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Short Communication

Preparation and Luminescent Properties of α-ZnSe Heterolayers with Surface Nanostructure

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A modified surface on α-ZnSe heterolayers was prepared by chemical treatment in H_2SO_4:H_2O_2 etchant. Visual observation with microscope magnification 150$^{\times}$ and AFM-topograms made it possible to determine the geometrical surface structure which is composed of nanocrystals – pyramids of various size from 20 to 100 nm. Photoluminescence studies revealed high quantum efficiency $\eta = 15 \div 20$ % and two radiation spectrum components. In the range of photon energies $\hbar\omega > E_g$ ($E_g = 2.89$ eV at 300 K) the wide band with a maximum at $\hbar\omega_m = 3.24$ eV is attributable to quantum size effects. The component at $\hbar\omega_m = 2.72$ eV is formed by radiation on pyramids of large size and determined by interband transitions of free charge carriers and the dominant annihilation of bound excitons. The properties are characterized by temporal and temperature stabilities.

Keywords: Zinc selenide of hexagonal modification, Optical reflection, Luminescence, λ-modulation.

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1. INTRODUCTION

Zinc selenide remains one of the promising materials of solid-state electronics. Its crystals serve the basis for manufacturing various types of radiators and detectors. The basic material in them is crystal lattice of cubic (β) modification. At the same time, it is known that in semiconductors transition from cubic to hexagonal modification causes a change in the energy gap and contributes to formation of basically different properties. They change essentially due to formation of geometrically structured surface. Under these conditions, properties caused by quantum-dimensional processes become apparent. Essential increase in the quantum yield of luminescence can be important for practical application. Hence, of great current interest is preparation of ZnSe layers of hexagonal (α) modification, as well as formation of surface nanostructure thereupon.

2. SAMPLES AND RESEARCH METHODS

The α-ZnSe heterolayers were obtained by isothermal annealing of the substrates of α-CdSe single crystals in saturated zinc vapour. The process took place in a specially evacuated to 10^{-4} Torr quartz ampoule. The weighted amount of Zn and α-CdSe substrate of standard size 4×4×1 mm^3 were arranged on different ends thereof. It allowed isovalent substitution to be performed according to reaction [1]

$$\alpha\text{-}CdSe_{Sol} + Zn_{Gas} \overrightarrow{\leftarrow} \alpha\text{-}ZnSe_{Sol} + Cd_{Gas} \qquad (1)$$

where indices "Sol" and "Gas" correspond to the solid and gaseous states of matter.

Formation of α-ZnSe heterolayer on the surface of α-CdSe is confirmed both visually and by integrated investigations of the optical properties – transmission, reflection, photoluminescence [2]. Their important advantage is the nondestructive interaction with matter. For this purpose use is made of MDR-23 diffraction instrument, photomultiplier and standard synchronous detection system. The resulting optical characteristics are corrected with the aid of spectral sensitivity of integrated research installation. It allows you to conduct research both in classical techniques and using λ-modulation [3]. The luminescence was excited by N_2-laser with the wavelength $\lambda_m = 0.337$ mkm.

To obtain a modified surface, the α-ZnSe heterolayers were specially treated in chemical etchant H_2SO_4:H_2O_2 = 3:1 [4]. Variation of time and temperature modes allowed changing the geometrical structure of the surface. This provides for the possibility of a significant change in the luminescent properties of isovalent-substituted layers of basic zinc selenide of hexagonal modification.

3. RESULTS AND DISCUSSIONS

Formation by isovalent substitution method of ZnSe layers of hexagonal modification is vividly confirmed by the research of λ-modulated spectra. On the corresponding differential curves one can observe peculiarities typical for the band structure of hexagonal lattice, Fig. 1.

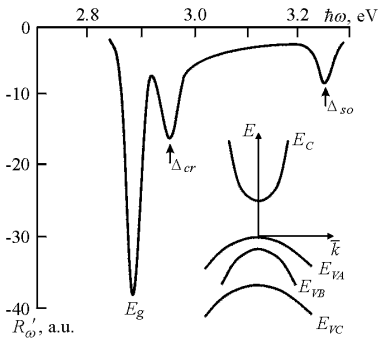

Fig. 1 – Differential optical reflection spectrum of α-ZnSe heterolayers. On the inset – the band structure of semiconductors with a hexagonal modification

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They are determined by splitting of valence band into subbands due to the effect of crystalline field $\Delta_{cr} = 0.07$ eV and spin-orbit interaction $\Delta_{so} = 0.37$ eV. The value $E_g = 2.89$ eV is in good agreement with the reported values for ZnSe hexagonal lattice [5]. Note that the hexagonal structure of layers obtained by isovalent substitution method is stable and not subject to phase transition of the type wurtzite → sphalerite that takes place when ZnSe single crystals are obtained by known classical techniques [6]. So, it becomes possible to study the possibilities of obtaining surface nanostructure of α-ZnSe heterolayers and to investigate their luminescent properties.

Surface modification was obtained as a result of chemical treatment. Visual observation with microscope magnification 150x revealed the formation of typical geometric structuring.

It is clearly observed experimentally on the AFM-topogram, Fig. 2. The thus obtained surface is composed of randomly arranged grains the lateral dimensions of which vary within 20-70 nm. Their shape reminds pyramids. To find out possible nature of such changes, special research is needed that goes beyond the scope of this work.

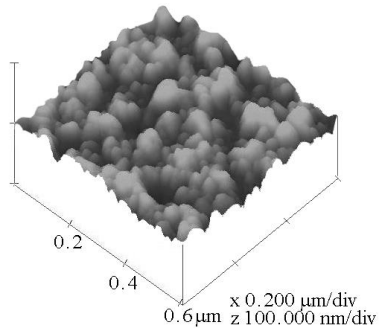

Fig. 2 – AFM-topogram of α-ZnSe layers with a modified surface

Research on the photoluminescence of α-ZnSe layers with a modified surface revealed some specific features. Let us consider the main ones. The radiation spectrum is composed of two bands conventionally designated by symbols A and B, Fig. 3.

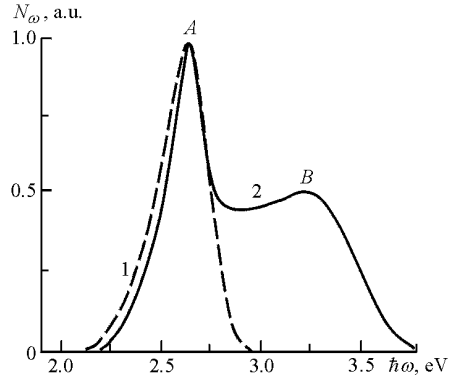

Fig. 3 – Photoluminescence spectra of basic (1) and modified (2) α-ZnSe layers

They are arranged in the region of photon energies $\hbar\omega$ larger than $E_g = 2.89$ eV and lower values. High-energy radiation ($\hbar\omega > E_g$) cannot be caused by formation of substance of different chemical composition. This is evidenced by the research on optical reflection R_ω of both types of samples. In conformity with it, the energy gap value does not change and corresponds to the obtained α-ZnSe layers.

It can be assumed that luminescence in the $\hbar\omega > E_g$ region is due to quantum-dimensional structure which is formed as a result of chemical treatment of α-ZnSe heterolayers. The respective self-organization processes cause the influence of geometric structuring on the character and nature of radiation. One of the provisions of this may be formation of dimensional quantization of the resulting nanostructures.The change in transition energy a result of dimensional quantization can be represented as [7]

$$\Delta E = \frac{\pi^2\hbar^2}{2d^2}\left(\frac{1}{m_n^*} + \frac{1}{m_p^*}\right), \qquad (2)$$

where m_n^* and m_p^* are effective masses of electron and hole, and d are dimensions of nanoobjects.

This is confirmed by the estimates of possible dimensions of nanoobjects with a change in transition energy [7]. From the empirically known potential well depth $\Delta E = \hbar\omega_m - E_g = 0.35$ eV the calculated dimensions make $d \approx 50$ nm. They correspond to the values of pyramid vertices, and their possible reduction causes the presence in the spectra of photons with the energies $\hbar\omega$ exceeding $\hbar\omega_m = 3.24$ eV.

Note that the dominant in intensity band A is caused by radiation from the large nanocrystals (d = 60-100 nm). Its properties are formed by the base layer of α-ZnSe. Prior investigations have shown [8] that photoluminescence spectra are determined by interband recombination of free charge carriers and annihilation of bound excitons, Fig. 4. The respective bands with the maxima of photon energy $\hbar\omega \sim 2.90$ eV and $\hbar\omega_m = 2.645$ eV become apparent in experience, especially when studying λ-modulation, curve 2, Fig. 4.

The exciton character of dominant radiation is confirmed by the following properties: a) maximum is shifted towards lower energies with increasing photoexcitation level L; b) intensity I depends on L by the law $I \sim L^{1.5}$. Interband recombination is confirmed by the independence of maximum position from L and the

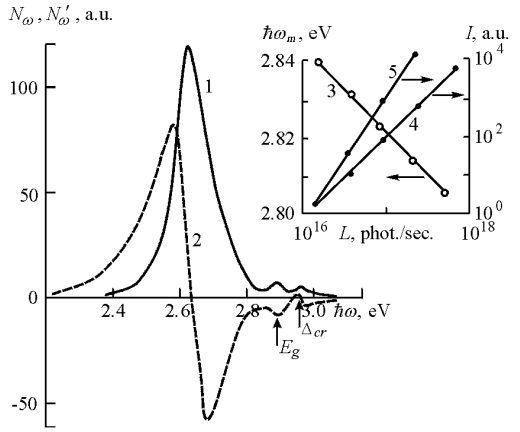

Fig. 4 – Conventional (1) and λ-modulated (2) photoluminescence spectra of α-ZnSe heterolayers. On the inset – dependence of position of maximum $\hbar\omega_m$ (3) and intensity I (4, 5) on the excitation level L; the low $I \sim L^{1.5}$ (4) and $I \sim L^2$ (5)

dependence of I on L by the law $I \sim L^2$. The above peculiarities are identical to the base α-ZnSe layers prepared by isovalent substitution method. Note that quantum efficiency of the luminescence of modified layers exceeds that of the initial samples and makes $\eta \sim$ 15-20 % (against 10-12 %).

4. CONCLUSIONS

Isovalent substitution method is used to obtain α-ZnSe heterolayers on the base substrates α-CdSe. The method of growing allows manufacture of material with a stable hexagonal structure ensuring the possibility of formation of surface nanostructure. It is characterized by intensive photoluminescence in photon energy region $\hbar\omega_m = 3.24$ eV which is caused by dimensional quantization of charge carriers energy. The dominant radiation is in the energy region of photons close to E_g value. It is determined by the radiative transitions of free charge carriers and the annihilation of bound excitons. Creation of surface nanostructure on α-ZnSe expands the spectral region of radiation and increases its quantum yield to $\eta = 15$-20 %.

Отримання та люмінесцентні властивості гетерошарів α-ZnSe з поверхневою наноструктурою

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Отримано модифіковану поверхню на гетерошарах α-ZnSe хімічною обробкою у травнику H_2SO_4:H_2O_2. Візуальне спостереження при збільшенні мікроскопа 150× та АСМ-топограми дозволили встановити геометричну структурованість поверхні, яка складається з нанокристалів – пірамід різних розмірів від 20 до 100 нм. Дослідження фотолюмінесценції виявили високу квантову ефективність $\eta = 15 \div 20$ % і дві складові у спектрах випромінювання. У діапазоні енергій фотонів $\hbar\omega > E_g$ ($E_g = 2{,}89$ еВ при 300 К) широка смуга з максимумом на $\hbar\omega_m = 3{,}24$ еВ пояснюється квантово-розмірними ефектами. Складова при $\hbar\omega_m = 2{,}72$ еВ формується випромінюванням на пірамідах великого розміру і визначається міжзонними переходами вільних носіїв заряду та домінуючою анігіляцією зв'язаних екситонів. Властивості характеризуються часовою і температурною стабільностями.

Ключові слова: Селенід цинку гексагональної модифікації, Оптичне відбивання, Люмінесценція, λ-модуляція.

Получение и люминесцентные свойства гетеослоев α-ZnSe с поверхностной наноструктурой

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Получено модифицированную поверхность на гетеослоях α-ZnSe химической обработкой в травителе H_2SO_4:H_2O_2. Визуальное наблюдение при увеличении микроскопа 150× и АСМ-топограммы позволили установить геометрическую структурированность поверхности, которая состоит из нанокристалликов – пирамид разных размеров от 20 до 100 нм. Исследования фотолюминесценции выявили высокую квантовую эффективность $\eta = 15 \div 20$ % и две составляющие в спектрах излучения. В диапазоне энергий фотонов $\hbar\omega > E_g$ ($E_g = 2{,}89$ эВ при 300 К) широкая полоса с максимумом на $\hbar\omega_m = 3{,}24$ эВ объясняется квантово-размерными эффектами. Составляющая при $\hbar\omega_m = 2{,}72$ эВ формируется излучением на пирамидах большого размера и определяется межзонными переходами свободных носителей заряда и доминирующей аннигиляцией связанных экситонов. Свойства характеризуются часовой и температурной стабильностями.

Ключевые слова: Селенид цинка гексагональной модификации, Оптическое отражение, Люминесценция, λ-модуляция.

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