

Free-exciton spectra in heteroepitaxial ZnSe/GaAs layers

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The free-exciton photoluminescence (PL) and reflection spectra of metal-organic vapor-phase-epitaxy grown ZnSe/GaAs epilayers with a thickness greater than that of the strain relaxation thickness were studied experimentally and theoretically for temperatures in the range $T=10\text{--}120$ K. Calculations were performed in the framework of absorbing and reflecting dead layer models, using single and two-oscillator models, both including and neglecting spatial dispersion. The results rule out the explanation that the fine structure in the free-exciton PL spectra derives from thermal strain splitting and polariton effects, if this structure is not accompanied by a corresponding structure in reflection. It was shown that this structure in the PL spectrum originates mainly from light interference caused by the presence of a dead layer in the near-surface region, with the thickness of the dead layer depending on the excitation intensity. A correlation between the measured and inherent free-exciton spectra was established.

I. INTRODUCTION

The fine structure of the free-exciton (FE) photoluminescence (PL) spectra is often observed in heteroepitaxial ZnSe/GaAs epilayers. It has been shown by many authors (see Ref. 1) that if the ZnSe layer thickness h is less than the strain relaxation thickness $d_{\text{rel}} \approx 1 \mu\text{m}$,² this fine structure is determined by the splitting of the valence band of ZnSe into light-hole (lh) and heavy-hole (hh) subbands, due to the compressive strain in ZnSe caused by the lattice mismatch between the epilayer and substrate. This splitting gives a corresponding structure in PL and reflection spectra. A similar fine structure in the PL spectrum is also observed, however, if $h \gg d_{\text{rel}}$. This effect has been attributed to the tensile strain caused by the difference in thermal-expansion coefficients of the ZnSe layer and the GaAs substrate,³ and this view has become the most popular explanation in recent years. Other authors believe that this structure relates to the peculiarities of the spatial and energetic distribution of polaritons⁴⁻⁷ (see also Refs. 53-57 in Ref. 1). However, nei-

ther point of view allows one to give a satisfactory explanation of experimentally observed phenomena like the increased distance between spectral features with rising temperature,^{4,8} the abnormally small value of the FE_{hh} band half-width [about 1.5 meV at $T=6$ K (Ref. 1)] together with the higher value of FE_{hh} half-width that is sometimes observed, as well as the change in the intensity relation between the lh and hh in the PL spectrum during the transition to the tensile strain, while no corresponding changes are seen in reflection.

A similar fine structure was previously observed in the FE PL cathodoluminescence and reflection spectra of cubic bulk crystals ZnSe, ZnTe, and CdSe, as well as in spectra of A excitons in CdS and CdSe.⁹⁻²⁰ This structure was explained both by polaritonic effects,^{5,14-17} and by absorption reversal effects.^{9,11,19,20} However, despite the large amount of work performed, a satisfactory agreement between the experimental results and theoretical description was not achieved within the framework of these models. The absorption reversal effects and their influence on the shape of FE PL line

were ignored in most papers devoted to the investigation of PL in ZnSe epilayers. The influence of the self-absorption on excitonic spectra in ZnSe/GaAs was investigated in Ref. 21, but only the intensity ratio between free- and bound-exciton emission was discussed. The nonuniqueness of the interpretations and considerations leads to an ambiguity in estimating the FE resonance position and the binding energies of bound excitons and, thus, of impurity ionization energies.

In this work we present the results of an experimental and theoretical investigation of the PL and reflection spectra of heteroepitaxial ZnSe/GaAs, carried out with the aim to establish the physical cause of the observed structure in FE PL spectra in epilayers with $h > 1 \mu\text{m}$.

II. EXPERIMENT

The ZnSe samples were grown on GaAs(110) substrates by metal-organic vapor-phase epitaxy in a horizontal reactor, at the temperatures between 330 and 480 °C. The growth details and precursor combinations are described in Ref. 22. The layer thickness was $h = 0.2\text{--}4 \mu\text{m}$. All the layers were undoped and of high resistivity ($\rho \approx 10^{10}\text{--}10^{11} \Omega \text{cm}$) as measured by capacity-voltage characterization. PL was excited using a cw He-Cd laser with $\lambda_{\text{exc}} = 325.0 \text{ nm}$ and in some cases 441.6 nm. The excitation intensity I_{exc} was varied between 0.02 and 10 W/cm². The measurements of polychromatic reflection spectra were performed using a glow band lamp. The spectra were recorded using a diffraction monochromator and a photomultiplier, and then corrected to include the spectral sensitivity distribution of the monochromator-photomultiplier system. The spectral resolution was typically less than 0.3 meV (10–80 K) and <1 meV (above 80 K). Several dozen samples were characterized by recording both the PL and reflection spectra.

III. CALCULATIONS

For calculation of the PL spectra reliable data about the spectral position of the excitonic resonance are necessary, which is only obtained from the analysis of the reflection spectra. For this analysis we used mainly the classical model of an excitonic oscillator²³ with the following parameters; resonance frequency ω_0 (or energy E_0), damping parameter Γ , exciton polarizability $4\pi\alpha$, and background dielectric constant ϵ_b . Distortion of the observed reflection spectrum can be caused by interference in near-surface layer (the so-called ‘‘dead layer’’^{23,24}). Its appearance can be determined by the finite size of the exciton itself,²⁵ as well as by the influence of the surface electric field.^{26,27}

We used both the reflecting dead layer model by Hopfield and Thomas²³ and the absorbing multilayer model taking into account the variable excitonic absorption coefficient inside of each j th sublayer. In the last case, the near-surface region was approximated by a set of thin homogeneous layers with equal thickness d_j . Thus the gradual change of excitonic absorption was replaced by a steplike one with a separate dielectric function in each j th layer. Our calculations showed that the reconstruction of a reflection spectrum based on a model of the inhomogeneous absorbing layer with thickness d_i gives the same result as in the case of using a model of a reflecting layer with thickness d_{eff} . The relation

d_i/d_{eff} is nearly constant, and is about 1.33.

To take into account the possible contribution of residual or thermal strain in reflection spectra, calculations were also performed in the framework of the two-oscillator model proposed in Ref. 25. The spatial dispersion was included in some cases by using the well-known formula for calculating the effective refractive index.²⁴ It was shown earlier that the reflectivity spectra are not very sensitive to the choice of additional boundary conditions (ABC’s)—it is possible to obtain similarly good fits with different ABC’s.²⁷ We used the ABC’s proposed by Pekar,²⁸ which are reasonable for Wannier-type excitons.

To calculate the reflection spectra $R(\omega)$ taking into account the interference in the dead layer, we used the methods described in Refs. 24 and 25. The resonance frequency ω_0 , the damping parameter Γ , and the effective width of dead layer d_{eff} were varied during the fitting of the experimental $R(\omega)$. The optimization of parameters was carried out by the method of coordinatewise descent.²⁹ In this procedure only one set of output parameters results from successive iterations, independent of the initial parameter values.

The evaluation of excitation levels used in our experiments shows (with a created carrier concentration of about 10^{12} cm^{-3} at $I_{\text{exc}} = 0.1 \text{ W/cm}^2$, estimated by the generation rate) that degeneracy does not take place. Thus the radiation line shape of free excitons is described in the steady-state case, in a one-coordinate approximation, by the equation³⁰

$$I_{\text{pl}}(\omega) = \rho(\omega)[1 - R'(\omega)] \int_0^h n_{\text{ex}}(x) \exp[-k(\omega)x] dx, \quad (1)$$

where h is the epilayer thickness, $\rho(\omega)$ is the probability per unit time of emitting a photon with the frequency ω by exciton annihilation, $R'(\omega)$ is the reflectivity of light with frequency ω incident on the surface from within the epilayer, $k(\omega)$ is the absorption coefficient of ZnSe, and $n_{\text{ex}}(x)$ is the exciton concentration. The probability $\rho(\omega)$ was calculated as the probability of the process reciprocal to the absorption of photons.⁹

Under the conditions of quasiequilibrium between the free-carrier gas and excitons, the value of $n_{\text{ex}}(x)$ can be obtained using:³⁰

$$n_{\text{ex}}(x) = \frac{I_{\text{exc}} k \tau}{L^2 - k^2 - 1} \left[\frac{k - \frac{S}{D_{\text{ex}}}}{\frac{1}{L} - \frac{S}{D_{\text{ex}}}} \exp\left(-\frac{x}{L}\right) - \exp(-kx) \right], \quad (2)$$

where S is the surface recombination rate, k is the absorption coefficient on the pump wavelength, τ is the total lifetime of the exciton, and D_{ex} and L are the diffusion coefficient and the diffusion length of the excitons, respectively.

The parameters ω_0 and Γ were obtained from the ‘‘best fitting’’ of the experimental reflection spectra, and were used to calculate $I_{\text{pl}}(\omega)$. Using these parameters, the reflection coefficient of excitonic radiation incident on the surface from within the epilayer $R'(\omega)$ was calculated.

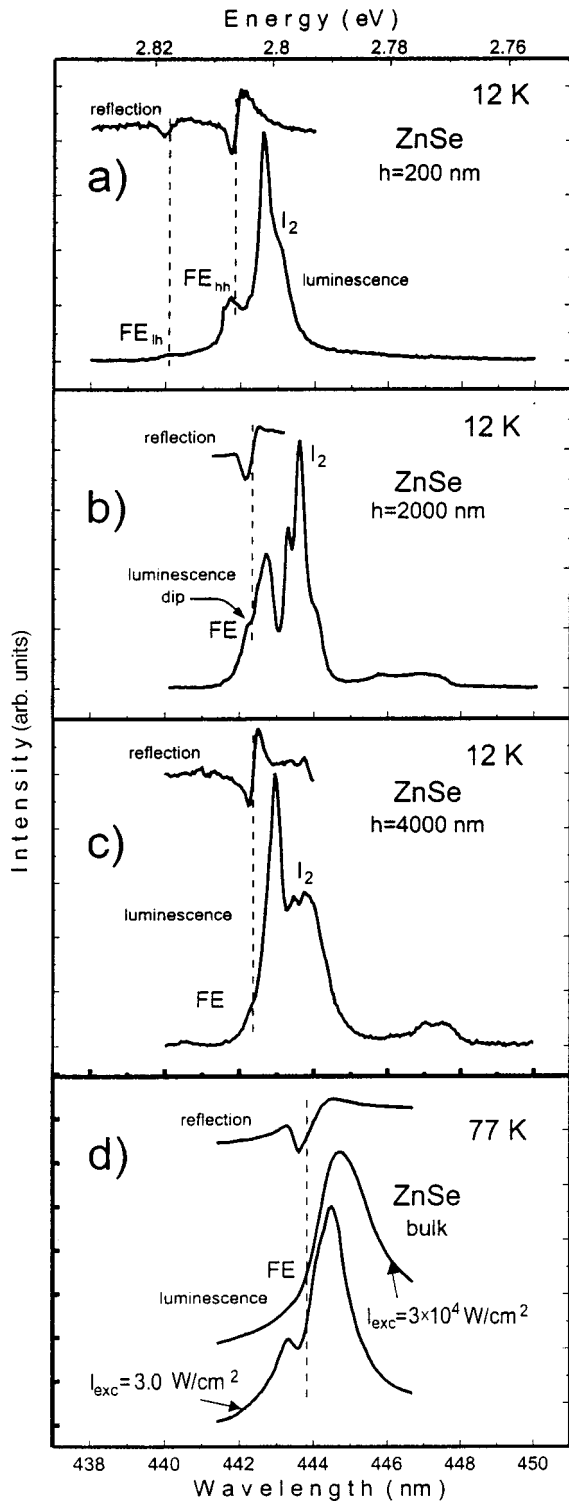


FIG. 1. PL and reflection spectra of three ZnSe/GaAs samples with different thicknesses h [(a)–(c)] and of bulk ZnSe at different excitation intensity (d). For PL in (a)–(c), $I_{\text{exc}}=0.1 \text{ W/cm}^2$.

IV. RESULTS AND DISCUSSION

Figure 1 shows the PL and reflection spectra in exciton region for ZnSe/GaAs layers with various thicknesses, grown under different conditions. For comparison, the spectra of bulk ZnSe are also included ($h=\infty$). The layer with a thickness of 200 nm shows well-resolved lh and hh excitonic features in both PL and reflection spectra [Fig. 1(a)], while

the reflection spectra of epilayers with a thickness greater than d_{cr} do not exhibit any such structures. The PL bands of these samples, however, show a fine structure with a dip corresponding to the excitonic resonance position according to the reflection spectrum [Fig. 1(b)]. In some cases the PL spectra have a structure similar to that described in Ref. 1 with the dominant emission line 2.799–2.800 eV having a half-width of about 3 meV [Fig. 1(c)]. A similar doublet structure is also present in PL spectra of the bulk samples, and is found to disappear with rising excitation intensity [Fig. 1(d)]. The reflection spectrum has no split structure, and shows a resonance position at 2.8025 eV, which is the typical value for the perfect bulk crystals.³¹

The displacement of the observed PL peak from the resonance position together with its relatively small half-width allows us to attribute this peak to the long-wave wing of a FE line modified, for example, by reabsorption, or to the bound exciton analogous to I_2^* reported in Ref. 32 (see also Ref. 17 in Ref. 1). To resolve this uncertainty, PL and reflection spectra of this sample were measured in the temperature range between 10 and 80 K. The result is shown in Figs. 2(a) and 2(b). At elevated temperatures the thermal quenching of all I_2 lines takes place. The 2.8-eV peak becomes dominant and shifts toward lower energies, with a concomitant shift in the band gap. Simultaneously, a dip appears on the short-wavelength wing of this peak, which becomes better resolved with increasing temperature. At $T>25 \text{ K}$ the doublet structure of the FE spectrum is formed. The distance between the peaks ΔE increases with temperature from $\Delta E=4.2 \text{ meV}$ at $T=30 \text{ K}$ to $\Delta E=7 \text{ meV}$ at $T=70 \text{ K}$ [Fig. 2(a)]. The calculation of ΔE caused by the thermal-induced tensile strain using formula and data from Ref. 3 yielded $\Delta E=4.2 \text{ meV}$ at $T=10 \text{ K}$ and $\Delta E=3.7 \text{ meV}$ at $T=80 \text{ K}$, showing the opposite tendency to the experimental observation. The reflection spectra remained unstructured and did not change their shape except for broadening [Fig. 2(b)]. The energetic position of the dip in the PL spectra corresponds well to the half-height position between maximum and minimum values in the reflection spectrum. This can then be used as a first approximation for the estimation of the FE resonance position.³³ From these results it is possible to attribute the 2.8-eV peak in emission spectra to the long-wave wing of the broader FE band. In the case represented in Fig. 1(b), the FE PL band is less distorted; however, the dip on the FE resonance position is also visible, and the PL maximum is shifted from the resonance position.

The increase of the distance between the components of the FE PL doublet with rising temperature, the persistent shape of the reflection spectra, and the increase of the distance between the PL maximum and the presumed FE resonance position with temperature contradict the explanation of the doublet structure by the thermal strain splitting. Moreover, the same structure is observed in bulk ZnSe, where such a splitting effect is definitively absent [Fig. 1(d)]. The numeric simulations of the experimental reflection spectra, in the framework of the two-oscillator model, give a satisfactory agreement with the experiment only if $\omega_1 \approx \omega_2$, with an accuracy ΔE less than 1 meV. The great difference between the expected and observed values of the splitting may be explained if we take into account that the investigated layers are in fact nonmonolithic, i.e., they contain at least three

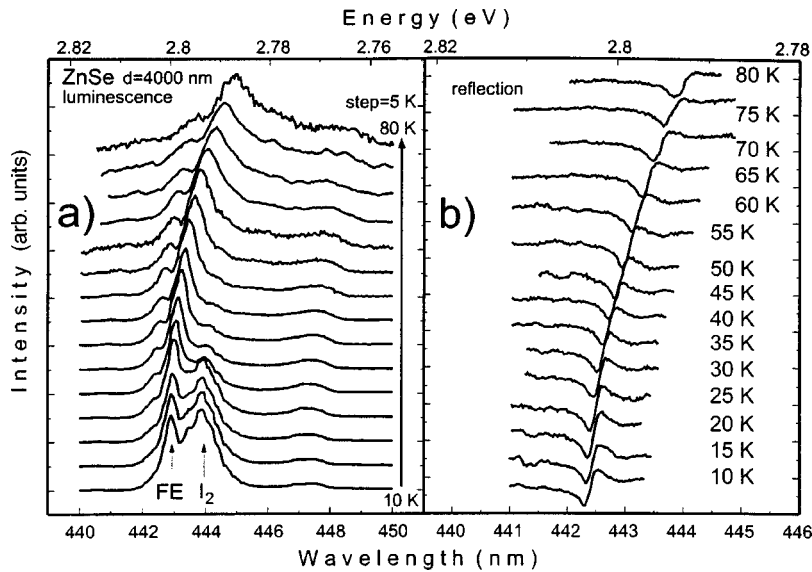


FIG. 2. PL (a) and reflection (b) spectra of the ZnSe epilayer with $h=4 \mu\text{m}$ in a temperature interval of 10–80 K.

sublayers: a lattice-matched strained layer near the substrate, a dislocation-rich relaxation region, and a relaxed upper layer. The presence of a the dislocation-rich region, which can be plastically deformed during cooling and heating of the sample, can reduce the thermal strain in the upper layer from which the PL spectra are observed. This can also explain why in some samples the ZnSe epilayers roll up after release from the substrate, while in other samples they do not.³⁴

From the above results we conclude that the observed doublet structure of the FE PL spectra cannot be explained by the thermal strain splitting. The remaining two mechanisms that can be employed to explain this behavior are polaritonic effects and the influence of reabsorption (or interference) of radiation in the near-surface region of crystal.

The temperature region where the effects of spatial dispersion should be taken into account can be estimated by calculating the temperature dependence of the Γ parameter. The critical temperature T_{ct} of the transition to classical dispersion model is marked by the beginning of a strong temperature broadening of the exciton absorption band (or, equivalently, of the increase of the Γ parameter).³⁵ From the temperature dependency of Γ calculated from the reflection spectra, the value of $T_{cr} \approx 55$ K was obtained. The observation that doublet structure in the FE PL spectra at the liquid nitrogen temperatures becomes even better resolved with rising temperature, and its persistence in our samples up to 150–180 K,²² together with the absence of the characteristic spike structure in reflection, allows us to rule out the polaritonic mechanism. As the energy position of the excitonic resonance E_0 does not depend on whether the spatial dispersion is included or neglected in the calculation procedure, we only used a model of free excitons, taking into account their diffusion, self-absorption, reabsorption, and interference effects for further calculations.

From the fitting of the reflection spectra, we calculated the values for the exciton resonance energy E_0 using both single-oscillator and two-oscillator models. The calculated values of E_0 are presented in Fig. 3. It is clear that E_0 agrees with the dip position in the PL spectra. In Fig. 4, some examples of experimental and calculated reflection spectra are given, demonstrating the excellent agreement between them. The values of the dead layer thickness d obtained from the

“best fit” to the experimental reflection spectra in the frame of the Hopfield-Thomas model is 8 ± 1.5 nm for the whole temperature region, which is comparable to the value of exciton diameter in ZnSe [about 9–10 nm (Ref. 36)]. Thus the shape of the reflection spectra could be explained entirely by the conventional model of the light interference in the dead layer, without the need to involve any additional mechanism.

Now we will discuss the role of excitonic self-absorption in formation of the observed structure in the FE PL spectra. Since the excitonic absorption coefficient at E_0 in ZnSe is high enough [10^4 – 10^5 cm^{-1} (Refs. 9, 37, and 38)], it leads not only to a change of the intensity ratio between the FE and bound-exciton emission discussed in Ref. 21, but to a significant modification of the FE PL line shape itself. Many attempts have been made in order to calculate the PL line shape for this case using models of the self-absorption and

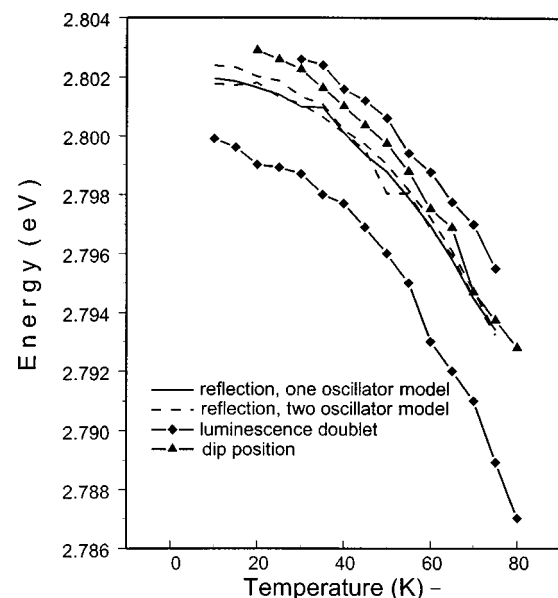


FIG. 3. The temperature dependence of the PL peak positions (diamonds), the dip position (triangles), and FE resonance position calculated using a single-oscillator model (solid curve) and a two-oscillator model (dashed curve).

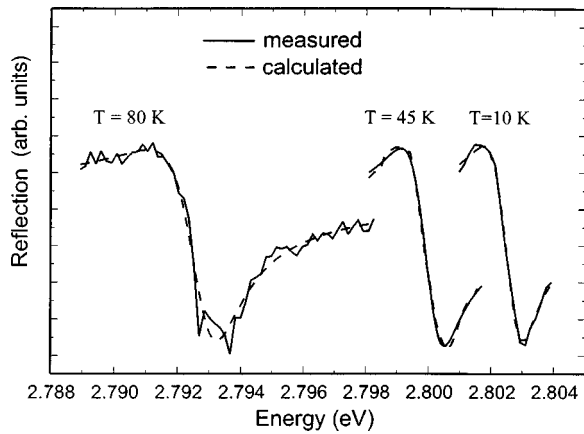


FIG. 4. Experimental (solid curves) and calculated (dashed curves) reflection spectra for different temperatures: $T=80$ K ($E_0=2.792$ eV, $\Gamma=1.865$ meV, and $d_{\text{eff}}=9.5$ nm); $T=45$ K ($E_0=2.799$ eV, $\Gamma=1.17$ meV, and $d_{\text{eff}}=7.8$ nm); $T=10$ K ($E_0=2.802$ eV, $\Gamma=1.05$ meV, and $d_{\text{eff}}=9.0$ nm).

diffusion of free excitons or polaritons (see, for example, Refs. 5, 9, 39, and 40). However, an acceptable agreement between theory and experiment was only obtained in these works by making the assumption of an anomalously high diffusion length (up to several micrometers⁹). Our own calculations of the PL spectra including only the diffusion of excitons and self-absorption of their radiation, also yield similar results. The diffusion length necessary to obtain an acceptable fit to the experimental spectrum is 8–10 μm , which exceeds even the highest layer thickness used in this work (4 μm). Thus this is unacceptable, and leads to the conclusion that to only consider self-absorption effects is an insufficient explanation of the observed results. An additional mechanism is required to obtain a good agreement with experimental data.

To our knowledge, nobody has attempted up to now to consider the influence of the light interference in the dead layer on the line shape of FE emission in ZnSe, although the interference effects in reflection spectra are well known. We performed the corresponding calculations in this work. By fitting the experimental PL spectra, the exciton diffusion coefficient D and the exciton lifetime τ were estimated ($D=30$ cm^2/s , $\tau=150$ – 200 ps), which gave the diffusion length $L=0.67$ – 0.77 μm . These values agree very well with the experimental results measured by other authors for ZnSe epilayers, $\tau=100$ – 150 ps,⁴¹ $\tau=164$ – 209 ps, $D=16.8$ – 28.4 cm^2/s , and $L=0.52$ – 0.77 μm .⁴² The corresponding spectra for $T=45$ K (at this temperature the I_2 excitonic emission is suppressed) are given in Fig. 5, demonstrating a quite good agreement between the experimental and calculated curves. It is possible to recover the real shape of inherent excitonic PL spectrum if we use $d_{\text{eff}}=0$ (curve 3 in Fig. 5). However, the value of the dead layer thickness obtained from the “best fit” is noticeably larger than that evaluated from the reflection spectrum for the same sample and temperature. For the spectra given in Fig. 5, $d_{\text{eff}}=29$ nm. The most probable cause of this discrepancy is the influence of the laser pump light on the charge state of the surface.

To check this assumption, the reflection spectra were recorded with and without laser illumination of the sample surface. The intensity of He-Cd laser illumination I_i was

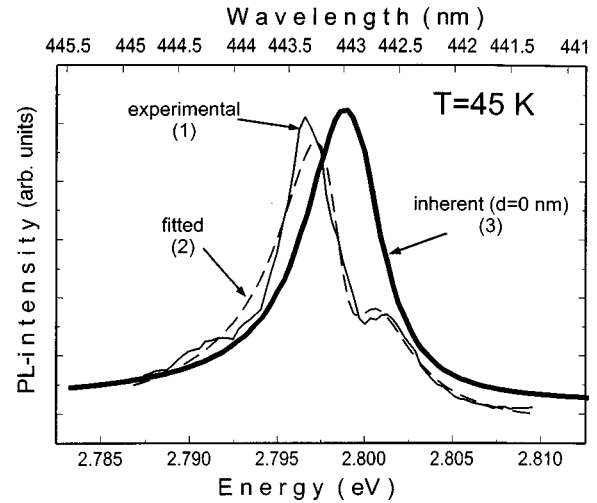


FIG. 5. Experimental (curve 1), fitted (curve 2), and inherent ($d_{\text{eff}}=0$) PL spectra of ZnSe/GaAs at $T=45$ K, when the bound excitonic emission is sufficiently quenched.

varied in order to estimate the dependence $d_{\text{eff}}(I_i)$. The spectra are given in Fig. 6. They demonstrate a significant change in the reflection spectra under illumination. The fitting of these spectra gives values of $d_{\text{eff}}=4$ nm (without illumination) and $d_{\text{eff}}\approx 17$ nm with illumination. In several samples, saturating values of d_{eff} up to 47 nm were calculated; this is

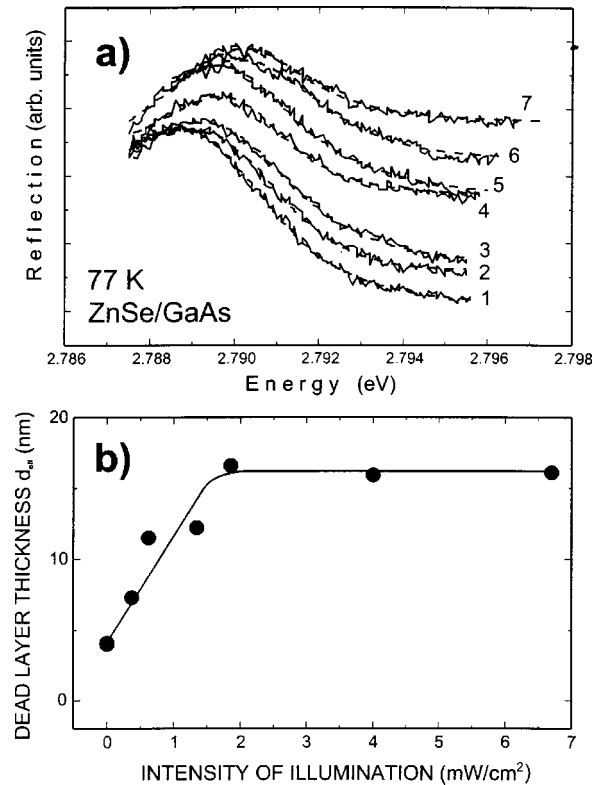


FIG. 6. (a) Experimental reflection spectra (solid curves) recorded without illumination of the sample (1) and with illumination by the He-Cd laser radiation (2–7), and the corresponding calculated spectra (dashed curves). Intensity of illumination I_i , 0.37 (2), 0.62 (3), 1.34 (4), 1.85 (5), 4.0 (6), and 6.7 (7) mW/cm^2 . (b) The calculated dependence of the value of d_{eff} on the illumination intensity.

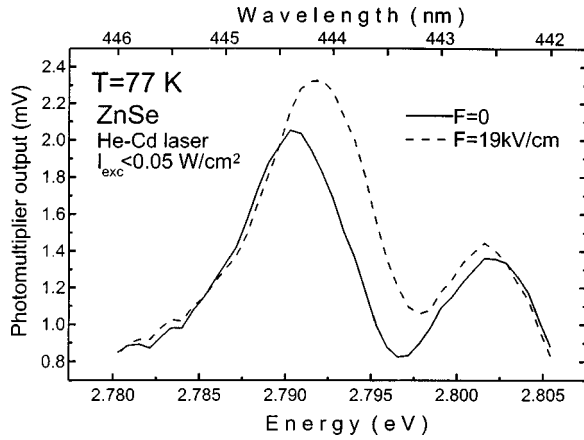


FIG. 7. The dip region of the FE PL spectrum of ZnSe without (solid curve) and with application of an external electric field whose direction is opposite to that of the surface field (dashed curve).

the same order of magnitude as the values estimated from the PL spectra. The changes in reflection disappear relatively fast after the illumination is stepped (the reflection spectra recorded immediately after cessation have the same shape as before the illumination). No differences in the reflection spectra recorded with different illumination times were detected. The changes in the reflection spectra were observed under illumination by laser radiation with both wavelengths of 325.0 and 441.6 nm. The dependence $d_{\text{eff}}(I_i)$ [Fig. 6(b)] saturates at relatively low I_i (about $2 \times 10^{-3} \text{ W/cm}^2$)—much less than the values of I_{exc} commonly used for recording PI spectra. These results provide an unambiguous evidence for the influence of laser pump light on the dimension of dead layer in our samples, and, thus, on the observed shape of the FE PL spectra.

The influence of the external illumination on the reflection spectra is well known, and widely used in photoreflectance spectroscopy. However, the most discussed mechanism of such influence is the screening of the near-surface electric field, formed by charged surface states and by the nonequilibrium carriers produced by the pump light.⁴³ The opposite case, when the illumination by light both with $h\nu > E_g$ and $h\nu < E_g$ leads to an increased surface field and to the broadening of a dead layer, was also observed and discussed by many authors for ZnSe (Ref. 10) and CdS,^{44–47} and confirmed by an investigation of photoconduction spectra in CdS.⁴⁸ In our case the concentration of excited carriers (about $10^{11}–10^{12} \text{ cm}^{-3}$) is not high enough to screen the electric field. If a N₂ laser is used for excitation, the dip in the spectra disappears because of screening of the surface field, as can be seen from Fig. 1(d). The conditions necessary for screening are discussed in Ref. 43. The most likely cause for the appearance and/or broadening of the dead layer during our PL measurements is that the near-surface electric field is formed by the surface states becoming charged during illumination.^{20,45–47} The resultant effect depends on the concurrence between this effect and the screening of the surface charge by the nonequilibrium carriers. In our case of a relatively low concentration of nonequilibrium carriers, an increase of the space-charge area during illumination takes place. Figure 7 gives direct evidence of the influence of electric field on the FE PL spectra in ZnSe excited by He-Cd

laser radiation with an intensity of about 0.05 W/cm^2 . If an external positive electric voltage is applied, subtracting the external field strength from the field formed by surface states, the dip in the PL spectrum decreases. From these measurements we found that the surface charge was negative. This effect was already investigated in more detail in CdS.¹⁹

The near-surface field can lead (i) to the ionization of FE states, (ii) to the drift of carriers, and (iii) to a decrease of an exciton binding parameter. The last two effects can lead to the decrease of FE concentration in the near-surface layer, and to the appearance of a gradient of concentration causing the self-reabsorption or self-reversal effect.¹⁹ They cannot lead to the appearance of a reflecting dead layer completely devoid of excitonic states at values of the electric field strength less than the FE ionization field F_{cr} . Therefore, the main mechanism in the formation of a dead layer is the ionization of the free excitons by the electric field. The surface field and the corresponding surface charged state density n_s could be roughly estimated assuming an electric-field distribution $F(x) = F_s \exp(-x/l)$, where l is the screening length and F_s is the surface field, if we set $x = d_{\text{eff}}$, $l = (\epsilon_0 \epsilon k T / n e^2)^{1/2}$, $n = I_{\text{exc}} \tau / h \omega_{\text{exc}} L$, and $F(d_{\text{eff}}) = F_{\text{cr}}$. For excitation by He-Cd laser radiation with $\lambda = 325 \text{ nm}$ and $I_{\text{exc}} = 0.1 \text{ W/cm}^2$ we obtain $n \approx 0.5 \times 10^{12} \text{ cm}^{-3}$ and $l \approx 2.3 \mu\text{m}$ (for $T = 80 \text{ K}$). The critical field of exciton ionization⁴⁹ $F_{\text{cr}} = 1.5 E_{\text{ex}} / e a_B \approx 50 \text{ kV/cm}$, for the exciton binding energy $E_{\text{ex}} = 20 \text{ meV}$ and the exciton radius $a_B = 4.87 \text{ nm}$.³⁶ Since $d_{\text{eff}} \ll l$, $F_0 \approx F_{\text{cr}}$ and $n_s = \epsilon \epsilon_0 F_0 / e \approx 2 \times 10^{11} \text{ cm}^{-2}$ if we assume the single-charged surface states. The corresponding volume concentration is about 10^{16} cm^{-3} , which is comparable to the typical value of the background impurity concentration. But the role of external atoms adsorbed on the surface seems to be more important. Since the surface density of adsorbed atoms such as oxygen^{50,51} often exceeds the background impurity concentration, the value of n_s seems to be quite reasonable. Knowing the values of n_s and I_i , corresponding to the saturation of the dependence $d_{\text{eff}}(I_i)$, and taking into account the steady-state excitation, one can estimate the effective time of discharge of the surface states τ_d . For the case illustrated by Fig. 6(b), $\tau_d \approx 0.1 \text{ ms}$. Thus from an investigation of the FE PL spectra the density of the charged surface states can be estimated.

V. CONCLUSION

From this work the following general conclusions can be drawn.

(i) The main cause of the doublet structure with a dip in the resonance position in FE PL spectra of ZnSe/GaAs epilayers with a thickness above $1 \mu\text{m}$ is light interference in a near-surface dead layer free of excitons. The width of this layer was estimated to be about 30–40 nm in our experiments.

(ii) The dead layer with a thickness $h \gg 2a_B$ appears to originate from the ionization of FE states by a surface electric field. The field is formed by surface states that becomes negatively charged due to illumination by the pump laser light used for PL excitation. The surface density of the single-charged states was evaluated to be about $2 \times 10^{11} \text{ cm}^{-2}$. These states can most probably be formed by atoms such as oxygen adsorbed on the surface.

(iii) The comparison between the FE PL and reflection spectra should be carried out taking into account the drastic change of reflection spectra under conditions when the PL spectra are recorded. The real position of the FE resonance could be estimated only by a detailed calculation of reflection spectra, taking into account the influence of the near-surface dead layer.

(iv) The position of FE resonance in ZnSe/GaAs epilayers with $h > 1 \mu\text{m}$ is the same as reported in the literature for perfect bulk ZnSe samples (2.802–2.8025 eV), although the observed FE PL peak can be shifted by several meV toward lower energies from this position.

(v) From the experimental PL and reflection spectra, the values of the excitonic lifetime τ , the diffusion coefficient D , and the diffusion length L were estimated as τ

$= 150\text{--}200 \text{ ps}$, $D = 30 \text{ cm}^2/\text{s}$, and $L = 0.67\text{--}0.77 \mu\text{m}$. These values are in very good agreement with experimental results recently obtained by other authors.

(vi) The fitting procedure used in this paper can be used as a tool to recover the shape of inherent excitonic emission from the PL spectra distorted by reabsorption, self-absorption, and interference effects, in cases when the spike structure caused by polaritonic effects or splitting is not observed in reflection.

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