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Light sources based on CdTe/CdS/ZnS heterostructures

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The optimal modes of isovalent substitution and the CdTe/CdS/ZnS heterostructure obtained for the first time were established, the main parameters of the band structure of the constituent heterolayers and the characteristics of the obtained radiation sources were determined. The high quantum efficiency $\eta \approx 12$-14 % of surface ZnS is caused by isovalent impurities. The band structure parameters of the obtained isovalently substituted CdS layers of atypical cubic modification and their luminescence efficiency of $\eta \approx 7$-8 % were established. The emission of the resulting layers is localized in the edge region of the material and is formed by interband emitting transitions and the dominant annihilation of bound excitons.

Keywords: CdTe/CdS/ZnS heterostructure, isovalent substitution, light sources, high quantum intensity.

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Introduction

Heterostructures based on CdTe and ZnS are widely used in solid-state electronics [1-2]. The corresponding devices manufactured on their basis using modern technologies are used in optoelectronics and fiber optics in the formation of photosensitive devices and radiation sources [3-5]. The direct gap nature of materials contributes to the high efficiency of generation and recombination processes, which determine the corresponding properties and characteristics of radiation sources. The need to further improve the parameters of devices makes the issue of developing technologies and manufacturing sources with high radiation efficiency urgent. Mastering the shortwave range remains relevant for them [6-7]. The use of CdTe as the base material of modern solid-state electronics necessitates technological and research work to create new devices [8-10]. A fundamental issue that arises is the variation of the spectral range of structures created on the basis of CdTe. For this purpose, wide-gap II-VI compounds, in particular CdS and ZnS, may be important in their creation [11-12]. Therefore, it is necessary to develop an appropriate technology for creating corresponding heterostructures (HSs) based on cadmium telluride with their participation and establishing the possibilities of their practical use. This paper presents the results of the production of CdTe/CdS/ZnS HSs and studies of their radiation parameters.

I. Experiment

1.1. Test samples

CdTe/CdS/ZnS heterostructures were obtained using the isovalent substitution method (IVS) [13-15]. For their formation, CdTe crystals of electronic conductivity (n-type) with a value of $\sigma \approx 10^{-6}$·10^{-12} Ohm^{-1}·cm^{-1} at $T = 300$ K were used, obtained by the classical Bridgman method [16]. It has been established that when growing GS it is important to carry out diffusion in a closed volume. For this purpose, quartz ampoules were used, in which specially prepared CdTe substrates and isovalent alloying elements S and Zn were placed, Fig. 1.

Diffusion of isovalent elements S and Zn was carried out at an annealing temperature of $T_A \approx 850$-950°C. Samples of base CdTe underwent preliminary chemical-mechanical treatment using well-known technology and were thoroughly washed in running distilled and deionized water. The condition of the resulting surface was monitored visually under an MBS-9 microscope at a magnification of at least 40X. The sample and a sample of the diffusant were located on opposite edges of a quartz ampoule, evacuated to more than 10^{-4} Torr [17].

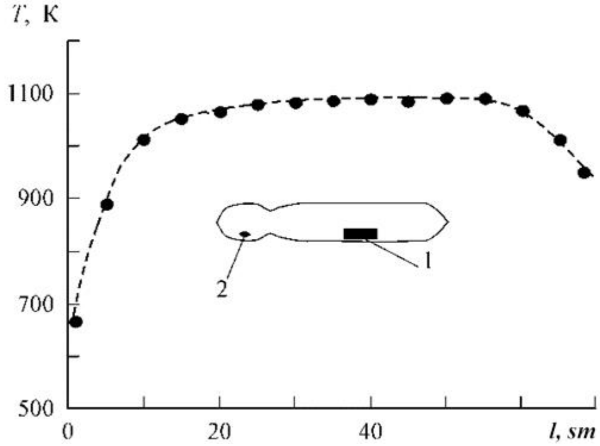

Fig. 1. Temperature distribution and position of ampoules when obtaining diffusion layers: 1 – substrate of the starting material; 2 – the sample.

According to the established regimes [14,18], the following isovalent substitution reactions occurred

$$CdTe + S \rightarrow CdS + Te \quad (1)$$

$$CdS + Zn \rightarrow ZnS + Cd \quad (2)$$

Diffusion was carried out in isothermal mode on a temperature plateau in repeated cycles. The annealing duration is t_a = 1–2 hours.

1.2. Research methods

The optical properties of heterolayers of the resulting β-CdTe/CdS/ZnS structure were studied. For this purpose, optical transmission Tω, reflection R_ω, and photoluminescence N_ω were studied. Complex measurements were carried out on a universal spectral installation, which made it possible to obtain the results of different measurements under the same experimental conditions. The installation consists of a spectral device MDR-23, a photodetector FEP-79, a synchronous detection system and an optical radiation source. To excite photoluminescence, a nitrogen laser LGN-21 with sb was used $\lambda_{зб.}$ = 0,337 nm and mercury lamp PRK-4. Optical transmission and reflection were produced under irradiation with a special ELC/C halogen lamp. The studies were carried out using classical measurement techniques, as well as using the λ-modulation method, which made it possible to obtain differential spectra T'_ω, R'_ω, N'_ω [16,18]. Based on them, the main parameters of the energy structure of the samples under study were determined.

The spectral setup was calibrated using a well-known standard lamp radiation technique, which made it possible to take into account the spectral quantum sensitivity of the setup S_ω during research. The research methods used are consistent with well-known ones [16,19]. Therefore, the study also made it possible to determine the possibilities of using the obtained samples to create light-emitting devices based on them.

II. Results and discussion

These methods for studying optical and luminescent properties made it possible to unambiguously determine the optimal technological conditions for obtaining the constituent layers, determine their parameters and features, and most importantly, their properties in order to establish the possibilities of their practical use. The CdTe/CdS/ZnS HSs obtained for the first time were formed by isothermal annealing in pairs of isovalent elements according to reactions (1) and (2). Accordingly, on a specially prepared CdTe substrate, CdS heterolayers (HLs) were obtained under appropriate conditions, and subsequently, under the invented substitution conditions, ZnS was obtained. The modes of substitution of atoms of the base substance under equilibrium conditions have been determined. This ensured the production of a complex combined heterostructure for the first time. Comprehensive studies of optical absorption T_ω and reflection R_ω using λ-modulation were carried out and the basic parameters E_g and Δ_{SO} of their energy structure were determined. The obtained values for CdTe and ZnS layers correlate with known literature data. Studies have been conducted for the first time obtained β-CdS layers of atypical cubic modification in CdTe/CdS/ZnS HS. Behind them, the band gap of β-CdS is Eg = 2.92 eV and the spinorbital splitting energy is Δ_{SO} = 0.28 eV. The obtained optical spectra are presented in Fig. 2.

Based on them, the main characteristics of the band structure of the resulting layers were determined. For β-CdTe base substrates, they are Eg = 1.50 eV and Δ_{SO} = 0,90 eV, which corresponds to generally known values [8]. The β-ZnS HLs obtained by the IVS method are characterized by the parameters Eg = 3.68 eV and Δ_{SO} = 0.072 eV, consistent with literature sources [20]. The correlation of certain parameters of the band structure with known values indicates the proper level of the technological process for obtaining the heterolayers under study.

Important for the practical use of materials obtained by the IVS method is the high quantum efficiency η of radiation. For the obtained ZnS surface HLs, the quantum efficiency is η = 12-14%. The value determined under the same experimental conditions for widely used cubic ZnS crystals is η = 1-2%. The significant difference in η indicates the fundamental importance of the IVS method in the manufacture of CdTe/CdS/ZnS HLs.

The luminescence spectrum of β-ZnS surface HLs covers a wide range of photon energies $\Delta\hbar\omega \approx$ 3.53-3.78 eV with a maximum at ħωm $\hbar\omega_m$ = 3.64 eV. The emission curve of HL β-ZnS is an asymmetric band. It covers both the photon energy region $\hbar\omega > E_g$ (E_g = 3.66 eV) and $\hbar\omega \leq E_g$. Let's consider the characteristic features.

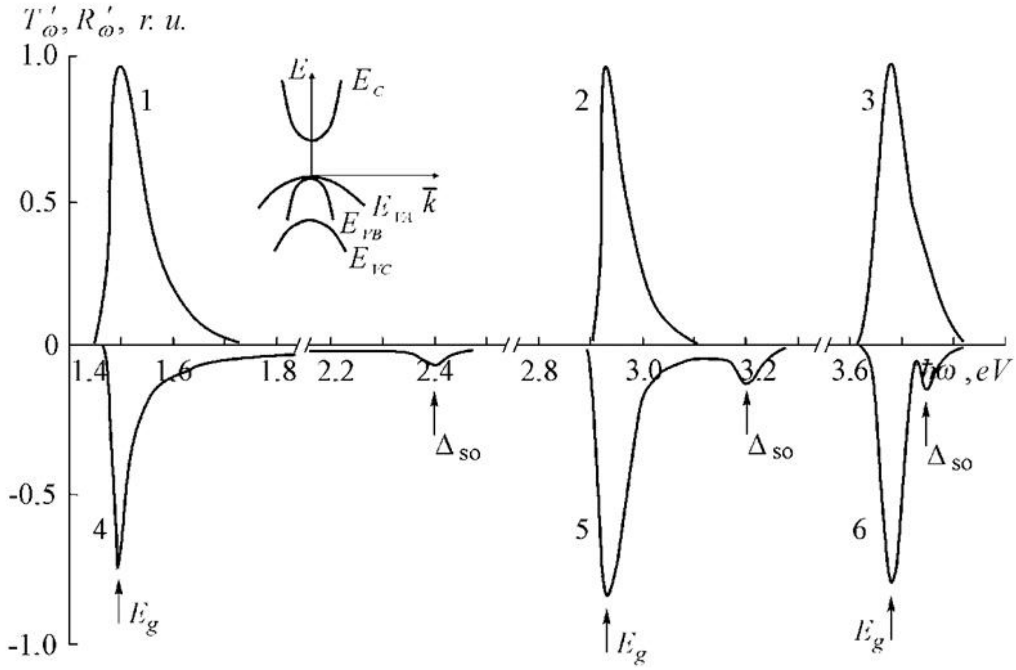

Fig. 2. Differential spectra of optical transmission T'_ω (1, 2, 3) and reflection R'_ω (4, 5, 6), CdTe semiconductor (1, 4), CdS films (2, 5) and ZnS (3, 6). Insets show the band structure of the cubic modification of crystals.

In the range $\hbar\omega > E$, the spectral distribution of radiation from the experimental curve is well approximated by the well-known analytical expression for interband transitions of free charge carriers [20,21].

$$N_\omega \sim (\hbar\omega)^2\sqrt{\hbar\omega - E_g}\,exp\left(-\frac{\hbar\omega - E_g}{kT}\right) \qquad (3)$$

where k is the Boltzmann steel, T is the temperature. In addition, the radiation is characterized by the independence of the position of the maximum of the radiation spectrum $\hbar\omega_m$ from the photoexcitation intensity L (when it changes by four orders of magnitude). The similarity of the temperature dependence $\hbar\omega_m$ to $E_g(T)$ is also important. The identified emission features in the region $\hbar\omega > E_g$ confirm the formation of β-ZnS HL radiation due to interband recombination of free charge carriers.

Analysis and comparison of the experimental emission curve and the component calculated by expression (3) allows us to identify the second component of the spectrum in the range $\hbar\omega \leq E_g$. It clearly manifests itself in modulation spectroscopy studies [19]. The maximum of the E band occurs at $\hbar\omega_m$=3.64 eV. The radiation is characterized by the following properties: 1) the intensity of the I band with the excitation level L varies according to the law $I \sim L^{1.5}$; 2) with increasing L, the maximum shifts to the region of lower photon energies $\hbar\omega$. Such characteristics are characteristic of exciton emission [22,23]. This is shown in the inset in Fig. 3. The experimental dependence $I \sim L^{1.0}$ for interband transitions is also indicated.

Note that the presence of highly efficient excitonic radiation is most likely due to isovalent substitution processes during the formation of the ZnS crystal lattice. According to equation (3), the atoms of the base compound are not completely replaced and when the content of residual atoms is up to 0.001%, they are isovalent impurities. According to their properties, excitons are localized on them, and therefore there is emission of excitons localized on isovalent impurities with their corresponding properties. The main ones are high temperature resistance [22,23] and high quantum efficiency η = 12-14% of radiation [13,24].

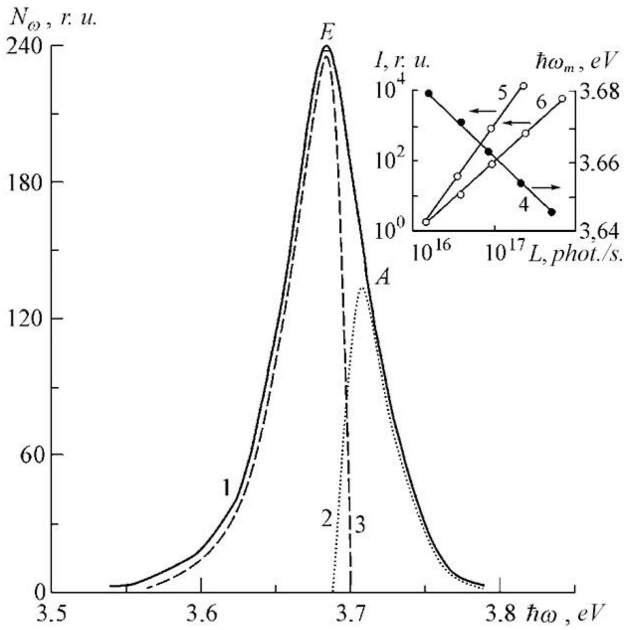

Fig. 3. Photoluminescence spectrum of β-ZnS heterolayers of the CdTe/CdS/ZnS structure T = 300 K. Inset – dependence of the position of the maximum of the E band on the excitation level L (4) and radiation intensity I on L (5), dependence of the intensity of interband radiation on L (6).

Under the same experimental conditions, the radiation of typical cubic ZnS crystals gives η = 1-2% and is also characterized by a spectrum in the range $\Delta\hbar\omega \approx$ 2.2-3.2 eV and a maximum at $\hbar\omega_m$ = 2.75 eV [24]. Therefore, establishing the conditions for growing the components of CdTe/CdS/ZnS HL for the first time using the IVS method and determining their basic parameters and properties is important.

Important for the gradual formation of a perfect ZnS crystal lattice is the formation of a transition CdS layer. The IVS method was used for the first time to obtain β-CdS heterolayers of atypical cubic modification. They are characterized by the stability of certain properties. It is the IVS method that makes it possible to obtain the indicated modification, in contrast to the typical hexagonal lattice compound for this type. For β-CdS, in the photon energy region $\hbar\omega \sim E_g$, an emission spectrum is observed with a maximum at $\hbar\omega_m$ = 2.9 eV. It is formed by two components in the photon energy regions $\hbar\omega > E_g$ and $\hbar\omega < E_g$ (Fig. 4).

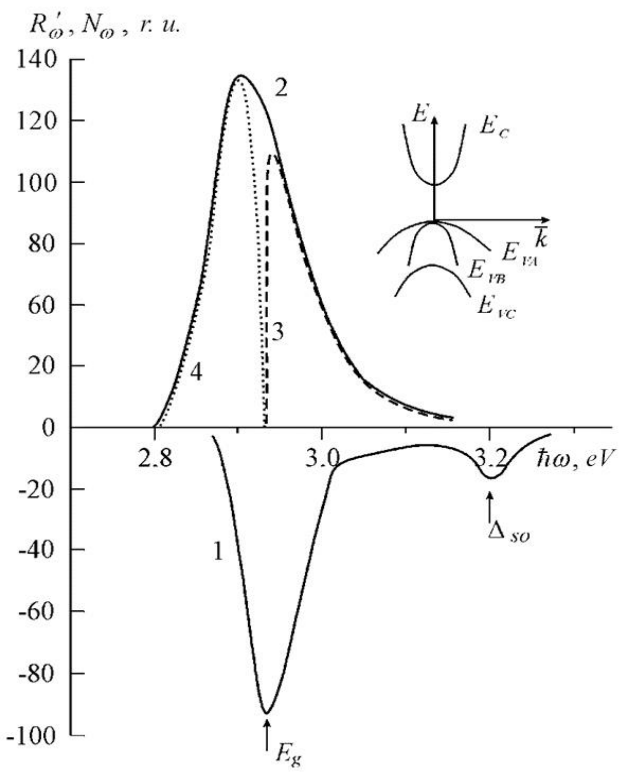

Fig. 4. Spectra of differential reflection (curve 1) and conventional photoluminescence (curve 2) of β-CdS/β-ZnS heterolayers. Curve 3 is the radiation component formed by interband radiative transitions, and curve 4 is the exciton component of the luminescence band. The inset shows the structure of energy bands inherent in the cubic modification of the crystal lattice.

Their presence is confirmed by studies of differential spectra, as well as corresponding calculations using the Alentsev-Fock method [23]. The component at $\hbar\omega > E_g$ is characterized by properties typical for interband recombination, as in the case of β-ZnS layers. Its shape is well approximated by analytical expression (3). For a band in the range $\hbar\omega < E_g$, an asymmetry of shape, a binding energy value of $E_g - \hbar\omega_{\mathrm{m}} \approx 0.03$ eV, as well as the dependence of the intensity at the maximum at $I \sim L^{1.5}$ and its position on L are observed. They are typical for exciton emission [23,25].

Thus, emission from layers of the atypical cubic modification β-CdS is observed in their edge region. It is characterized by high intensity with η = 7-8 %. Such properties are determined by the growth processes of layers when they are produced by the IVS method. The residual atoms of the tellurium sublattice from the β-CdTe substrate are decisive for the formation of the emissive properties of β-CdS.

Conclusions

Thus, replacing the components of the base CdTe compound with isovalent substances Cd and S under appropriate temperature and time conditions makes it possible to obtain a double heterostructure CdTe/CdS/ZnS. The constituent heterolayers are characterized by high structural perfection, which is confirmed by luminescence with a quantum efficiency of η = 12-14% for β-ZnS and η = 7-8% for β-CdS. The parameters of the band structure of the resulting β-CdS layers of an atypical cubic modification of the crystal lattice were determined: E_g = 2.92 eV and Δ_{SO} = 0.28 eV. The emission of grown heterolayers is formed by interband transitions of free charge carriers in the photon energy region $h\omega \geq E_g$ and the annihilation of bound excitons at $h\omega \geq E_g$. Based on β-ZnS heterolayers, it is possible to obtain radiation sources with high intensity in the short-wave region $h\omega$ = 3.5-3.8 eV and a maximum at $h\omega_m$ = 3.64 eV.

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[1] A. Sadao Properties of Semiconductor Alloys: Group-IV, III-V and II-VI Semiconductors. (New Jersey: Wiley, 2009).

[2] T.M. Mazur, M.M. Slyotov, V.V. Prokopiv, O.M. Slyotov, M.P. Mazur, *Light emitters based on II-VI chalcogenides with nanostructured surface*, Molecular Crystals and Liquid Crystals, 752(1), 95 (2023); https://doi.org/10.1080/15421406.2022.2091276.
[3] O. Ermakov Applied optoelectronics. (M.: Tekhnosfera, 416, 2004).
[4] M. Slyotov, T. Mazur, V. Prokopiv, Oleksii Slyotov, Myroslav Mazur, *Sources of optical radiation based on ZnTe/ZnSe/ZnS heterostructures*, Materials Today: Proceedings, 62, 5763 (2022); https://doi.org/10.1016/j.matpr.2022.03.476.
[5] H. Nykyforchyn, V. Kyryliv, O. Maksymiv, V. Kochubei, R. Boyko, V. Dovhunyk, *Wear resistance of the surface nanocrystalline structure under an action of diethyleneglycol medium*. Applied Nanoscience, 9(5), 1085 (2019); https://doi.org/10.1007/s13204-018-0690-3.
[6] A.N. Georgobiani and M.K. Sheinkman, Physics of A2B6 compounds (M. Mir, 320, 1986)
[7] T. Mazur, M. Mazur, M. Halushchak, *Surface-Barrier CdTe Diodes for Photovoltaics*, Journal of Nano- and Electronic Physics, 15(2), 02004-1 (2023); https://doi.org/10.21272/jnep.15(2).02006.
[8] D.V Korbutyak, S.V. Melnichuk, E.V Korbut, & M.M. Borisyuk, Cadmium telluride: impurity-defect states and detector properties (Ivan Fedorov: Kyiv, 198, 2000).
[9] I.V. Gorichok, P.M. Fochuk, Y.V. Verzhak, T.O. Parashchuk, D.M. Freik, O.E. Panchuk, ... & R.B. James, *Compensation mechanism of bromine dopants in cadmium telluride single crystals*, Journal of Crystal Growth, 415, 146 (2015); https://doi.org/10.1016/j.jcrysgro.2014.11.005.
[10] B. Naidych, T. Parashchuk, I. Yaremiy, M. Moyseyenko, O. Kostyuk, O. Voznyak, ... & L. Nykyruy, *Structural and thermodynamic properties of Pb-Cd-Te thin films: Experimental study and DFT analysis*, Journal of Electronic Materials, 50, 580 (2021); https://doi.org/10.1007/s11664-020-08561-5.
[11] R. Ahiska, D. Freik, T. Parashchuk, & I Gorichok, *Quantum chemical calculations of the polymorphic phase transition temperatures of ZnS, ZnSe, and ZnTe crystals*, Turkish Journal of Physics, 38(1), 125 (2014); https://doi.org/10.3906/fiz-1301-7.
[12] Y. P. Saliy, L. I. Nykyruy, R. S. Yavorskyi, & S. Adamiak, *The surface morphology of CdTe thin films obtained by open evaporation in vacuum*, Journal of nano-and electronic physics, 9(5) (2017); https://doi.org/10.21272/jnep.9(5).05016.
[13] V.I. Fistul, Atoms of dopants in semiconductors (state and behavior), (Fizmatlit: Moskva, 432, 2004).
[14] T. Mazur, V. Prokopiv, L. Turovska, *Quasi-chemistry of intrinsic point defects in cadmium telluride thin films*, Molecular Crystals and Liquid Crystals, 671(1), 85 (2018); https://doi.org/10.1080/15421406.2018.1542088.
[15] M. M. Slyotov, A. M. Slyotov, *The sources of radiation in the short-wave range on the basis of II-VI heterolayers*, Journal IAPGOS, 4(4), (2018).
[16] Yu.V. Vorobiev, V.I. Dobrovolsky, V.I. Stryha, Semiconductor research methods. (Vyshcha schola: Kyiv, 232, 1988).
[17] S.V. Bulyarskiy, V.I. Fistul, Termodinamika i kinetika vzaimodeystvuyushchikh defektov v poluprovodnikakh. (M. Nauka. Fizmatlit, 352, 1997).
[18] T. M. Mazur, M. M. Slyotov, O. M. Slyotov, M. P. Mazur, *Light Emitters Based on CdTe Doped with Isovalent Impurities*, Physics and chemistry of solid state, 23(2), 317 (2022); https://doi.org/10.15330/pcss.23.2.317-321.
[19] V.P. Makhniy, M.M. Slyotov, E.V. Stets, I.V. Tkachenko, V.V. Gorley, P.P. Horley, *Application of modulation spectroscopy for determination of recombination center parameters*, Thin Solid Films, 450, 222 (2004).
[20] Gavrilenko V.I, Grekhov A.M., Korbutyak D.V., Litovchenko V.G. Optical properties of semiconductors. Directory (Naukova Dumka, Kyiv, 608, 1987).
[21] V.P. Gribkovsky, The theory of absorption and emission of light in semiconductors (Science and technology, Minsk, 464, 1975).
[22] Ya.E. Pokrovsky, Radiative recombination in semiconductors (M. Science, 304, 1972)
[23] Era Koh, D.W. Langer, *Luminescence of ZnSe near the band edge under strong laser light excitation*. J. Luminescence, 1-2, 514 (1970)
[24] S. Zi, Physics of semiconductor devices (M. Mir, 352, 1984).
[25] P. Yu, M. Cardona, Fundamentals of semiconductor physics (M. Fizmatlit, 560, 2002).

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Джерела світла на основі гетероструктур CdTe/CdS/ZnS

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Встановлено оптимальні режими ізовалентного заміщення і вперше отримано гетероструктуру CdTe/CdS/ZnS, визначено головні параметри зонної структури складових гетерошарів і характеристики отриманих джерел випромінювання. Висока квантова ефективність $\eta \approx 12\text{-}14\,\%$ поверхневого ZnS обумовлена ізовалентними домішками. Встановлено параметри зонної структури отриманих ізовалентно заміщених шарів CdS нетипової кубічної модифікації і ефективність $\eta \approx 7\text{-}8\,\%$ їх люмінесценції. Випромінювання отриманих шарів локалізується у крайовій області матеріалу і формується міжзонними випромінювальними переходами і домінуючою анігіляцією зв’язаних екситонів.

Ключові слова: гетероструктура CdTe/CdS/ZnS, ізовалентне заміщення, джерела світла, висока квантова інтенсивність.