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THE SOURCES OF RADIATION IN THE SHORT-WAVE RANGE ON THE BASIS OF II-VI HETEROLAYERS

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Abstract. The possibility of obtaining zinc selenide and zinc sulfide layers of hexagonal modification by isovalent substitution method is shown. They are characterized by intensive luminescence which is formed by the dominant annihilation of bound excitons for α -ZnSe and recombination on donor-acceptor pairs for α -ZnS. The resulting radiation covers the violet wavelength range. Quantum radiation efficiency reaches $\eta = 10$ –12% for α -ZnSe and $\eta = 5$ –8% for α -ZnS. The radiation is characterized by high temperature stability and repeatability of characteristics and parameters.

Keywords: cadmium sulfide, zinc selenide, zinc sulfide, hexagonal modification, reflection spectrum, photoluminescence

ŹRÓDŁA PROMIENIOWANIA W ZAKRESIE KRÓTKOFALOWYM NA PODSTAWIE HETEROWARSTW GRUP II-VI

Streszczenie. Pokazano, że możliwe jest uzyskanie heterogennych warstw selenku i siarczku cynku o modyfikacji heksagonalnej za pomocą metody izowalentnego podstawienia. Charakteryzują się one intensywną luminescencją, która powstaje w wyniku anihilacji związanych ekscytonów dla dominującego pasma α -ZnSe i rekombinacji na parach donor-akceptor w przypadku α -ZnS. Otrzymane promieniowanie pokrywa fioletowy zakres optyczny. Sprawność kwantowa promieniowania wynosi $\eta = 10$ –12% dla α -ZnSe i $\eta = 5$ –8% dla α -ZnS. Promieniowanie charakteryzuje się wysoką stabilnością temperaturową oraz powtarzalnością charakterystyk i parametrów.

Słowa kluczowe: siarczek kadmu, selenek cynku, siarczek cynku, modyfikacja heksagonalna, mieszanie widma, fotoluminescencja

Introduction

An important direction of optoelectronics is creation of various types of systems for the formation, transmission and processing of information. The use of optical communication in them can greatly improve the speed, significantly increase the throughput, the density of recording information and its noise immunity, and, most importantly, the ability to visualize the transmitted information. Therefore, it is important to obtain materials and create devices on their basis that extend the optical region to the short-wave range. Such requirements are met by wide-gap II-VI compounds the direct band nature of which assures high efficiency of generation and recombination processes in various types of light-emitting diodes and photodetectors [10]. Therefore, the study of the possibility of obtaining α -ZnSe and α -ZnS layers with a time-stable structure and the investigation of their optical properties and photoluminescence appears to be relevant. The heterostructures based on such layers can play an important role in the creation of various types of optoelectronic devices with the stable and repetitive properties.

1. Measurement procedure

The optical properties and photoluminescence (PL) of the α -ZnSe and α -ZnS heterolayers were studied. For this purpose a universal optical setup was used, Fig. 1. It allowed integrated measurements to be carried out under the identical conditions of optical reflection spectra and luminescence, using the classical procedure and the λ -modulation method [8]. The latter method significantly increased the sensitivity to spectral distribution features. In the case of optical reflection studies, this provided an opportunity to determine the type and parameters of the band structure of the resulting material. PL measurements made it possible to establish both important properties, characteristics and parameters of generation and recombination processes, and the opportunities of practical application of the obtained α -ZnSe and α -ZnS heterolayers. When constructing PL plots, the hardware function of the setup was taken into account.

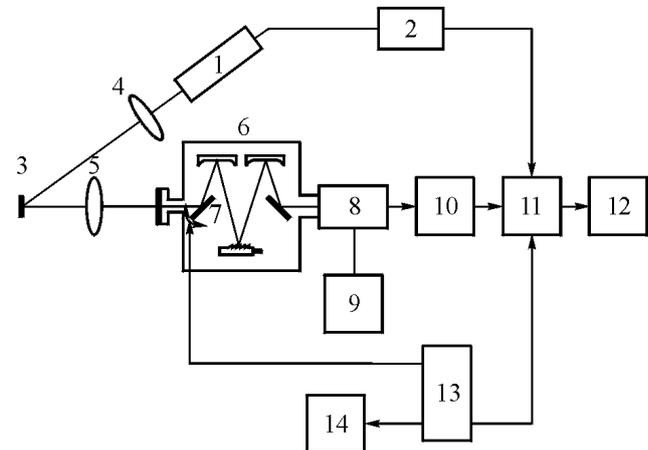
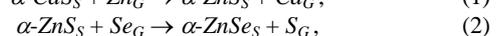
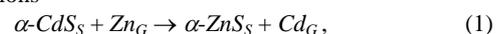


Fig. 1. Schematic diagram of experimental universal optical setup: (1) source of radiation (laser or lamp) with its power source (2); (3) sample; (4, 5) lenses; (6) monochromator MDR-23; (7) oscillating mirror (modulator); (8) photodetector with its power source (9); (10) selective amplifier; (11) synchronous detector; (12) plotting device; (13) sound generator; (14) millivoltmeter

2. Formatting of heterolayers components

The α -ZnSe and α -ZnS heterolayers of hexagonal modification were obtained on α -CdS crystals by isovalent substitution method [7]. Isothermal annealing took place consecutively in two steps in saturated vapours of Zn and Se elements. The diffusion character of the processes of substitution by isovalent elements causes growth of the layer deep into the substrate, which assures the necessary conditions for it to repeat the crystalline structure of the substrate.

The reaction of formation of heterolayers is described by the following equations



where indices "S" and "G" correspond to the solid and gaseous states of reagents.

Also, isovalent substitution method provided formation by reaction (1) on the surface of α -CdS single crystals of hexagonal α -ZnS heterolayers. Note that at the present time the properties of the resulting α -ZnSe and α -ZnS heterolayers remain poorly understood.

3. Results and discussions

The α -ZnSe and α -ZnS heterolayers, which were obtained by isovalent substitution method, have hexagonal lattice structure. Their formation in the case α -ZnSe is confirmed by the generation on the surface of α -CdS of a film characterized by zinc selenide yellow-red colour. But in the case of α -ZnS heterolayers, obtained films were characterized by the absence of colour. X-ray studies showed a pattern of diffraction maxima typical of the hexagonal lattice. Formation of a hexagonal modification of the crystalline structure of the obtained heterolayers is also confirmed by the studies of differential optical reflection spectra, Fig. 2. The structure of energy bands at point Γ of the Brillouin zones is exhibited which is typical of the hexagonal lattice. The main maximum corresponds to the optical transitions between the bands of allowed energies $E_g = 2.89$ eV for α -ZnSe and $E_g = 3.86$ eV for α -ZnS [3]. For the first time, the values of the valence band splitting into subbands with the participation of the crystalline field $\Delta_{CR} = 0.07$ eV and the spin-orbital interaction $\Delta_{SO} = 0.37$ eV were determined. In the case of α -ZnS these values are as follows: $\Delta_{CR} = 0.055$ eV and $\Delta_{SO} = 0.092$ eV.

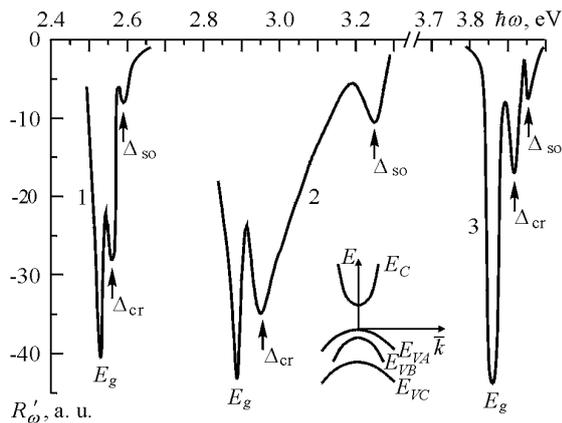


Fig. 2. Differential optical reflection spectra of basic α -CdS substrates (1) and annealed α -ZnSe (2) and α -ZnS (3) heterolayers. The inset shows the energy band structure of hexagonal structure semiconductors

The α -ZnSe heterolayers are characterized by intensive photoluminescence in a short-wave range with the photon energies $\hbar\omega = 2.72$ – 3.3 eV at 300 K. Determination of its quantum efficiency by the known method gives the values of $\eta = 10$ – 12% [5]. For the widely used β -ZnSe crystals its value does not exceed 0.1–0.4%.

The radiation of the obtained α -ZnSe heterolayers is characterized by maxima $\hbar\omega_m = 2.82$ eV and $\hbar\omega_m = 2.92$ eV in the violet range which correspond to two photon energy regions, Fig. 3 curve 1. Their spectral ranges are divided by the value of $E_g = 2.89$ eV. In the range $\hbar\omega \geq E_g$ the luminescence has the following features: a) independence of the position of maximum $\hbar\omega_m$ of photoexcitation level L ; b) quadratic dependence of intensity I on L , that is, $I \sim L^2$, Fig. 3 curve 4. Spectral shape is well approximated by the analytic expression which describes interband transitions of free charge carriers [9]

$$N = (\hbar\omega)^2 \sqrt{\hbar\omega - E_g} \exp\left(-\frac{\hbar\omega - E_g}{kT}\right), \quad (3)$$

where k is the Boltzmann constant, T is temperature. When substituting the value $E_g = 2.89$ eV, the band A is obtained, Fig. 3. Its mismatch with the experimental curve indicates the presence of the second component. It is determined by the optical

transitions involving a subband that was split by crystalline field $\Delta_{CR} = 0.07$ eV. The substitution of the value $E_g + \Delta_{CR}$ into (3) yields the calculated band B the shape of which is in good agreement with the experiment, Fig. 3.

This testifies to the active role of generation and recombination processes in the region $\hbar\omega > E_g$, with the participation of the main allowed energy bands and the valence subband, that is split into Δ_{CR} due to the action of the crystalline field. The presence of these components is confirmed by the experiment in the study by experimental λ -modulation. A typical differential curve of the first derivative N'_ω with two singularities is observed, the position of which is consistent with the analytical calculations of bands A and B , Fig. 3 curve 2.

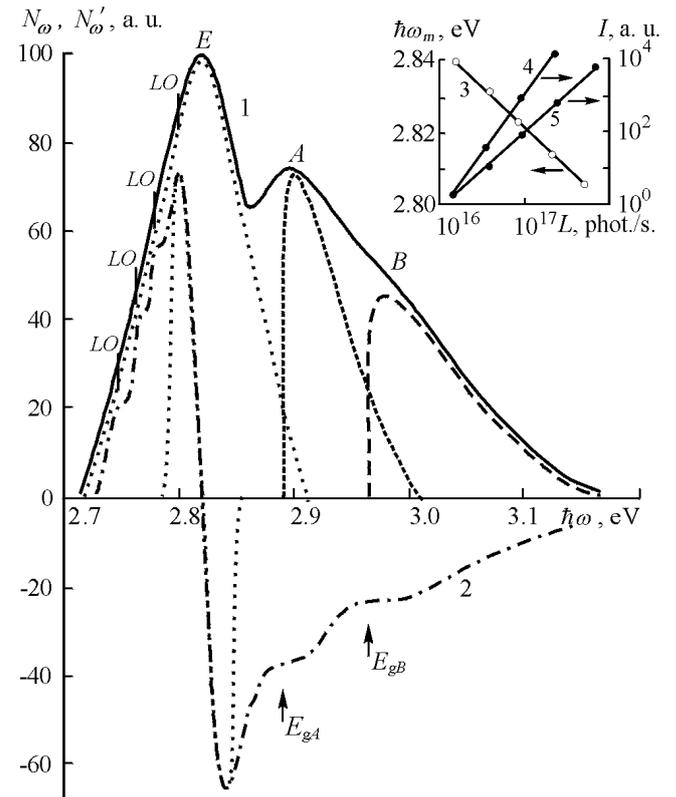


Fig. 3. The normal (1) and λ -modulated (2) photoluminescence spectrum of the α -ZnSe heterolayers. In the inset – maximum position (3) and intensity (4, 5) versus photoexcitation level L : 4 – $I \sim L^2$, 5 – $I \sim L^{1.5}$, $T = 300$ K

The singularity E on the curve 2 at its intersection with the axis of energies $\hbar\omega = 2.82$ eV corresponds to the maximum of the dominant band E in the region $\hbar\omega < E_g$. The position of the maximum $\hbar\omega_m$ is shifted to the region of lower energies with increasing L (Fig. 3, curve 3), and the intensity $I \sim L^{1.5}$ (Fig. 3, curve 5). These properties of band E are characteristic of radiation due to the annihilation of excitons [6]. Its observation at 300 K is caused by the processes of isovalent impurities formation in the formation of α -ZnSe heterolayers by the isovalent substitution method. These are the residual (not completely substituted) atoms of the base substance.

As a result of short-range potential of isovalent impurities, the exciton is localized thereupon, that is, bound excitons are formed. So, the resulting heterolayers are characterized by high quantum radiation efficiency. It is also defined by “purification effect” of the obtained material α -ZnSe [8]. At the same time, excitons localized on isovalent impurities are temperature-resistant. Therefore, in experiment one could observe radiation even at $T = 580$ K, though under such conditions the PL of β -ZnSe crystals is completely quenched. PL intensity of the resulting α -ZnSe heterolayers obtained by isovalent substitution decreased insignificantly. It should be noted that after cooling the nature of the spectra and the intensity were completely restored.

The α -ZnS heterolayers obtained by isovalent method are characterized by intensive photoluminescence at 300 K. Its quantum efficiency is $\eta = 7\text{--}8\%$. In so doing, the radiation spectrum covers a wide range of photon energies from 2.5 to 3.30 eV. The maximum falls on $\hbar\omega_m = 2.90$ eV, Fig. 4.

The specific feature of radiation is the shift of the maximum towards higher photon energies with increase in photoexcitation level from 10^{16} phot/sec to 10^{18} phot/sec. This testifies to recombination on donor-acceptor pairs (DAP) [9]. According to studies of the second derivative of the PL spectra, the main components of the radiation spectrum were determined, Fig. 4, curve 2. Their presence is confirmed by calculations according to the well-known Alentsev-Fock method [1]. In Fig. 4 they are shown by corresponding dashed lines.

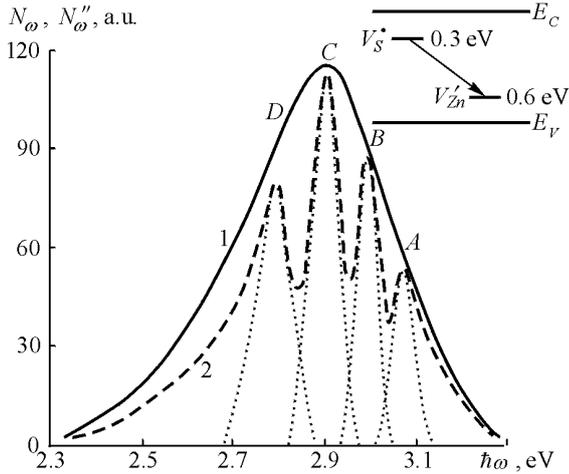


Fig. 4. The normal (1) and λ -modulated at a frequency of 2Ω (2) PL spectra of α -ZnS heterolayers. On the inset – the energy structure of simple centres, $T = 300$ K

The investigations of the differential spectra of optical reflection made it possible to reveal the specific features at the energies of 3.86 eV, 3.56 eV, 3.26 eV and 2.90 eV, Fig. 5.

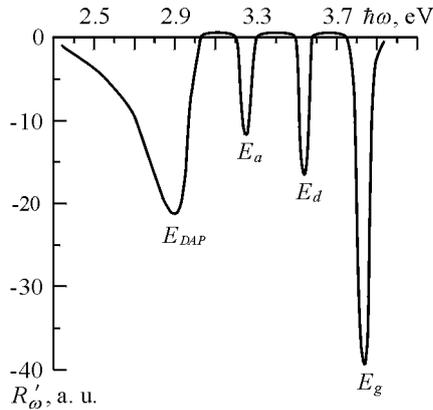


Fig. 5. λ -modulated spectra of optical reflection of α -ZnS heterolayers, $T = 300$ K

They correspond to the bandgap width of α -ZnS and the depth of the donor E_d and acceptor E_a states. The theoretical analysis of the spectral distribution of luminescence with the participation of the DAP (V'_{Zn} , V'_S) was carried out according to the known equation [6, 10]

$$\hbar\omega = E_g - E_d - E_a + E_k = E_g - E_d - E_a + \frac{e^2}{4\pi\epsilon_0\epsilon R_i}, \quad (4)$$

where E_a and E_d are the depths of corresponding acceptor and donor levels; ϵ_0 is dielectric constant, ϵ is the dielectric permittivity of the material (semiconductor), R_i is the distance between the DAP partners.

The revealed components of the α -ZnS luminescence spectra are located in a non-equidistant fashion with the

maxima at photon energies 3.072 eV (A), 2.989 eV (B), 2.904 eV (C), 2.795 eV (D). They were used to calculate the corresponding distances between the DAP partners with the participation of which the radiation transitions take place. They are 7 Å, 8.4 Å, 10.5 Å, 15.6 Å. The high-energy edge of the PL spectrum corresponds to the distance of $R_i = 4.1$ Å.

The resulting α -ZnSe and α -ZnS heterolayers are characterized by the anisotropy of optical properties. It is due to the hexagonal structure of crystalline lattice. This determines polarization of the optical transmission and reflection, as well as radiation of heterolayers in the short-wave range.

Important for practical application of the resulting α -ZnS and α -ZnSe heterolayers is a weak temperature dependence of their radiation (high-temperature properties). Integrated research has shown that maximum intensity of their luminescence is reduced not more than by a factor of 2 on heating from room temperatures to $T = 480\text{--}500$ K. Moreover, the character of the spectral distribution of radiation is almost unchanged when heated in the specified temperature range. Experimentally, as an example, typical dependences of their intensity and spectrum for α -ZnSe can be found in Fig. 5. A similar type of the dependence of the above characteristics on temperature is also valid in the case of α -ZnS.

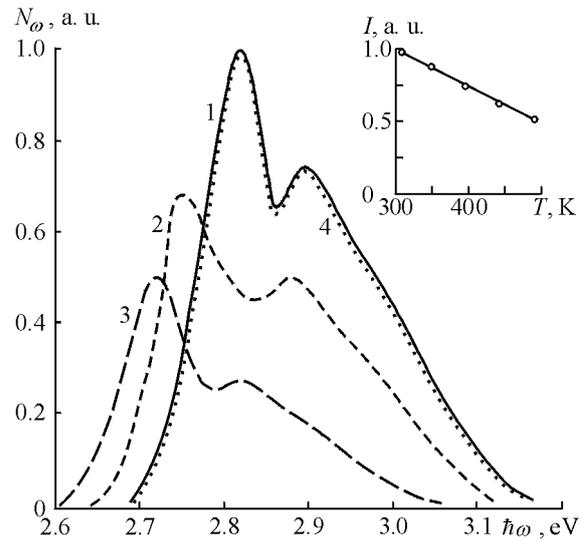


Fig. 6. PL spectra of α -ZnSe at $T = 300$ K (1), 490 K (2), 490 K (3) and after cooling to $T = 300$ K (4). On the inset – the dependence of radiation integral intensity versus temperature.

Note that the wavelength in the maximum of the given α -ZnSe radiation when heated to 490 K changes its position from $\lambda_m = 0.439$ μm to $\lambda_m = 0.455$ μm . Such shear value is in good agreement with the experimentally determined temperature coefficient of the change in the band gap of zinc selenide with a hexagonal modification of the crystal lattice, namely $dE/dT = 5.3 \cdot 10^{-4}$ eV/K. In the case of α -ZnS heterolayers the position of maximum changes from $\lambda_m = 0.427$ μm to $\lambda_m = 0.440$ μm , which corresponds to the well-known value of its shear ratio $dE/dT = 3.8 \cdot 10^{-4}$ eV/K.

Note that the resulting luminescence spectra of the investigated heterolayers testify to permanence of radiation range 0.37–0.46 μm with a change in higher than room temperature range. It is noteworthy that the temperature mode used for the investigations revealed high temperature stability of the characteristics and parameters of materials obtained.

It was also found that the variation of temperatures in the range of their high values (up to 500 K) leaves unchanged the mechanism that determines the processes of formation of radiation of the grown heterolayers. For α -ZnS, the established properties of their luminescence at $T = 300\text{--}500$ K indicate the above discussed recombination on donor-acceptor pairs. The corresponding radiation is also formed by the components A, B, C and D, which

are determined by certain distances between the partners of the DAP. Note that their respective contribution to the total spectrum does not undergo fundamental (strong) changes. In the case of α -ZnSe, radiation is formed by the components that are due to interband recombination of free charge carriers and annihilation of bound excitons. The latter determines the nature of the dominant band with a maximum of 2.82 eV (0.439 μm) at 300 K. The analysis of its properties at $T = 390$ K also revealed the dependence of luminescence intensity I on the excitation level L , which is described by $I \sim L^{1.5}$. The specific shear of maximum $\hbar\omega_m$ with increase in L (see Fig. 3) additionally confirms the exciton nature of the dominant band. It is determined by the annihilation of bound excitons. The possibility of such localization and its temperature stability are due to the properties characteristic of isovalent impurities [2]. This is indicative of the fact that the proposed and employed isovalent substitution method allows not only growing heterolayers of unstable hexagonal crystallographic modification, but also their doping with residual isovalent impurities.

It has been experimentally established that the character of the spectra and the change in radiation intensity are repeated at multiple measurements, Fig. 5. Investigations conducted in the course of two years did not reveal the features distinct from those considered during operation of heterolayers at high temperatures, which indicates not only the stability, but also the repeatability of characteristics. Such high temperature and temporal stability and repeatability of properties, characteristics of parameters can be used not only in the information and communications systems of various types, but also in the manufacture of various sensors, in particular for temperature recording.

4. Conclusions

The use of isovalent substitution method allows obtaining zinc sulfide and zinc selenide heterolayers of hexagonal modification. They are characterized by intensive luminescence with quantum efficiency $\eta = 6\text{--}8\%$ and $\eta = 10\text{--}12\%$, respectively. The radiation covers the violet optical range $\Delta\lambda = 0.37\text{--}0.46 \mu\text{m}$. It is formed by recombination on donor–acceptor pairs for α -ZnS and dominant annihilation of bound excitons in isovalent impurities and interband recombination of free charge carriers in the case of α -ZnSe. The resulting radiation is characterized by high temperature stability and repeatability of characteristics and parameters, which can be used in various information and communications systems and sensors.

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