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Preparation and luminescent properties of zinc sulfoselenide thin films

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The preparation of zinc sulfoselenide heterolayers is considered. The possibility of obtaining a hexagonal modification of the crystal lattice by the method of isovalent substitution was shown. The λ-modulated optical reflection was studied and the parameters of the energy structure of α-ZnSe, α-ZnS, α-$ZnS_{0.45}Se_{0.55}$ were determined. It has been established that the obtained heterolayers are characterized by intense photoluminescence with a quantum yield η = 8–12% in the blue-violet region. It is formed by constituent bands, the nature of which is determined by the annihilation of bound excitons and interband transitions of free charge carriers. It is shown that the selection of temperature regimes allows obtaining radiation with $\hbar\omega_m$ maxima in the violet 2.80 eV, blue 2.70 eV and green 2.45 eV spectral regions. It is determined by the generation-recombination transitions involving donor and acceptor states formed by intrinsic point defects of the crystalline lattice $V_{Se}^{\bullet}$, V_{Zn}' i Zn_i, respectively. The models of radiative recombination are discussed.

Key words: Isovalent elements, isothermal annealing, hexagonal structure, heterolayers, energy structure, photoluminescence, polarization.

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Introduction

Thin layers of wide-gap II-VI semiconductors are widely used in various electronic devices. Among them, light-emitting and photosensitive optoelectronics devices occupy an important place. The various types of structures made on their basis require further improvement of their functional capabilities. Among them, it is important to expand the spectral range in the short-wave region, reduce the intrinsic noise, increase both the quantum efficiency and the resistance of parameters and characteristics to the influence of external factors, in particular temperature and radiation exposure. This is especially important for basic semiconductor materials when they are based on devices for operation in extreme conditions. Among these materials, special attention should be paid to zinc selenide and sulfide. Their direct-gap feature is an important condition for obtaining high efficiency of generation and recombination processes in the devices created on their basis. In addition, the large band gap ZnSe and ZnS is a prerequisite for the development of little mastered short-wave area of the optical range. Solving these tasks is possible with the use of high quality layers with the corresponding properties. It should be noted that widely used epitaxy and ion implantation processes for films of III-V compounds, Ge and Si are substantially complicated in obtaining II-VI compounds and are often poorly suitable for obtaining films due to the large inconsistency of parameters of crystalline lattices of substrates and heterolayers and their coefficients of thermal expansion. Therefore, the urgent issue is the search for new methods for the production of zinc sulfoselenides of hexagonal (α) modification with stable properties. In addition, it is important to study the properties of materials with hexagonal crystalline lattice, as well as the possibilities for further creation of electronic devices on their basis.

The purpose of this work is to study the possibility of obtaining and development of a method for growing hexagonal α-ZnSe and α-ZnS_xSe_{1-x} hexagonal heterolayers, determining their parameters and characteristics using non-destructive optical control

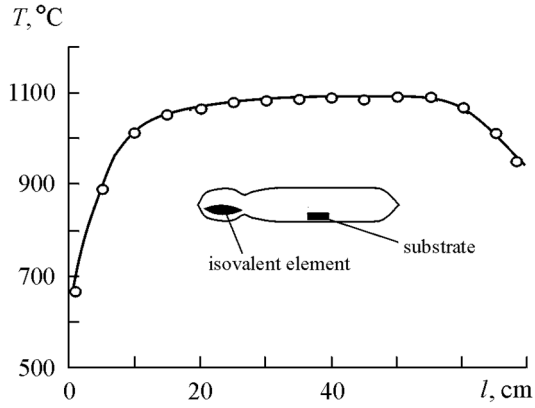

Fig. 1. The distribution of temperature and the position of the ampoules wn preparing diffusion layers.

methods and studying radiation properties and possibilities of practical use.

I. Objects and research methods

The α-ZnSe, α-ZnS heterolayers and α-ZnS_xSe_{1-x} substitutional solid solutions were formed by isothermal annealing in pairs of isovalent elements [1]. The technological process was carried out in quartz ampoules pre-evacuated to a pressure of at least 10^{-4} Torr. The weighed portions of Zn or (and) Se isovalent elements and α-CdSe or α-CdS substrates were located on opposite sides of the working object and were at the same temperatures, which could vary in the range of 800 ÷ 1100 °C, Fig. 1.

Under these conditions, diffusion of elements into the substrate occurred. Its hexagonal structure determined the design of the crystalline lattice of the resulting heterolayers. The heterolayers were formed according to the following reactions

$$a\text{-}CdS_S + Zn_G \rightarrow a\text{-}ZnS_S + Cd_G, \quad (1)$$

$$a\text{-}ZnS_S + Se_G \rightarrow a\text{-}ZnSe_S + S_G, \quad (2)$$

where indices "*S*" and "*G*" correspond to the solid and gaseous states of reagents. The formation of the heterolayer is provided by selecting the appropriate annealing time, temperature, and initial amount of alloying elements. Under such conditions, thin layers were formed by isovalent substitution by the mechanism of "epitaxy in depth" [2, 3]. The formation of a transition graded-gap layer between the substrate and the heterolayer ensures the stability of the structure, which is confirmed by the conducted studies.

The optical properties of the obtained hetero-layers were studied. Measurements were made on a specially designed universal optical installation. It provided the possibility of measuring both by classical methods and using the λ-modulation method [4, 5]. The main units are the diffraction device MDR-23, photodetectors FEP-79 or FEP-39A, a system of synchronous detector. When measuring spectra of optical reflection R'_ω, the source of continuous radiation was the ELC/C lamp. Photoluminescence was excited by radiation of a nitrogen laser with $\lambda = 0.337$ μm. In analyzing their spectra N_ω and N'_ω, the spectral sensitivity of the setup S_ω was taken into account. To analyze the influence of the possible anisotropy of the properties of the hexagonal lattice on the properties of heterolayer, studies were conducted in polarized light. For this, the polarizer was located next to the laser (obtaining linear polarization). The polarization of the heterolayer radiation was evaluated using the analyzer according to the known method [6].

II. Research results and their discussion

By the method of isovalent substitution, α-ZnSe, α-ZnS and α-ZnS_xSe_{1-x} heterolayers were obtained. The formation of a hexagonal crystal lattice is confirmed by studies of λ-modulated optical reflection, Fig. 2. The structure of the energy bands at the Brillouin point which is characteristic of this type of lattice is observed. The main maximum of the differential curves corresponds to the value of the band gap E_g. In the case of α-ZnS, it is $E_g = 3.89$ eV, and for α-ZnSe, $E_g = 2.89$ eV. The obtained values are consistent with known literary data [7]. The near-to-main peak is due to optical transitions involving the valence subband split by the crystalline field Δ_{CR}. The spin-orbital interaction Δ_{SO} defines the nature of the third maximum in the optical reflection spectra. The corresponding values are $\Delta_{CR} = 0.055$ eV and $\Delta_{SO} = 0.092$ eV in the case of α-ZnS. For α-ZnSe these values are determined for the first time and make $\Delta_{CR} = 0.07$ eV and $\Delta_{SO} = 0.37$ eV. The selection of appropriate regimes for isothermal annealing of the basic α-CdS sequentially in Zn and Se pairs ensures the formation of solid substitutional solutions α-ZnS_xSe_{1-x}. The width of the bandgap of one of these hetero-layers is $E_g = 3.20$ eV. It is established that their band gap width is linearly dependent on the content of the components. A similar linear dependence is observed for the parameters

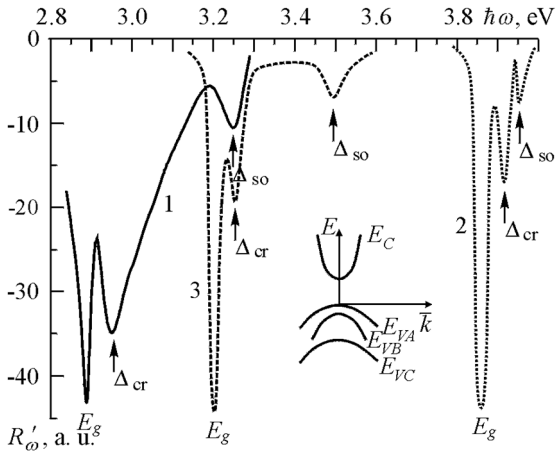

Fig. 2. Differential spectra of optical reflection R'_ω of α-ZnSe (1), α-ZnS (2) and α-$ZnSe_xS_{1-x}$ (3) heterolayers. On the inset: band structure of semiconductors of hexagonal modification. $T = 300$ K.

Δ_{CR} and Δ_{SO} of the band structure. The values of splitting of the valence band into subbands are Δ_{CR} = 0.066 eV and Δ_{SO} = 0.311 eV. These properties and their values allow us to determine the composition of the investigated solid solution, namely x = 0.45. The respective chemical formula for zinc sulfoselenide is as follows: $ZnS_{0.45}Se_{0.55}$.

An important property of the obtained hetero-layers of zinc sulfoselenides with a hexagonal crystalline lattice is intense luminescence in the short-wave blue-violet region. The study of the dependence of the properties of radiation on the conditions of excitation allowed establishing the constituent nature of the boundary

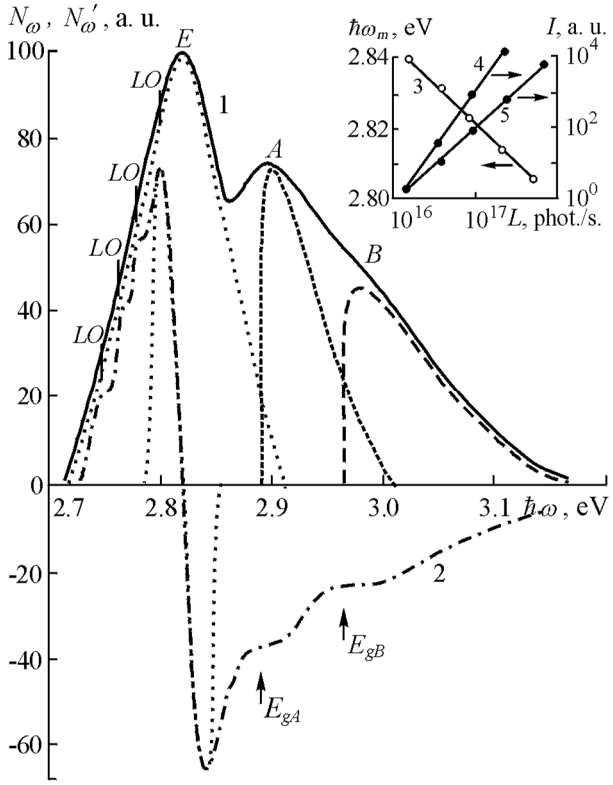

Fig. 3. The normal (1) and λ-modulated (2) photoluminescence spectrum of the α-ZnSe heterolayers. In the inset – maximum position (3) and intensity (4, 5) versus photoexcitation level L: 4 – $I \sim L^2$, 5 – $I \sim L^{1.5}$. T = 300 K.

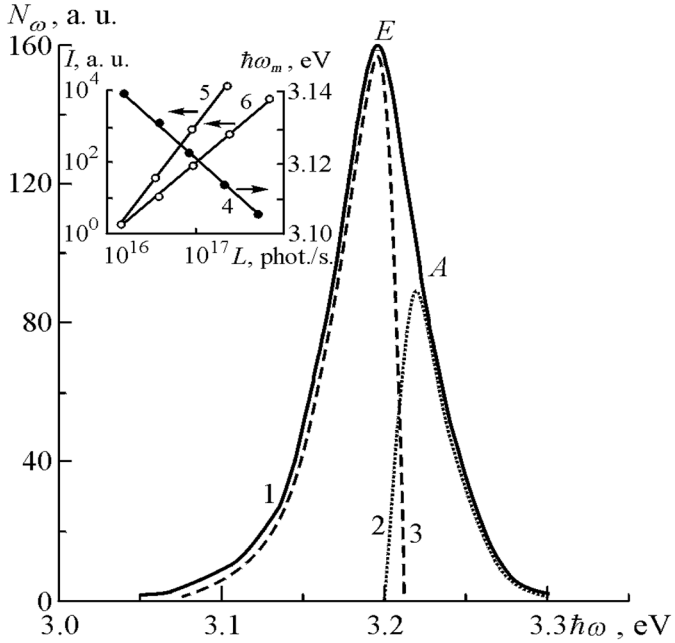

Fig. 4. The photoluminescence spectrum of the α-$ZnSe_{0,45}S_{0,55}$ (1) heterolayers and the A (2) band component of interband recombination and the E (3) band of exciton annihilation. T = 300 K. On the inset: the dependence of the position of the maximum $\hbar\omega_m$ (4) and the radiation intensity I (5, 6) of the excitation level for the resulting heterolayers: 5 – $I \sim L^2$; 6 – $I \sim L^{1.5}$.

radiation. As shown in [4], the dominant band *E* of the luminescence of the α-ZnSe hetero-layers is formed as a result of the annihilation of Cd-excitons bound on isovalent impurities, Fig. 3. In the region of photon energies $\hbar\omega > E_g$, the radiation is determined by the interband transitions of free charge carriers. They carry out the emitted transition both through the main valence subband (band *A*) and the subband, split off by the crystalline field (band *B*). Research using λ-modulation allowed to reveal these components by the characteristic features of the differential curve N'_ω (designated by the symbols *A* and *B*, respectively). In addition, the use of the modulation technique has allowed the exciton-phonon interaction to be established in the processes of formation of the radiation of the dominant band *E*. There are equidistantly located features. The distance between them allows you to determine the energy of an optical phonon. For α-ZnSe it is $\hbar\omega_{LO} = 28$ meV, which is determined by the known method [8]. The quantum yield of luminescence α-ZnSe is $\eta = 10 - 12$ % [9]. For widely used zinc selenide crystals, cubic modification $\eta = 0{,}1$ - 0,4 %.

Intense radiation in the short-wave region is also observed on α-$ZnS_{0.45}Se_{0.55}$ heterolayers, Fig. 4. The determined quantum yield is η = 6-8%. The spectrum of photoluminescence covers the range $\Delta\lambda$ = 0.36-0.40 μm, and the maximum is λ_m = 0.387 μm. The study of the dependence of the intensity of radiation *I* on the excitation level *L* revealed the regularity of $I \sim L^{1.5}$. The dominant band maximum $\hbar\omega_m$ is shifted to a region of lower energies with increasing *L*. Such main properties indicate the annihilation of excitons [10]. Accordingly, the dominant band *E*, as in the case for α-ZnSe, is formed as a result of the annihilation of bound excitons.

In the photon energy region of $\hbar\omega \geq Eg$, interband recombination of free charge carriers takes place. The latter is confirmed by the coincidence of the experimental curve with a curve calculated by the analytical expression [11]

$$N_w \sim (\mathbf{h}w)^2 \sqrt{\mathbf{h}w - E_g}\, \exp\left[-\frac{\mathbf{h}w - E_g}{kT}\right] \quad (1)$$

Such type of recombination processes and high quantum efficiency can indicate the high quality of the obtained α-ZnS_xSe_{1-x} heterolayers, as well as the basic binary components of α-ZnSe and α-ZnS.

For the resulting heterolayers of hexagonal modification, the characteristic feature is the possibility of changing the emission spectrum with variations in the temperature of isothermal annealing of the base substrate, Fig. 5. For α-ZnSe, when it changes in the range of 850-1050 °C, effective radiation is obtained with maxima in the violet ($\hbar\omega_m$ = 2.80 eV), blue ($\hbar\omega_m$ = 2.70 eV) and green ($\hbar\omega_m$ = 2.45 V a) spectral regions [12]. This can be explained by restructuring of the ensemble of intrinsic point defects of the crystalline lattice with isovalent substitution [3].In particular, the generation of single charged selenium vacancies $V_{Se}^{\bullet}$ ($E_a \approx 0.036$ eV) causes the formation of the violet colour of radiation due to recombination using the Lamb-Clique model [13]. Diffusion of the isovalent type of elements in semiconductors causes the generation of various types of intrinsic point defects.

Therefore, with a change in temperature, the role of single-charge zinc vacancies increases. They form acceptor centers with ionization energy $E_a \approx 0.14$ eV and the recombination with their participation in accordance with the Shen-Klasens model causes blue radiation. An increase in temperature to 1050 °C causes the transition of zinc atoms in the Zn_i, intermediate zone, in the middle of which deep centers are formed. With their participation, radiation is formed in a green area whose properties are described in the framework of the Kopylov-Pikhtin model [14]. This is confirmed by such signs as, firstly, the asymmetry of the contour with a rapid decrease in the intensity in the high-energy region, and secondly, the large half-width $\hbar\omega_{1/2}$, which increases with increasing *L* (excitation level); third, the independence of the maximum position $\hbar\omega_m$ on *L*. It

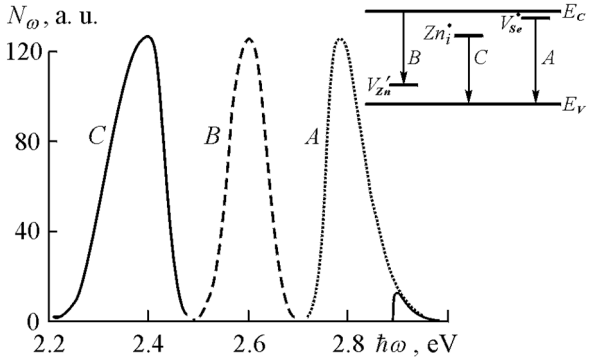

Fig. 5. The photoluminescence spectra of α-ZnSe hetero-layers obtained with T_A = 80-1040 °C. *T* = 300 K. On the inset: The energy diagram of the radiative transitions of charge carriers.

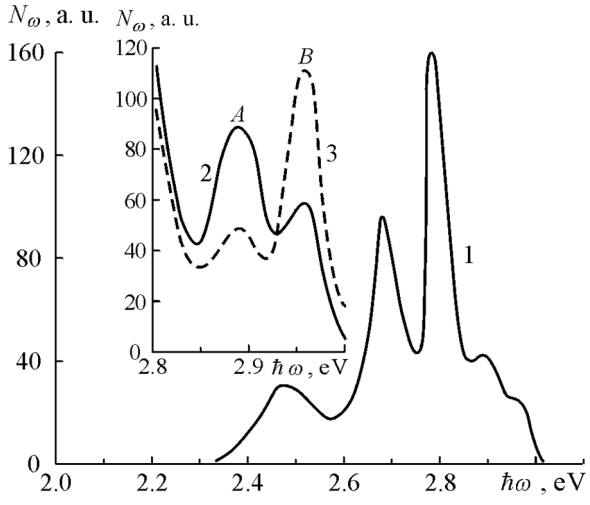

Fig. 6. Spectrum of polarized luminescence of α-ZnSe hetero-layers (1). On the inset - the dependence of the intensity of the edge radiation bands on the angle of polarization of the exciting laser radiation: the solid curve (2) 0°, and the dashed curve (3) 90°.

should be noted that the temperature studies of electrical conductivity allowed to determine the ionization energy of deep centers E_i = 0.583 eV. The value of the obtained magnitude is close to the depth of Zn_i in β-ZnSe (~ 0.6 eV) [2]. The values of the ionization energy of the centers formed $V_{Se}^{\bullet}$ and V_{Zn}' were obtained from the results of studies of the temperature dependence of the intensity of photoluminescence $I(T)$ and electrical properties.

A characteristic feature of the luminescence of hexagonal hetero-layers of zinc sulfoselenides is the polarization of radiation. It is determined by the anisotropy of the crystalline lattice. Investigation of the photoluminescence spectra at the characteristic positions of the analyzer, namely 0° and 90°, revealed the above violet, blue and green bands, Fig. 6. They are determined by the orientation of the respective centers. The characteristic orientation of the centers formed creates a radiation band with a maximum $\hbar\omega_m$ = 2.78 eV. The hexagonal lattice of heterolayers also causes the respective orientation of the location of its defects V_{Zn}' and Zn_i. This leads to the formation of polarized radiation bands with maxima of 2.68 eV and 2.47 eV, respectively. A detailed definition of the influence of the features of the hexagonal symmetry of heterolayers on the orientation of these centers requires special careful research. The anisotropy of the crystal lattice also affects radiative transitions involving the subzones. This determines the dependence of the nature of the spectral distribution of the boundary radiation on the orientation of the exciting linearly polarized light of the laser. The change in the polarization planes leads to a redistribution of the intensities of the constituent bands, which are determined by the interband transitions of free carriers through the main valence subband (band A) and that split under the action of the crystalline field Δ_{CR} (band B), inset in Fig. 6

Note that with a corresponding initial orientation of the laser beam, component A dominates at $\hbar\omega_m$ = 2.89 eV. A change in orientation by ~ 90° causes the component to have an advantage with $\hbar\omega_m$ = 2.96 eV. The difference in energy is ~ 0.07 eV, which corresponds to the Δ_{CR} value. This determines the structure of the spectrum of the edge radiation with features at the above photon energies. Note that a similar structure also manifests itself in the study of optical reflection in polarized light using λ-modulation [15]. Such a correlation of the results indicates the decisive role of the symmetry of the field of the ions forming the crystalline lattice.

Conclusions

Thus, thin layers of zinc sulfoselenides can be obtained by high-temperature annealing of hexagonal α-CdSe and α-CdS in pairs of isovalent elements Zn and (or) Se. They are characterized by intense luminescence with a quantum yield η = 8 – 12 %. The radiation covers the short-wave blue-violet region and is formed by the annihilation of excitons and interband transitions of free charge carriers. A change in the temperature of isovalent substitution predetermines the possibility of varying the colour of the radiation. This is determined by the change in the conditions of the formation of intrinsic point defects $V_{Se}^{\bullet}$, V_{Zn}' and Zn_i.. The parameters and characteristics of the received radiation are stable and repeating in time.

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Отримання і люмінесцентні властивості тонких плівок сульфоселенідів цинку

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Розглядається отримання гетерошарів сульфоселенідів цинку. Показано можливість отримання гексагональної модифікації кристалічної гратки методом ізовалентного заміщення. Досліджено λ-модульоване оптичне відбивання і визначено параметри енергетичної структури α-ZnSe, α-ZnS, α-$ZnS_{0,45}Se_{0,55}$. Встановлено, що отриманим гетерошарам властива інтенсивна фотолюмінесценція з квантовим виходом η = 8 - 12 % у синьо-фіолетовій області. Вона формується складовими смугами, природа яких визначається анігіляцією зв'язаних екситонів і міжзонними переходами вільних носіїв заряду. Показано, що добір температурних режимів дозволяє отримати випромінювання з максимумами $\hbar\omega_m$ у фіолетовій 2,80 еВ, синій 2,70 еВ і зеленій 2,45 еВ областях спектру. Воно визначається генераційно-рекомбінаційними переходами за участю донорних і акцепторних станів утворених власними точковими дефектами кристалічної гратки $V_{Se}^{\bullet}$, V_{Zn}' і Zn_i відповідно. Обговорюються моделі випромінювальної рекомбінації.

Ключові слова: ізовоалентні елементи, ізотермічний відпал, гексагональна структура, гетерошари, енергетична структура, фотолюмінесценція, поляризація.