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Photoluminescence of ZnSe–ZnS Single Quantum Wells Grown by Vapour Phase Epitaxy *

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We study the photoluminescence (PL) of ultra thin layer ZnSe quantum wells in ZnS barriers. Samples with different well widths are grown by vapour phase epitaxy and the PL spectra of these samples are measured by the excitation of a 500 W Hg lamp. The peak positions of the bands coming from the excitonic luminescence show a larger blueshift with respect to the energy of free excitons in the ZnSe bulk material. The observed variation of the full width at half maximum and peak position of the bands in the spectra with the well width are interpreted to the formation of the ZnS_xSe_{1-x} alloy layer due to the interdiffusion in the interfaces between ZnSe and ZnS. According to the behaviour of the excitons in the smaller conduction band offset, the exciton binding energy is estimated from the dependence of the PL intensity on the temperature. From this result, excitons seem to show nearly three-dimensional characteristics.

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In recent years, ZnSe-based quantum well structures have attracted more interest due to their extensive applications in short wavelength light emitting devices.[1,2] The quality of these devices depends to a large extent on the quality of the interfaces between the two materials in the quantum well structures. Photoluminescence (PL) is extensively studied in these quantum wells because the spectral line shape and width of the excitonic luminescence bands are very sensitive to the quantum well structures.

For example, Yao *et al.*[3] reported that the luminescence broadening in quantum wells was caused by fluctuations associated not only with the quantum confinement effect along the growth direction, but also with the lateral quantum confinement effect in the quantum slabs formed on islands and valleys at the interface. Tishchenko *et al.*[4] observed the spectrum which related to the shift in the ground energy level of excitons with the quantum well width due to the formation of localized excitonic states in the interface of the quantum wells. In this letter we report the PL results of ZnSe–ZnS single quantum wells (SQWs) grown by vapour phase epitaxy (VPE). Luminescence peaks for the quantum well structures show a larger blueshift and broadening with respect to that of free exciton emission in the ZnSe bulk material. This is attributed to the formation of the ZnS_xSe_{1-x} alloy layer in the interfaces of the quantum wells due to the diffusion between the ZnSe and ZnS layers. In such a structure, the behaviour of three-dimensional (3D) like excitons is caused by the delocalization of the electron in the smaller conduction band offset. The exciton binding energy is estimated by measuring the PL spectra at different temperatures, indicating nearly 3D characteristics for the free excitons.

In our experiment, ZnSe–ZnS SQWs were grown by VPE on a (100) GaAs substrate. The source materials were ZnSe and ZnS powders. Each of these was filled into completely separate tubes and was supplied through completely separate paths. The samples were grown by alternating feeding of each source with H_2 carrier gas. The source temperatures of ZnS and ZnSe were 900°C and 980°C, respectively. The GaAs(100) substrate temperature during growth was 550°C. The sample structure consists of a 500 nm thick ZnS layer followed by a ZnSe SQW and a 100 nm ZnS layer. The thicknesses of the ZnSe well layers used in this study were 14, 25 and 36 Å. PL spectra of the above samples were measured by the excitation of a 500 W Hg lamp. The sample was immersed directly into liquid nitrogen in an optical Dewar, or was attached to the cold finger of an optical cryostat in conjunction with a cryogenic refrigerator. The latter system can cool the sample down to ∼10 K. The PL from the sample was dispersed through a monochromator and detected by a photomultiplier tube followed by a photon counter. The light from the Hg lamp was suitably attenuated by a neutral density (ND) filter to change the excitation intensity. Figure 1 shows the typical PL spectra of a ZnSe–ZnS SQW with a 25 Å thick ZnSe well width. The solid and dashed lines in Fig.1 present the spectra at 77 K excited by a Hg lamp at 313 and 365 nm, respectively. From Fig.1, we notice that an intense band in the high-energy region and a weaker broadband in the lower-energy region are located at 391 and 478 nm, respectively. The result indicates that the luminescence comes from the same energy level or centre under two excitation energies, although the PL intensity under 313 nm line excitation is stronger than that of PL under 365 nm line excitation.

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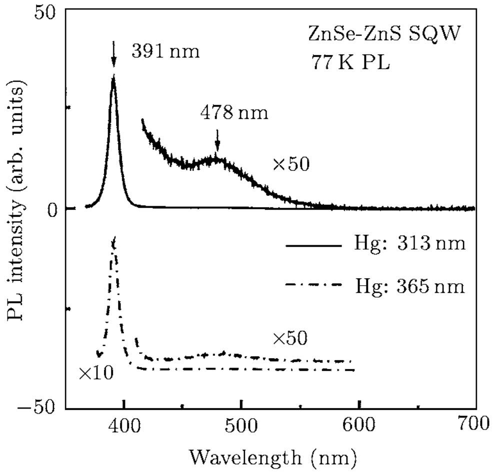

Fig. 1. PL spectra of a ZnSe–ZnS SQW with a 25 Å well width at 77 K excited by 313 and 365 nm lines of a Hg lamp.

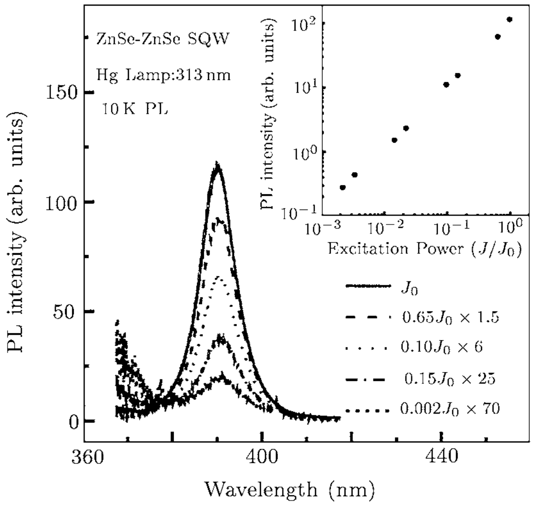

Fig. 2. PL spectra with different excitation powers of a ZnSe–ZnS SQW with a 25 Å well width at 77 K. The inset shows the dependence of excitation powers J on the PL intensity I at the peak position of 391 nm.

Figure 2 gives the spectra at 77 K excited by 313 nm with different excitation intensities. With the increasing excitation power, the PL intensity becomes increasingly stronger and no peak shift is observed. The insert in Fig. 2 shows the dependence of excitation power J on the PL intensity I for the band at 391 nm. The luminescence intensity is linearly proportional to the excitation power in the above excitation range, which seems to suggest that the measured PL band at 391 nm originates predominately from an exciton recombination process.[5] Under 313 nm light excitation, the absorption occurs dominantly in the ZnS layer, since the ZnS layer is much thicker than the ZnSe layer. Excitons created in ZnS layers flow into the ZnSe well layer and then recombine together with excitons created in ZnSe layer to give luminescence. Actually, we observed the free excitonic luminescence from the ZnS layers in a short wavelength region. More detailed results will be reported elsewhere. When the photon energy of the excitation light source is less than the bandgap of ZnS, only the ZnSe layer can absorb the excitation light. Therefore, the PL intensity of the band given by the broken line in Fig. 1 is weaker by approximately one order of magnitude. As for the band at 478 nm in Fig. 1, it may be caused by the interface disorder or mismatch dislocation. However, the origin is not clear.

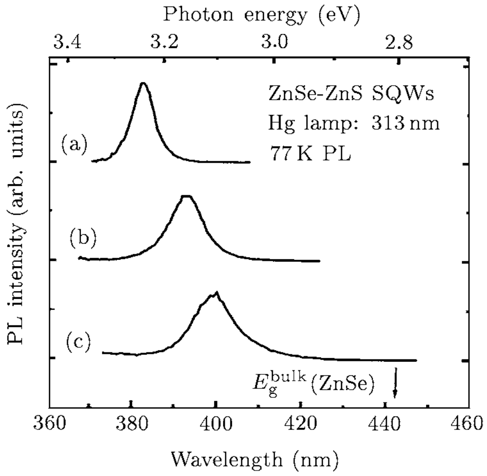

Fig. 3. PL spectra of ZnSe–ZnS SQWs with different well widths at 77 K. The arrow indicates the bandgap energy of the ZnSe bulk material with ZnSe layer thicknesses of: (a) 14 Å; (b) 25 Å; (c) 36 Å.

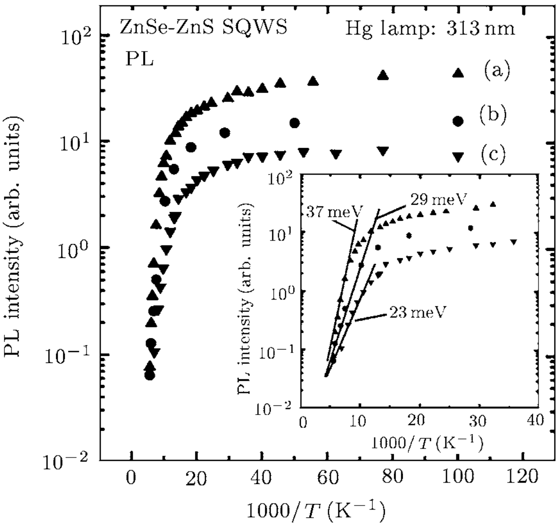

Fig. 4. Temperature dependences of PL intensity for samples excited by the 313 nm Hg line. The inset gives the thermal activation energies estimated in the higher-temperature region for the above samples with ZnSe layer thicknesses of: (a) 14 Å; (b) 25 Å; (c) 36 Å.

Figure 3 exhibits the spectra of samples (a)–(c) with 14 Å, 25 Å and 36 Å thick ZnSe well widths, respectively, which are measured at 77 K by using the excitation of 313 nm light. The bands observed in Fig. 3 are located at 383 nm (3.23 eV), 391 nm (3.17 eV) and 400 nm (3.10 eV) for the 14 Å, 25 Å and 36 Å SQW systems, respectively. These results show that the peak positions of the band shift to the higher-energy side with the decreasing well width, suggesting that the band is related to the quantum energy level of the ZnSe well layer. From Fig. 3, it is found that the full width at half maximum (FWHM) of the bands becomes broader with the increasing well widths, which are 52, 76 and 87 meV for samples (a), (b) and (c), respectively. This result differs from that reported in Ref. [6], in which the linewidth broadening for the PL band with the decreasing well width is due to the fluctuation of the well width. Compared to the result of Ref. [6], the peak position in our experiment is a distinct blueshift for the samples with the same well width. To explain the observed blueshift and broadening of the bands, we suggest that the interdiffusion is caused in the interfaces between the ZnSe layer and ZnS layer due to the higher growth temperature (550°C). For ultra-thin quantum wells, such diffusion leads to the formation of the $\mathrm{ZnS}_x\mathrm{Se}_{1-x}$ alloyed well layer. Because the composition x decreases gradually with the increase of the depth within the ZnSe well layer, the x value in the thicker well layers is larger than that in the thinner well layers. This results in the broadening of the PL band with the increasing well width.

In order to verify this point, temperature dependences of the PL spectra are analysed for the above three samples (a)–(c), as shown in Fig. 4. We can see that the thermal activation energies equal 23, 29 and 36 meV for the quantum wells with ZnSe well layers of thicknesses of 36, 25 and 14 Å, respectively. Because the confined quantum energy levels are enhanced with decreasing well width, thermal quenching of the luminescence in the high-temperature region cannot be explained by the electron release from the well layer to the barrier layers. For the ZnSe and ZnS systems, the conduction band offset is so small that the electrons cannot be effectively confined in an electronic well. Particularly, the formation of the $\mathrm{ZnS}_x\mathrm{Se}_{1-x}$ alloy layer by interdiffusion between ZnS and ZnSe results in a very small conduction band offset. In our quantum well structure, the excitons are created dominantly by Coulomb interaction between the electrons and holes. In contrast, for the deep potential well system, the dominant contribution to the electron–hole pair (exciton) is the confinement effect of the quantum wells. Thus, the spread of the electrons into the ZnS barrier partially preserves a 3D characteristic; the excitons seem not to be purely 2D quasi-particles. The thermal quenching in the high-temperature region (Fig. 4) is considered to be due to the decomposition of the excitons. The experimental values obtained in Fig. 4 really reflect the exciton binding energy. The exciton binding energy is known to be enhanced with the decreasing well width due to the confinement effect. Liu *et al.*[7] reported the binding energy of excitons bound to neutral donors in two-dimensional semiconductors numerically by the spherical effective mass approximation. In Ref. [8], the free-exciton binding energy can be expressed by $E_b = 4E_0/(\alpha - 1)^2$, where E_0 is the effective Rydberg constant for the bulk exciton and α is the dynamic space fractional dimension which measures the anisotropy of the electron–hole Coulomb interaction. $\alpha = 3$, 2 or 1 gives, respectively, $E_b = E_0$, $4E_0$ or ∞, corresponding to the well-known results of the integer dimension models. In a real quantum well structure, α changes continuously between 3 and 2. For $E_0 = 21$ meV from the exciton binding energy of a ZnSe bulk material,[6] our results calculated by Eq. (1) give $\alpha = 2.51$, 2.70 and 2.91 for $E_b = 37$, 29 and 23 meV, respectively. These values are higher than those reported in Ref. [9], in which $\alpha = 2.35$ was given for the ZnSe(11)–ZnS(60) SQW. Therefore, we believe that the free excitons are of nearly 3D characteristics in our quantum well structures. On the other hand, the enhancement of the exciton binding energy with decreasing well width indicates a partly 2D characteristic due to holes confined in a higher potential well.

In conclusion, we have studied the optical properties of ZnSe–ZnS SQWs grown by VPE. The photoluminescence at 77 K exhibits a strong excitonic emission with a larger blueshift with respect to the energy of the free excitons in a ZnSe bulk material. It is considered that the $\mathrm{ZnS}_x\mathrm{Se}_{1-x}$ alloy layers are caused by the interdiffusion between the two materials building quantum structures. This leads to the formation of quite a small conduction band offset and the exciton seems not to be a purely 2D particle in this structure. The excitonic binding energy is estimated from the dependence of the PL intensity on the temperature according to the behaviour of excitons in the smaller conduction band offset. The blueshift of a PL emission peak with decreasing well width is attributed to the $\mathrm{ZnS}_x\mathrm{Se}_{1-x}$ alloy layer formed in the well layer and the confinement effect of holes in the hole well.

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