the presence of these defects, the electric and elastic strain fields are produced in ZnTe layers. Such fields can shift the existing energy levels caused by the intrinsic defects and residual impurity atoms. Usually, the PL spectra of ZnTe show Y$_1$- and Y$_2$-bands, where the first band is related to the structural defects created at the grain boundary or zones of high dislocation density [68]. For the film deposition at $T_s = 573$ K, the Y$_2$-band was not observed, and therefore, these structural defects in this sample are not formed. It should be noted that the presence of dislocations and stacking fault defects into the crystallites of ZnTe and CdTe films was observed using the X-ray methods in Refs. [32, 69-70].

The ZnTe films grown at $T_s = 623$ K exhibits a strong Y$_2$-band emission at 2.1557 eV and relatively weak exciton-relative lines at 2.381 eV (I$_X$), 2.370 eV (I$_{A2}$), and 2.363 eV (I$_{A3}$). The I$_{A2}$-peak is attributed to the emission of excitons bound to neutral acceptor due to the residual impurities such as Li, Na or P [71]. The exciton binding energy is 11.4 meV and 18.6 meV for I$_{A2}$-lines and I$_{A3}$-lines, respectively. According to Ref. [66], the appearance of I$_{A3}$-lines is attributed to an acceptor complex, namely, a donor associated to a substitutional IV-group atom (C or Si) on a Te site or a Zn vacancy. Since, this line is also observed in the group of samples prepared under Zn-rich ZnTe conditions, the first notation is more likely [66]. Thus, this line is due to the emission of excitons bound to a carbon atom on a Te site, i.e., C$_{Te}$ acceptor. As it could be seen in Figure 3,
in the excitonic energy region of the PL spectra, three shoulders at 2.360 (I_{A4}) eV, 2.350 eV (I_{A5}), and 2.344 eV were also observed. The line at 2.344 eV corresponds to 1LO-phonon replica of I_{A2}-line, while I_{A4}- and I_{A5}-lines may be connected with other neutral acceptors of unknown nature. In particular, these lines may be ascribed to the presence of Cl-related centres, namely to a complex composed of Zn vacancy and Cl on the Te site (V_{Zn–Cl_{Te}}) [65-66]. The exciton binding energies associated with these acceptor centres are 20.9 meV and 30.7 meV, respectively. The line at 2.333 eV (I_{DAP}), which is attributed to the DAP recombination, followed by 1LO- and 2LO-phonon replicas.

At $T_s = 673$ K, an intense I$_{A2}$-line appears in the PL spectra at 2.371 eV to the weak free exciton emission (I$_X$-line) at 2.383 eV. The I$_{A2}$-line, ascribed to the radiative recombination of an excitonic emission bound to neutral shallow acceptor, is significantly dominant in the PL spectra. The DAP emission bands also appear in the spectra energy range of 2.324 eV, 2.298 eV, and 2.272 eV. The last two bands are connected to the 1LO- and 2LO-phonon replicas of the line at 2.324 eV. In this spectrum, there can also be observed a Y$_2$-band followed by its LO-phonon replica. Another I$_{Y1}$-band at 2.191 eV may also be caused by the structural defects, like dislocations. This band is observed for the films grown at different $T_s$, but its energy position depends on the films growth conditions and corresponds to the energy region of $E = 2.191–2.213$ eV.

A further increasing of the substrate temperature to $T_s = 723$ K leads to a strong increase of the intensity of Y$_2$-band at 2.153 eV. This effect indicates a significant increasing of the density of dislocations in the layer. The 1LO-phonon replicas of this band at 2.130 eV were also observed in the spectrum. Similar to the spectrum obtained for the samples grown at $T_s = 673$ K, in this case the intensive I$_{A2}$-line at 2.372 eV is also observed, which has been attributed to an exciton bound to neutral acceptor. This acceptor may be due to the residual impurities such as Li, Na or P [71]. It should be noted, that some mismatch in energy for the I$_{A2}$-line for films grown at different $T_s$ may be caused by the influence of dislocations on the energy position of the impurity levels. The PL bands observed at (2.356–2.229) eV are associated with the DAP recombination and their LO-
phonon replicas. The most intensive $I_{A2}$-line for the film grown at $T_s = 873$ K appears at 2.370 eV and is followed by 1LO-phonon replicas at 2.345 eV. The shoulder on the low-energy edge of the $I_{A2}$-line appears at 2.363 eV, which corresponds to the $I_{A3}$-line similar to the spectrum obtained for the sample grown at $T_s = 623$ K. The presence of the $I_{A3}$-line confirms the occurrence of $C_{Te-D_{Zn}}$ complex in the films. This line is followed by the 1LO- and 2LO-phonon replicas at 2.336 eV and 2.231 eV, respectively. Along with the band-edge region emission, other PL bands can be identified at 2.153 eV and 2.213 eV, which occur due to the dislocations presence in the films. The weak $I_{O}$-band at 2.054 eV, which is observed in the PL spectra for the film grown at $T_s = 873$ K, is associated with the presence of oxygen, mainly, $O_{Te}$-centres and their complexes [72]. Since this band appears in the film grown at higher substrate temperatures, it indicates that the oxygen concentration strongly depends on the vacuum conditions of the film deposition. In this case, the oxygen concentration is low for the different growth conditions.

**CdSe Films**

Figure 4 shows the PL spectra of the CdSe polycrystalline films at 4.5 K for the samples obtained at different $T_s$ (curves 1–4 correspond to the films obtained at $T_s$ equal to 893 K, 773 K, 473 K and 373 K, respectively. As it can be seen from Figure 4 (curve 1), relatively broad group of PL bands in the spectral range (1.65–1.75) eV are observed. The highest intense $I_{DAP1}$-line at 1.736 eV is observed, which can be caused by the free-to-band or band-to-band optical transitions. It should be noted, that there are other lines with the energy of 1.710 eV, 1.683 eV and 1.657 eV corresponding to the 1LO-, 2LO- and 3LO- phonon replicas of the $I_{DAP1}$-line. The presence of these lines is characteristic of the bound-to-bound transitions with the participation of DAPs [73-75]. In this case the energy of the emitted light, which is associated with the zero-phonon $I_{DAP1}$-line, is given by the following equation [76-77]:

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where $E_g$ is the BG energy; $E_D$ and $E_A$ are the ionization energies of donor and acceptor centers, respectively; $e^2/\varepsilon_0 \varepsilon_R$ is the Coulomb energy of the two ionized impurity centers (donor and acceptor pairs) separated by distance $R$; $\varepsilon_0 \varepsilon$ is the dielectric constant of the investigated material; $e$ is the elementary charge. The ionization energy of shallow acceptors in CdSe is 109 meV [53]. This acceptor center is associated with Li or Na substituted into the cation sites, i.e., Li$_{\text{Cd}}$ or Na$_{\text{Cd}}$ centers. These impurity atoms are the typical residual impurities in II–VI films [78]. The ionization energy of shallow donor centers, which can be caused with the interstitial Li atoms (Li$_i$), is 19.0 meV [79]. Using in the Eq. (1) the values of 109 meV and 19.0 meV for the acceptor and donor binding energies, respectively, 1.841 eV [69] for the BG energy and 10.0 [80] for the dielectric constant the value $R_1 = 6.3$ nm was obtained.

Figure 4. Low-temperature ($T = 4.5$ K) PL spectra of CdSe thin films grown by the CSVVS technique under the following deposition conditions: $T_e = 973$ K; curves 1–4 correspond to $T_e = 873, 773, 473$ and 373 K, respectively [87].
As it can be seen from Figure 4, the bends at 1.727, 1.701 and 1.675 eV are observed on the long-wavelength wing of the I_{DAP1}-line and its LO-phonon replicas. They can be also caused by the DAP2 recombination process which arises from another set of donor or acceptor levels with the energies close to the conduction or the valence bands. It should be noted that the presence of P atoms in CdSe induces the appearance of the shallow acceptor level with the energy $E_V = 0.083$ eV [81].

Thus, it may be possible that the DAP2 recombination with the participation of this acceptor center took place. Usually, in this case the band at 1.753 eV appears in PL spectrum of CdSe containing P atoms [53]. As it can be seen from Figure 4, the bend at 1.753 eV is observed in the investigated spectrum which may be identified with the I_{DAP2}-zero-phonon line. Other lines at 1.727 eV, 1.701, and 1.675 eV correspond to 1LO-, 2LO-, and 3LO- phonon replicas of this line. The observation of this emission allows us to indicate the presence of a small concentration of the residual P atoms in CdSe film.

Usually, CdSe has excess Se vacancies over Cd vacancies and thus exhibits deviation from stoichiometry. Therefore, it is expected that excess Cd in the CdSe film produces Se vacancies and/or Cd interstitial (Cd_i), which induces the appearance of donors. The donor level for the DAP2 recombination may corresponds to the interstitial Cd_i atoms with the energy of $E_c = 0.014$ eV [81]. According to Eq. (1), and taking into account the energy of the acceptor center which is caused by the presence of P atom ($E_V = 0.083$ eV) and the energy of the donor centers ($E_c = 0.014$ eV), it is possible to get for DAP2 the values of $R_2$ to be 15.2 nm.

In addition to the shallow donor and acceptor levels CdSe films can also contain the deeper levels. Usually, the presence of these states leads to the appearance of PL bands located in the long-wavelength spectral region at 1.500 eV and 1.330 eV, which are associated with the Ag and Cu residual atoms, respectively [75]. As it can be seen from Figure 4, the PL bands in this spectral region don't appear. This indicates the absence of these impurity atoms in the investigated CdSe films. Other deep donor levels are due to the presence of Se vacancies with the energies $E_c = 0.220$ eV and $E_c = 0.400$ eV [82]. There are also deep donor levels with the
following energies: $E_c = 0.120$ eV and $E_c = 0.280$ eV, they are the result of the structural defects introduced during the growth process [68]. As it can be seen from the PL spectrum, presented in Figure 4, these intrinsic defects are also absent in the investigated CdSe films.

In addition to PL bands caused by the participation of point intrinsic defects and residual impurities in the recombination process, the emission associated with extended defects like dislocations may arises in semiconductor polycrystalline films [83-84]. The appearance of dislocations in CdSe films can be caused by the appearance of microstresses during the film deposition. The transformation of the low-temperature PL spectra of CdSe crystals during their plastic deformations was observed in Ref. [58]. In particular, the emergence of the PL bands at 1.765 eV and 1.792 eV is caused by the presence of the motion of dislocations in the prismatic slip and the dislocations slip in the basic plane, respectively [58].

As it can be also seen from Figure 4 (curve 1), PL spectrum of CdSe films deposited at $T_s = 873$ K shows only the structure of low intensity in the spectral region 1.750 – 1.810 eV. It is caused by the fact that the dislocation density in CdSe films deposited at this temperature is relatively small. The obtained results correlate with the microstress calculations of the investigated films, since the microstress level for the films grown at $T_s = 873$ K is minimal in comparison with the films obtained at lower substrate temperatures.

More information on the presence and nature of intrinsic defects and residual impurities can be obtained from the analysis of the PL spectra in the exciton region. As it can be seen from Figure 4 (curve 1), the sharp line of high intensity is observed in the short-wavelength region of PL spectrum at 1.822 eV. The energy position of this line indicates the appearance of the recombination of donor bound excitons, i.e., the presence of the $D^0X$-line which is characteristic for CdSe single crystals of $n$-type [76]. In this case the binding energy of bound exciton equals to 3.4 meV because the energy of free exciton in CdSe single crystals is 1.825 eV [33]. Earlier, this PL line is also observed in the CdSe films deposited by the laser ablation technique on a sapphire substrate [33]. In this case the intensity of $D^0X$-line was very small in comparison with the intensity of
emission located at 1.750 eV which is caused by DAP recombination involving shallow acceptor levels. It should be noted, that it’s full width at half maximum (FWHM) was about 10 meV [33]. In our case the FWHM of the D0X-line is more than three times smaller and corresponds to about 3.0 meV. The fact that we are able to observe the sharp intensive excitonic line in the PL spectrum indicates that the CdSe films are of high optical quality. Furthermore, the presence of the D0X-line shows that the films, obtained at $T_r = 873$ K, are of $n$-type conductivity. Thus, it leads us to expect that the concentration of the neutral acceptor centers in the CdSe films is negligible. The appearance of the D0X-line in the PL spectrum of the film may be the result of the presence of the donor levels caused by the Cd$_i$ centers or Na(Li) interstitial (Na(Li)), residual impurity. It should be noted, that these donor centres were observed in bulk CdSe [75]. Other narrow lines of small intensity close to D0X-line at 1.817 eV and 1.813 eV were also observed. They can be associated with the radiative recombination of excitonic emission bound to shallow acceptors (I$_1$-line) caused by the presence of Li, Na or Cu atoms. First line is in a good agreement with the energy of I$_1$-line which appear in CdSe single crystals lightly doped by Li or Na atoms [75]. The presence of P atoms in CdSe induces the appearance in PL spectrum of I$_1$-line at 1.819 eV [75]. As it can be seen from Figure 4 this line is not practically observed in PL spectrum of CdSe films deposited at $T_r = 873$ K.

In the case of the films obtained at $T_r = 773$ K (Figure 4, curve 2) the intensity of D0X-line at 1.824 eV is insignificant. This indicates that the donor concentration for CdSe films deposited at $T_r = 773$ K is considerably smaller than for the film obtained at $T_r = 873$ K. It should be noted, that in this case the intensity of A0X-line at 1.816 eV is comparable with that for D0X-line. According to Ref. [85] the decreasing of the donor concentration may be caused by increasing of the dislocations concentration for the film obtained at $T_r = 773$ K. At the same time, increasing of the intensities of PL lines at 1.804 eV and 1.788 eV, which can be associated with unknown acceptors, is observed. In this case, exciton-binding energies correspond to 21.1 meV and 37.0 meV, respectively. So, taking into account the fact that there is correlation between the acceptor ionization energy $E_A$ and the
exciton binding energy $E_{ex}$, namely $E_{ex} = 0.1 \cdot E_A$ [86] it allows us a possibility to estimate the value of $E_A$. In our case it was found $E_{A1} = 0.211$ eV and $E_{A2} = 0.370$ eV, respectively. The appearance of these acceptor levels may be caused by increase the dislocation density, since it was found that the microstress level increases from $0.1 \cdot 10^{-3}$ to $4.0 \cdot 10^{-3}$ for CdSe films deposited at $T_s = 873$ K and $T_s = 773$ K, respectively. The high intensity PL bands at 1.733 eV and 1.708 eV are also observed which corresponds to zero-phonon $I_{DAP1}$-line and its 1LO-phonon replica. There are also 2LO-phonon and 3LO-phonon replicas located at 1.681 eV and 1.655 eV, respectively. It is evident that the long-wavelength shift of the $I_{DAP1}$-line is observed in comparison with the CdSe films obtained at $T_s = 873$ K. It may be caused by increase of the distance $R_1$ between donor–acceptor pairs of DAP1 type. In this case using Eq. (1) the value $R_1 = 7.0$ nm was estimated. This indicates that the concentration of Li(Na) residual impurities for the films obtained at $T_s = 773$ K is significantly smaller than that for deposited at $T_s = 873$ K. This fact may be due to a higher diffusion of impurity atoms from the charge container at $T_s = 873$ K.

**CZT Films**

The low-temperature PL measurements [58, 68, 87] allow us to determine the nature and energy levels of both the intrinsic defects and the residual impurities as well as the relative concentration of dislocations in semiconductor materials [40, 86]. In this case, the excitonic PL lines are very sensitive to a wide-range of defects in semiconductors. The excitation energy of free excitons (bound electron-hole pairs) is slightly lesser than the BG energy $E_g$ of semiconductors. Usually, intensive PL lines caused by the BE appear in the low-temperature PL spectra for semiconductors of high optical quality. It should be noted, that the energy of BE is less than the energy of free excitons by the amount equal to its binding energy and is slightly depends on the nature of the impurity or intrinsic defects. So, the energy position of the BE allows us to determine the nature of the defects participating in the formation of the excitonic complexes.
In the case of semiconductor alloys, crystal potential field fluctuations (CPFFs) due to the random distribution of alloy components occur [88-90]. Excitonic states are localized at these fluctuations and the low-energy tails in the density of excitonic states arise [91-92]. The energy position of the localized excitons (LE) is some shifted to the low-energy region relative to the energy of free excitons by the amount corresponding to the energy about 1/2 of the FWHM of the LE band [93]. Taking into account the binding energy of free exciton for CdTe and ZnTe crystals, which corresponds to about 10 meV, we can determine the BG of the semiconductor films.

Earlier, the formation of LE associated with the presence of strong inhomogeneity in the distribution of component composition for semiconductor films was not considered. Further analysis of the PL spectra, presented below, takes into account the presence in CZT semiconductor films both the bound and localized excitons.

Figure 5. PL spectra of the samples: CdTe (a), CZT1 (b), CZT2 (c), CZT3 (d), CZT4 (e) and ZnTe (f) measured at 4.5 K [94].
PL spectra of the films obtained for CdTe, ZnTe and CZT1-CZT4 samples are presented in Figure 5. In this case, CdTe and ZnTe samples were obtained by CSVS method under growth conditions similar to CZT films. It should be noted, that these CdTe and ZnTe materials were used for the deposition of the films.

PL spectra for CdTe thick film are shown in Figure 5a. Analysis of the observed PL spectrum reveals intensive excitonic emission at $E = 1.591$ eV, which is associated with the recombination of excitons bound on a neutral acceptor ($A^0X$-line) with the participation of cadmium vacancy ($V_{Cd}$) [95]. Since the binding energy of BE ($A^0X$-line) is equal ~5 meV [53], the BG of CdTe film is equal to 1.606 eV that coincides with the corresponding energy for bulk CdTe crystal. The presence of intensive excitonic line indicates a fairly good optical quality of the investigated semiconductor films [96]. The PL band at 1.547 eV is caused by the recombination of free electrons and acceptor centers ((e-A)-transition) [9, 22].

Thus, knowing the energy of this PL line and the value of $E_g (4.5 \text{ K}) = 1.606$ eV for CdTe film, we can determine the energy of the acceptor level as it was done in Ref. [40]. Thus, we obtain the energy of the acceptor center associated with (e-A)-transition, namely $E_A = 59.0$ meV. This value is close to the acceptor energy of Li or Na (58.0 meV and 58.7 meV, respectively) [59]. The energy of both exciton acceptor complexes is about 1.589 eV [59]. This indicates that $A^0X$-line is complex and consists of the overlapping emission of several exciton acceptor complexes. However, the intensity of $A^0X$-line is mainly determined by the emission from the exciton complex involving cadmium vacancy.

The broad band at 1.495 eV can be caused by the DAP recombination with the participation of complexes ($V_{Cd}$-D), where D is residual donor (atoms of III or VII group metals) and $V_{Cd}$ is a cadmium vacancy. The difference between the value of $E_g = 1.606$ eV ($T = 4.5$ K) for CdTe and the peak position of the band is equal to 111 meV. The energy of the shallow donor in CdTe is equal to 14 meV [97]. Using these parameters accordingly to the procedure described in Ref. [54] we obtained the energy of the acceptor center, which participates in the DAP emission, which
value was 117 meV. This energy is close to the energy of Ag acceptor center (107 meV) [59]. In the PL spectra, another intensive PL band at 1.477 eV and its 1LO- and 2LO- phonons replicas are observed at 1.456 eV and 1.435 eV, respectively. In this case, the energy of LO-phonon is about 21 meV. In according to the data presented in Refs. [98-101], the PL band at 1.477 eV is due to Y-center which corresponds to the excitons bound on Te glide dislocations. Thus, the intensity of the Y band may be used as an indicator of the presence of dislocations in CdTe.

The intensive exciton emission line at 1.653 eV is observed in the PL spectra for CZT (CZT1 sample), which is shown in Figure 5b. This PL line is generally caused by the recombination of excitons bound on a neutral acceptor (A^0X-line). It should be noted, that this line has a high-energy asymmetry that can be caused by some overlapping of A^0X-line with the lines of localized excitons appearing on its high-energy wing. Another line observed at 1.619 eV is due to the (e-A)-transition with the participation of the cadmium vacancy acceptor with the energy equal to 49.0 meV. The FWHM of this line is smaller than for CdTe sample. We think that in the latter case other acceptors with different ionization energies are involved in these optical transitions. This may be the residual impurities such as Li, Na, N and P with the energies of 58.0, 58.7, 56.0 and 68.2 meV, respectively [59]. As it can be seen from Figure 5b 1LO-phonon replica of (e-A)-transition is observed at 1.597 eV. Other very broad PL-band at 1.497 eV corresponds to so-called D PL band, which is caused by the presence of point and extended defects of dislocation type as well as microstrains in the films [99, 102]. It is found that the value of $E_g$ for CZT1 sample is equal to 1.668 eV at $T = 4.5$ K.

On Figure 5c the PL spectrum of CZT2 sample is shown. Similar to the previous film sample, the most intensive line is the exciton line at 1.820 eV. It should be noted, that its FWHM is equal to 24 meV, i.e., practically coincides with the similar value for CZT1 sample (23 meV). It is obvious that the rising of Zn concentration above $x = 0.10$ leads to the increasing of the contribution of the LE. Thus, for CZT2 sample, the emission of the LE is dominant in the PL spectrum. Taking into account the energy value of 1/2 FWHM which is equal of 12 meV for the LE we
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determine the BG for CZT2 sample which corresponds to 1.842 eV. The PL spectrum also includes other broad bands at 1.778, 1.657 and 1.593 eV. The first band may be caused by (e-A)-transition, where the acceptor energy is equal to 64 meV and can correspond to the ionization energy of residual impurities (Li, Na and P) [59]. It is obvious that the PL bands at 1.657 and 1.593 eV correspond to the emission of DAP with the participation of A-centers and D-band associated with the presence of dislocations.

For CZT3 sample, the high-energy PL line at 1.974 eV is shown on Figure 5d, which also corresponds to the recombination of LE. Taking into account the energy value of 1/2 FWHM for this exciton line (12 meV), we can determine the value $E_g$, which is equal to 1.996 eV. Another PL band at 1.921 eV may be caused by DAP recombination with participation of donor and acceptor centers with the energies of 14 meV and 61 meV, respectively. The last energy is close to the energy of the Li or Na acceptors. The broad PL bands at 1.872 and 1.817 eV correspond to the DAP recombination and the emission of Y-band, respectively. Therefore, it is expected that the energy of acceptor center is about 110 meV, which is close to the energy of Ag acceptor center (107 meV) [59].

On Figure 5e the PL spectrum for CZT4 sample with the highest concentration of zinc atoms is shown. In this spectrum, the emission exhibits in the spectral region, which is typical for CdTe film. Particularly, the line at 1.585 eV is very close to the energy position of (A^0X)-line in CdTe. Other line at 1.546 eV may be caused by (e-A)-transition. The emission at 1.495 eV also coincides with the recombination of DAP which is very similar to CdTe. The broadening of these lines is caused by the presence of high concentration of microstrains in the investigated sample. This is supported by the presence of a broad band at 1.796 eV, which is most likely related to the emission with the participation of various extended defects, especially dislocations. In the high-energy spectral range the blurred PL band is observed at the energy of about 2.100 eV. This band can be determined as strongly broadened line of LE with the value of 1/2 FWHM, approximately 40 meV. Thus, the BG for Zn-rich region film of CZT4 sample can be equal to about 2.150 meV.
The line with the highest energy at 2.365 eV for ZnTe sample shown on Figure 5f, corresponds to A0X-line and is caused by the zinc vacancy acceptor exciton complex [78]. The energy position of free exciton in ZnTe films corresponds to 2.384 eV [78]. Since the binding energy of free exciton is 11 meV, the BG of ZnTe film is equal of 2.395 eV. The most intensive line at 2.317 eV is caused by the emission of DAPs and is the zero-phonon line. Other lines observed on the long-wavelength part of the spectrum at 2.291 eV, 2.265 eV, 2.238 eV, 2.213 eV and 2.186 eV are due to 1LO-, 2LO-, 3LO-, 4LO and 5LO-phonon replicas of the line at energy of 2.317 eV. The broad band at 1.622 eV may be caused by the emission with participation of deep impurity level.

**CdS:Dy Films**

Figure 6 shows PL spectra of the CdS polycrystalline films doped with Dy at 4.5 K for the samples obtained at different T (curves a–c correspond to 573, 623 and 673 K, respectively). As it can be seen from Figure 6a (sample 1), the group of relatively broad PL bands in the spectral range (2.250–2.500) eV are observed. The highest intensity of the band at 2.406 eV (G-band) can be caused by the free-to-band or band-to-band optical transitions. It should be noted, that other lines at 2.375 eV, 2.337 eV, 2.299 eV and 2.261 eV are actually observed, and their positions correspond to 1LO-, 2LO-, 3LO- and 4LO-phonon replicas of the G-band. In this case, the average energy of LO-phonon corresponds to 37.2 meV, which is close to the value of the energy of LO-phonon in bulk CdS [103]. It should be noted that the maximum of the G-band is somewhat broader in comparison with the similar maxima presented in Figure 6b and Figure 6c for the samples 2 and 3, respectively. This effect may be connected with the overlapping of two bands which have approximately equal intensity. As can been seen from the curve presented in Figure 6a, other PL band can be located at the energy of 2.413 eV. The analysis of the shape of 1LO-, 2LO and 3LO-phonon replicas shows that there are two bands which appear as bends on the long-wavelength edges of these phonon replicas at the
energies 2.368 eV, 2.330 eV and 2.292 eV, respectively. Thus, a careful analysis of the shape of the PL spectrum indicates the presence of two zero-phonons (ZP) bands at the energies of 2.413 eV (ZP1) and 2.406 eV (ZP2) and their LO-phonon replicas. Thus, the PL bands at 2.375 eV, 2.337 eV, 2.299 eV and 2.261 are the phonon replicas of ZP1 band. At the same time, the PL-bands at 2.368 eV, 2.330 eV and 2.292 eV are the phonon replicas of ZP2 band, as shown in Figure 6a.

Figure 6. PL spectra of CdS:Dy thin films deposited at the following deposition conditions: $T_e = 1173$ K, $T_s = 573$ K (a), $623$ K (b) and $673$ K (c) at 4.5 K. Curves 1 and 2 correspond to the PL and exciton reflection spectra, respectively [105].
Earlier, it was found that in the above mentioned spectral range (so-called “green” range) for CdS bulk crystals and thin films, two PL-bands were observed at the energies ranges of (2.410–2.417) eV and (2.398–2.405) eV, which were associated with the (e-A) and DAPs optical transitions, respectively [103–108]. Since the LO-phonon replicas for (e-A)-transitions have higher intensity than for the bound-to-bound transitions, the value of electron-phonon interaction in the former case is significantly greater than in the latter one. We may to assume that the ZP1 band, which we observed, is caused by (e-A)-transitions. Thus, the energy position of the ZP1 band makes it possible to determine the ionization energy of the acceptor level. According to [9, 109–110] the energy of (e-A)-transition can be presented by the following equation:

\[ E(e-A) = E_g - E_A + \frac{1}{2}kT, \] (2)

where \( E_g \) is the BG and \( E_A \) is the acceptor energy. The value \( \frac{1}{2}kT \) determines the kinetic energy of free electrons near the bottom of the conduction band. At the low temperatures (4.5 K) this value is equal to 0.4 meV.

The analysis of the PL spectra in the exciton region allows us to determine the BG of the films. As can be seen from Figure 6 for the investigated thin films, the exciton lines are observed both in the PL and reflection spectra at low temperatures. It should be noted that the energy position of the free excitons, which appears in the reflection spectrum, allows us to determine the energy of the BG for CdS:Dy films. The difference between these energies corresponds to the binding energy of free excitons, which equals to 28 meV [111]. Therefore, the BG of the CdS:Dy thin film (sample 1) corresponds to the energy of free exciton labelled as A (2.554 eV) plus the binding energy of exciton (0.028 meV), i.e., 2.582 eV. It should be noted, that this energy practically coincides with the respective value for bulk CdS crystals at low temperature (4.5 K), which equals to 2.583 eV [112]. Then, using the Eq. (2) we obtain the energy of the acceptor center, which is associated with (e-A)-transition, namely \( E_A = 169 \) meV. This value is practically coincides with the acceptor
energies of Li(Na) impurities atoms (165 meV and 169 meV, respectively) [108, 112].

Another ZP2 band is due to the bound-to-bound transitions with the participation of DAP [44, 104, 113]. In this case, the energy of the emitted light, which is associated with the ZP2 band, is given by the Eq. (1).

As it was established above, the ionization energy of shallow acceptors in CdS is 169 meV. This acceptor center is associated with Na substituted into the cation sites, i.e., NaCd centers. This impurity atom is the typical residual impurity in II–VI compounds [51, 113].

Usually, CdS has a higher number of S vacancies than Cd vacancies and thus exhibits deviation from stoichiometry [114-116]. Therefore, it is expected that excess of Cd in the CdS film produces S vacancies and/or Cd interstitial (Cd$_i$), which induce the appearance of donors. The ionization energy of shallow donor centers in CdS is about 30 meV [103, 107]. The donor centers having the similar energy are usually observed in optical and photoelectric studies of CdS bulk crystal and polycrystalline thin films [117-119]. Thus, for Eq. (1), we used the BG energy of 2.582 eV, the dielectric constant of 8.9, the acceptor and donor binding energies of 169 meV and 30 meV, respectively. As the result, the $R_1 = 7.05$ nm was obtained.

In Figure 6b and Figure 6c the PL spectra for other films samples are presented. In particular, Figure 6b corresponds to the CdS thin films obtained at $T_s = 623$ K. In this case, the PL band at 2.411 eV is due to the zero-phonon band, which is associated with (e-A)-transition, i.e., ZP1 band. As can be seen from Figure 6b, other bands at 2.374 eV, 2.339 eV and 2.300 eV are also observed in the long-wavelength range and are caused by the LO-phonon replicas of the ZP1 band. It should be noted, that any other PL bands on the long-wavelength edges of these bands were not observed. This indicates that the DAP recombination of the film sample is considerably smaller than the recombination caused by (e-A)-transitions, i.e., the relative concentration of free electrons near the bottom of the conduction band is larger than that of DAPs.

In Figure 6c the PL spectrum corresponds to the film obtained at $T_s = 673$ K. Here, the ZP1 zero-phonon band is observed at 2.412 eV. Other
bands at 2.376 eV, 2.339 eV, and 2.301 eV correspond to 1LO -, 2LO -, and 3LO - phonon replicas of this band. As in the case of sample 1, other bands are also observed at the long-wavelength edge of the above mentioned bands at the energies equal to 2.402 eV, 2.364 eV and 2.326 eV. The first band could be associated with the ZP2 band which is due to the recombination of DAP. It should be noted, that the difference in the energy between the ZP2 bands for the film samples 1 and 3 may be caused by the difference of the values of $R$ between the DAPs in both cases. It is obvious that this value must be larger in the case of sample 3. According to Eq. (1) and taking into account the energy of the ZP1 band, it allows us to get the value of $R_2 = 8.55$ nm.

A detailed analysis of the PL spectra in the exciton region allows us to obtain more information about the presence and nature of intrinsic defects and residual impurities in the investigated thin films. The reflection spectrum of CdS:Dy for the sample 1 at 4.5 K showing the peaks due to the formation of free excitons is shown in Figure 6a. The peaks labelled as A, B and C at 2.5541 eV, 2.5711 eV and 2.632 eV correspond to direct-allowed excitons. The existence of the peaks is due to the crystal field and spin-orbit splitting of the valence band, which is the result of the hexagonal (wurtzite) crystal structure of CdS. The polarization of the peaks is due to the symmetry of the valence bands. For CdS crystal, the conduction band and the top valence band have $\Gamma_7$- and $\Gamma_9$- symmetry, respectively. At the same time, other valence bands have $\Gamma_7$- symmetry. Thus, the $\Gamma_9$ valence band is active only for light with polarization $E \perp C$, where $C$ is the optical axis of the CdS crystal. In this case, an A exciton for polarization $E \perp C$ appears. Another valence bands interact strongly with both modes of polarization ($E \perp C$ and $E \parallel C$). Therefore, B and C excitons are observed for both light polarizations. Since in the reflection spectrum (Figure 6a) the intensities of A and B excitons is similar, this fact indicates about that crystalline grains of CdS polycrystalline films were grown with the optical axis perpendicular to the substrate. This result coincides with the data obtained from X-ray diffraction spectrum. The energy positions of A, B and C excitons let us determine the crystal field and spin-orbit splitting for the investigated CdS:Dy thin films. These values correspond to the
energies of 0.017 eV and 0.061 eV, respectively, and they match the corresponding quantities for a bulk CdS crystal (0.015 eV and 0.063 eV) [119].

As can be seen from Figure 6a, sharp lines are observed in the short-wavelength region of PL spectrum (exciton range) at 2.548 eV and 2.536 eV. The energy position of the first line indicates the appearance of the recombination of donor bound excitons, i.e., the presence of the D⁰X-line, which characterizes CdS single crystals as those of n-type conductivity. The appearance of the D⁰X-line in the PL spectra of the film may be caused, as a result, of the presence of the donor levels caused by the Cdᵢ centers, the sulfur vacancies, or the residual impurity of III group [103, 116]. The line at the energy of 2.556 eV, which is observed on the short-wavelength edge of D⁰X-line, coincides with the position of minimum for A-exciton in the reflection spectrum and corresponds to the emission of free excitons from the lower polariton branch. Another line at 2.536 eV is associated with the emission of excitons bound on the neutral acceptor, i.e., A⁰X-line. This line is in a good agreement with the energy of A⁰X-line, which appears in CdS single crystals lightly doped with lithium [108]. Earlier it was also found that undoped CdS crystals also show A⁰X-line at similar energy, which is associated with the presence of Li(Na) residual impurities. These atoms form in CdS the shallow acceptor centers [108]. Thus, this line correlates with the presence of the “green” emission, which, as was established above, is due to DAPs recombination and (e-A)-transitions, where the acceptors are also associated with Li(Na) residual atoms. In this case, the intensity of “green” luminescence is much stronger than the luminescence of excitons bound to neutral donors or acceptors. This is typical of highly compensated crystals [108].

The acceptor binding energy $E_A$ may be estimated from the position of A⁰X-line relative to the energy of free excitons, i.e, the exciton binding energy $E_{ex}(A)$, since there is correlation between these values, namely, $E_{ex}(A) \approx 0.1 \cdot E_A$ [120]. In this case, the value of $E_{ex}(A)$ is 0.018 eV. Thus, the acceptor binding energy $E_A \approx 177$ meV, which is close to the ionization energy of the acceptors caused by Na(Li) residual atoms. For D⁰X-line there is also a connection between the value of $E_{ex}(D)$ and the donor

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binding energy $E_D$, namely, $E_{ex}(D) \approx 0.2 \cdot E_D$. Using $E_{ex}(D) = 0.006$ eV for relative position of D$^0$X-line, we may to obtain $E_D = 29$ meV, that matches the energy of shallow donors in CdS (30 meV). It should be noted that FWHM of D$^0$X- and A$^0$X-lines was about 4.0 meV. The fact that we are able to observe the sharp intensive excitonic lines in the PL and reflection spectra indicates that the CdS thin films are of high optical quality. Furthermore, the presence of the D$^0$X-line shows that the investigated films are of $n$-type conductivity.

As can be seen from Figure 6, another two PL lines are observed in the long-wavelength range relative to the positions of D$^0$X- and A$^0$X-lines at 2.498 eV and 2.453 eV. The first line is 1LO-phonon replica of A$^0$X-line. In our point of view, the last line is associated with (e-A) transitions with the participation of another acceptor level. In this case, the energy of acceptor level is equal to 0.131 eV, which coincides with the value of the acceptor ionization energy (0.132 eV), caused by the presence of interstitial sulfur atoms (S$_i$) and is close to the energy of P residual impurity in CdS (0.120 eV) [121].

CONCLUSION

The low temperature photoluminescence spectra of II-VI semiconductor thin films prepared by the close-spaced vacuum sublimation technique under different growth temperatures were investigated and the structure of the films was analyzed. Thus, the study of the PL spectra of the investigated CdTe, ZnTe and CdSe films makes it possible to determine their optimal growth conditions in order to obtain the films of good optical quality. The obtained results are in good agreement with the structural investigations, which we have carried out earlier using the X-ray diffraction technique.

The PL spectra of CdTe, ZnTe as well as Zn-poor CZT1 and CZT2 samples show most intense A$^0$X line appeared due to the radiative recombination of acceptor bound excitons with the participation of cadmium vacancy. The presence of intensive excitonic line indicates a
fairly good optical quality of these samples. In a case of Zn-rich CZT samples, the broad PL bands caused by dislocations became dominant while relative intensity of A°X line significantly decreased. The presence of narrow lines of bound and free excitons in the PL spectra of CdS:Dy semiconductor films, as well as free excitons in the reflection spectra, indicates a remarkable optical quality of the films studied, grown at \( T_s = (573–673) \) K. This allowed us also to determine the BG of the CdS:Dy films with high accuracy, which coincides with that for bulk CdS crystals. It was found that the PL spectra of the investigated thin films also show other bands caused by (e-A)-transitions and donor-acceptor pairs recombination with the participation of Na(Li) residual impurities. The improvement of the crystal and optical quality of the investigated films is provided by both the optimization of the technological conditions of their growth and the “gettering” effect by dysprosium on the residual impurities such as Cu, P, N, Ag and Au. These results correlate with the decrease of the micro-stress level in CdS:Dy thin films in comparison with the undoped CdS films.

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