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FABRICATION, TREATMENT, AND TESTING OF MATERIALS AND STRUCTURES

Formation and Reconstruction of Se Nanoislands at the Surface of Thin Epitaxial ZnSe Layers Grown on GaAs Substrates

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Abstract—Strained epitaxial ZnSe layers are grown on GaAs substrates by the method of vapor-phase epitaxy from metal-organic compounds. It is found that Se nanoislands with a density of 10^8 to 10^9 cm^{-2} are formed at the surface of such layers. It is established that an increase in the size of Se islands and a decrease in their density take place after completion of growth. Annealing in a H_2 atmosphere at a temperature higher than 260°C leads to the disappearance of Se islands and to a decrease in the surface roughness. It is shown that annealing does not lead to deterioration of the structural perfection of the epitaxial ZnSe films; rather, annealing gives rise to a decrease in the intensity of impurity–defect luminescence and to an increase in the intensity of intrinsic radiation near the bottom of the exciton band.

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1. INTRODUCTION

In recent years, semiconductor nanostructures useful for the fabrication of coherent-radiation sources of a new type (polaritonic lasers) have been actively studied. In contrast to conventional lasers, the coherence of emission in a polariton laser is attained due to the Bose–Einstein condensation of exciton polaritons. As a result of the extremely small effective mass of polaritons (four–five orders of magnitude smaller than the mass of a free electron), their Bose condensation can take place at high temperatures and at a low density of polariton gas. In order to fabricate a polariton laser, it is possible to use exciton polaritons in microcavities with an active medium of semiconductor quantum wells and wires [1], of carbon nanotubes [2], and also of organic materials [3, 4]. At present, we have experimental samples of polariton lasers based on GaAs [5], CdTe [6], ZnO [7, 8], and GaN [9].

In order to fabricate polariton lasers, it is necessary to use active media with a fairly high exciton-binding energy. In this respect, wide-gap II–VI semiconductor compounds, in particular ZnSe [10] with an exciton-binding energy of 20 meV, are most promising. Microcavities with a high Q factor $Q \sim 1000$ and larger are necessary. Such cavities can be obtained on the basis of epitaxial layers with a very high surface quality. It was expected that epitaxial ZnSe layers (with subcritical thickness) grown on GaAs substrates under conditions of two-dimensional growth would feature the required surface quality. However, it was established that hillocks are formed at the surface of epitaxial ZnSe layers; the density of these hillocks exceeds 10^8 cm^{-2} [11–14]. An analysis of the time dynamics of the surface pattern in these samples showed that the material of the hillocks is subject to redistribution at room temperature; this redistribution is similar to so-called Oswald ripening [11]. Lopez-Lopez et al. [12] related the origination of hillocks to the formation of Ga drops at the surface of a substrate after deoxidation. It was assumed that the formation of hillocks occurs in regions enriched with gallium by the vapor–liquid–crystal mechanism. Smathers and Kneedler [13] assumed that the hillocks consist of SeO_2. A study of the composition of large hillocks with the use of dispersive X-ray structural analysis showed that, most probably, they consist of pure Se [11].

Independently of the composition, hillocks detected at the ZnSe surface impose fundamental limitations on the Q factor of microcavities since they give rise to the pronounced scattering of radiation. Therefore, for the development of the technology of the fabrication of high Q-factor microcavities based on ZnSe films, it is necessary to have a method for the removal of hillocks from the surface and/or their suppression directly during growth. The development of such a method applicable to the surface of thin (70–210 nm)

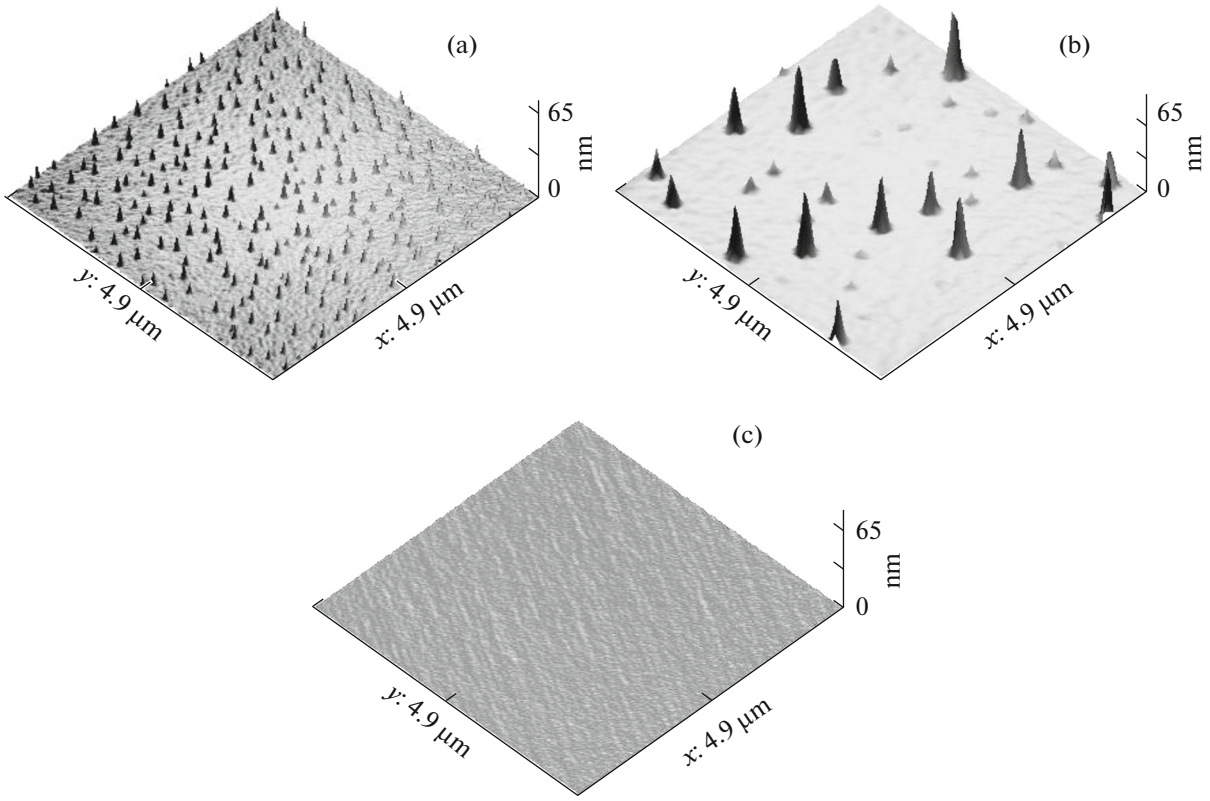

Fig. 1. Patterns of the surface of epitaxial ZnSe layers with a thickness of 140 nm (a) 2 and (b) 53 days after growth and also after annealing in a hydrogen atmosphere for three hours at a temperature of 263°C for 3 h at a temperature of 263°C (c).

ZnSe/GaAs epitaxial films is the main aim of this study.

2. METHODS OF GROWTH AND CHARACTERIZATION OF STRUCTURES

Thin epitaxial ZnSe layers were grown by the method of vapor-phase epitaxy from metal-organic compounds at temperatures of 455–485°C and at ratios of VI/II fluxes from 1.5 to 6 on GaAs substrates with a deviation of 10° from the plane (001) toward the plane (111)*A*. For layer growth, we used a horizontal quartz reactor equipped in situ with reflectometric control, which made it possible to control the layer thickness and the quality of the surface. Growth was performed in a H_2 atmosphere at atmospheric pressure; $ZSnEt_2$ and Et_2Se were used as precursors. The typical thicknesses of the ZnSe epitaxial layers amounted to about 70, 140, and 210 nm. In order to improve the quality of the surface of the epitaxial layers, some of the grown films were annealed in the hydrogen atmosphere for 1–2 h at temperatures of 260–320°C. The annealed and unannealed structures were studied using atomic-force microscopy (AFM), photoluminescence (PL), reflection of light, and X-ray diffractometry. The AFM measurements were performed using a SmartSPM AIST-NT microscope. The structural quality of the grown epitaxial layers was determined using a Panalytical X'Pert Pro MRD Extended X-ray diffractometer [15]. Measurements of the PL and reflection were performed in the temperature range 5–300 K using a grating spectrograph (Princeton Instruments Spec [10]) equipped with a multichannel CCD detector. The spectral resolution in the vast majority of experiments was no worse than 0.1 meV. The source of optical excitation was a semiconductor laser with an emission wavelength of 405 nm; the typical level of the excitation-power density was 0.2–2 W/cm^2.

3. RESULTS AND DISCUSSION

3.1. Characterization of ZnSe Epitaxial Layers Using AFM

Studies with the use of AFM showed that nanoscale hillocks are present at the surface of all of the grown samples. The density of the hillocks varied from 0.8×10^8 to 1×10^9 cm^{-2} depending on the growth conditions and the layer thickness. The height of the hillocks the first day after growth was 10–15 nm. 50 days after growth the height of some hillocks increased to 50 nm, while the density of hillocks decreased by an order of magnitude compared with

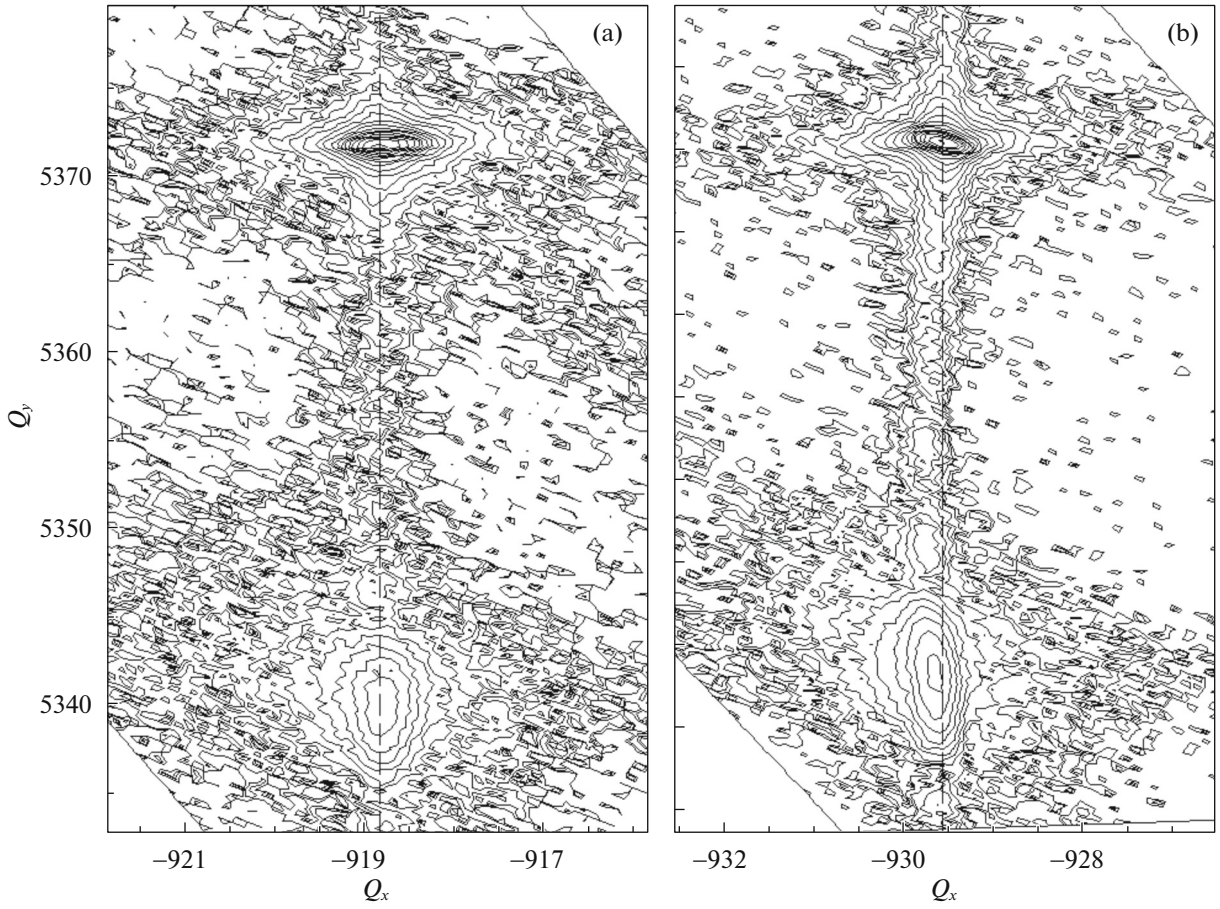

Fig. 2. Two-dimensional pattern of X-ray diffraction for the initial (a) and annealed (b) samples in the vicinity of the site (004) of the reciprocal lattice.

the initial value. The variations in the density and height of the hillocks are illustrated in Figs. 1a and 1b.

Since there are considerations [11] indicating that the hillocks on the surface of ZnSe epitaxial layers are formed of Se, we annealed some of the samples in a H_2 atmosphere at temperatures exceeding that of Se melting. Studies performed by the AFM method after annealing showed that the Se hillocks disappeared (Fig. 1c) and the roughness of the surface decreased to 0.48 nm.

3.2. X-ray Structural Characterization of ZnSe Epitaxial Films

Since the epitaxial layers grown on unoriented (001)GaAs substrates are subject to monoclinic elastic deformation [16], we used two asymmetric reflections (444) and ($\overline{4}44$) and reflection (400) in order to calculate the structural parameters of the ZnSe layers. Using such a procedure, we established that plastic relaxation is lacking in both the initial and annealed samples with a layer thickness as large as 220 nm. The lattice parameter $a_\perp$ of the ZnSe layers is equal to 5.6869 Å. However, in the vicinity of the lattice site (004) in the reciprocal lattice, a slight shift of the two-dimensional diffraction pattern corresponding to the ZnSe layer (along the horizontal axis) is observed, see Fig. 2. This means that insignificant plastic relaxation takes place during annealing. At the same time, annealing leads to an improvement in the observation of satellite peaks and to a decrease in diffusive scattering, which can be interpreted as the disappearance of Se precipitates.

3.3. Optical Characterization of ZnSe Epitaxial Films

We now consider typical spectra of the low-temperature PL of epitaxial ZnSe layers and their modifications as a result of annealing. The survey spectrum of low-temperature PL for the initial ZnSe film with a thickness of 140 nm is shown in Fig. 3. The PL spectra of this film after annealing for 90 min in a hydrogen atmosphere at a temperature of 260°C, and also after additional annealing in a H_2 atmosphere for 60 min at a temperature of 330°C are also given in Fig. 3.

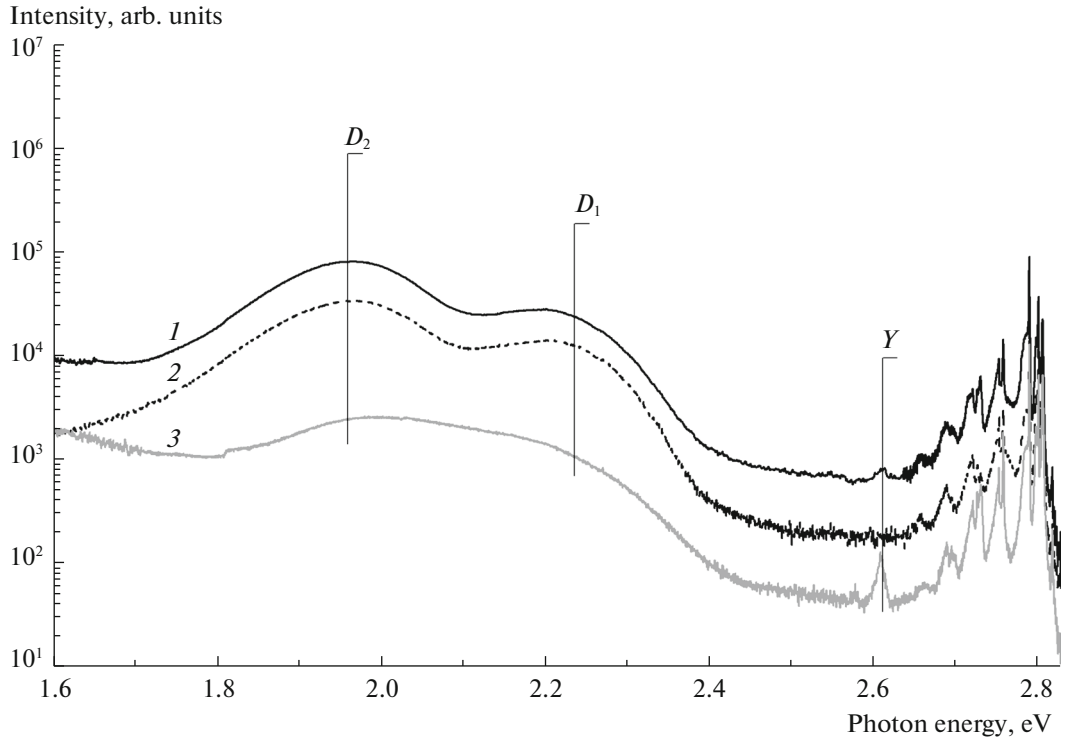

Fig. 3. Photoluminescence spectra of a ZnSe-film sample before annealing (*1*), after first annealing (*2*), and after second annealing (*3*).

In the short-wavelength part of the PL spectra for the initial sample, we observe the emission of free excitons and excitons bound to neutral impurities (exciton-related luminescence will be discussed in somewhat more detail in what follows), whereas structureless bands D_1 and D_2 are dominant in the long-wavelength region. Broad PL bands in the range of 1.7–2.3 eV are typical for bulk samples and epitaxial ZnSe films. These bands are conventionally related to impurity–defect emission, i.e., the luminescence of donor–acceptor pairs with the involvement of a deep acceptor (vacancy in the Zn sublattice, a complex defect with the involvement of a vacancy in the Zn sublattice or a number of impurities) and a shallow-level donor [17]. For the D_2 band, the position of the PL maximum (1.96 eV) coincides with good accuracy with the emission of the known "red" band, which is related to copper; however, the presence of appreciable concentrations of copper in the crystal leads, as a rule, to the appearance of two emission bands [18, 19], the "red" and "green" bands (with a maximum at 2.34 eV) (the "green" band is not observed in the structures under study). The position of the maximum of the band D_1 (2.22 eV), taking into account the considerable half-width of this band, is close to the position of the band maximum, which is observed in the spectra of the low temperature PL of both bulk ZnSe and relaxed ZnSe epitaxial films doped with Ga (2.27 eV). Also, an emission band with a maximum in the region of 2 eV is observed in the case of doping ZnSe with a Ga impurity. It is assumed that these PL bands are related to complex defects of the Ga_{Zn}–V_{Zn} type [20].

It is known that the interdiffusion of Ga and Zn takes place in the vicinity of the heterointerface during the heating of ZnSe/GaAs heterostructures to temperatures higher than 400°C. In addition, Ga released as a result of Ga_2Se decomposition (appears as a result of the interaction of selenium with the open surface of the substrate) can gradually be introduced into the lattice due to segregation effects. As a result of these two effects, deep PL bands related to the formation of complex defects with the involvement of Ga [21] appear in the ZnSe emission spectra. Since the growth of thin epitaxial ZnSe films under study took place at temperatures higher than 450°C, one can expect that complex defects of the Ga_{Zn}–V_{Zn} type are formed in these films and related deep bands of impurity–defect emission appear.

Subsequent annealing at 260 and 300°C results in an appreciable decrease in the level of defect–impurity emission. A decrease in the intensity of the D_1 and D_2 bands by 1.5–2 orders of magnitude is observed in the long-wavelength region of the spectrum (Fig. 3). In the edge region, the redistribution of the emission intensity from localized states to free ones occurs; in this case, each annealing is accompanied by an insignificant reduction in the absolute intensity of the radi-

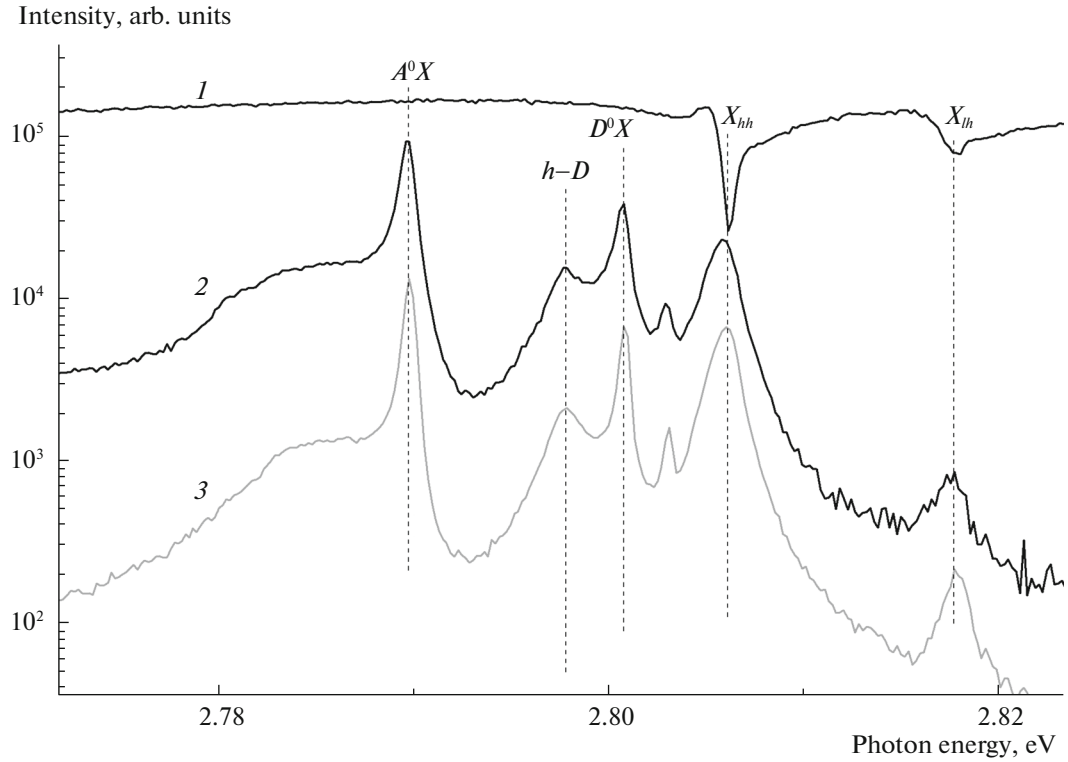

Fig. 4. Spectra of reflection (*1*) and exciton luminescence of the initial sample (*2*) and the sample after annealing (*3*) at 5 K. A^0X and D^0X designate the emission of excitons localized at neutral acceptors and donors, respectively.

ation of free excitons. It is worth noting that the line (*Y*, 2.61 eV) related to extended defects is clearly detected after secondary annealing in the spectrum of the epitaxial layers [22]. This is consistent with the data of X-ray structural analysis, which show that prolonged annealing leads to the appearance of signs of plastic relaxation. However, the analysis of exciton emission confirms that epitaxial films remain unrelaxed even after annealing.

Figure 4 shows the spectra of exciton-related PL of the sample under consideration before and after annealing and also the reflection spectrum. The characteristic (of strained films) splitting of hole states is observed in the shown spectra: two high-energy lines (at 2.8059 and 2.8176 eV) represent the PL of free excitons with the involvement of heavy (X_{hh}) and light (X_{lh}) holes, respectively. The identification of these lines with emission from heavy and light excitons is supported by the presence of sharp resonances in the reflection spectrum; the positions of these resonances coincide with those of luminescence lines and the ratio of the intensities of these resonances correspond to this ratio for the resonance lines (see curve *1* in Fig. 4). The positions of these lines and the difference in energy between them are typical of the case of the pseudomorphous growth of ZnSe on GaAs [23, 24]. The observed width of the excitonic resonances (1.5–2 meV) is sufficient for attaining the mode of strong binding of excitons and photons in microcavities based on epitaxial ZnSe films, which can be of interest for the fabrication of polariton lasers based on the above structures.

4. CONCLUSIONS

It is found that Se hillocks formed (with a density on the order of 10^8 cm^{-2}) on the surface of epitaxial ZnSe films can be removed by annealing in a hydrogen atmosphere at a temperature higher than 260°C. The roughness of the surface of the epitaxial layers significantly decreases as a result of annealing and does not exceed 0.5 nm. Annealing in a hydrogen atmosphere leads to a drastic decrease in the intensity of impurity–defect emission in relation to edge luminescence and also to narrowing of the emission lines related to free excitons and to an increase in their intensity compared to the emission lines of bound excitons. Thus, all obtained data indicate that annealing in a hydrogen atmosphere leads to a significant improvement in the structural properties of epitaxial layers. In this case, any deterioration in the luminescence properties of epitaxial ZnSe films is not observed. The attained width of exciton-related resonances is sufficient for attaining the mode of strong binding of excitons and photons in microcavities based on epitaxial ZnSe films.

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