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Well-width dependence of the emission linewidth in ZnO/MgZnO quantum wells

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Abstract

Photoluminescence (PL) spectra were measured as a function of well width (L_W) and temperature in ZnO/$Mg_{0.1}Zn_{0.9}O$ single quantum wells (QWs) with graded thickness. The emission linewidth (full width at half maximum) was extracted from the emission spectra, and its variation as a function of L_W was studied. The inhomogeneous linewidth obtained at 5 K was found to decrease with increasing L_W from 1.8 to 3.3 nm due to the reduced potential variation caused by the L_W fluctuation. Above 3.3 nm, however, the linewidth became larger with increasing L_W, which was explained by the effect related with defect generation due to strain relaxation and exciton expansion in the QW. For the homogenous linewidth broadening, longitudinal optical (LO) phonon scattering and impurity scattering were taken into account. The LO phonon scattering coefficient Γ_{LO} and impurity scattering coefficient Γ_{imp} were deduced from the temperature dependence of the linewidth of the PL spectra. Evident reduction of Γ_{LO} with decreasing L_W was observed, which was ascribed to the confinement-induced enhancement of the exciton binding energy. Different from Γ_{LO}, a monotonic increase in Γ_{imp} was observed with decreasing L_W, which was attributed to the enhanced penetration of the exciton wave function into the barrier layers.

Keywords: ZnO/MgZnO quantum well, photoluminescence, linewidth

Background

ZnO has been attracting much attention recently due to its potential applications in light-emitting devices in the ultraviolet spectral region. An important issue in enhancing the emitting efficiency of optoelectronic devices is the bandgap engineering to form a low-dimensional structure [1-4]. ZnO/MgZnO quantum well (QW) has been considered as one of the most promising structures due to its larger oscillation strength, enhanced binding energy in the excitonic region[1], and tunability of operating wavelength[2]. Up to now, this structure has been demonstrated on various substrates such as $ScAlMgO_4$ [5], ZnO [6], sapphire [2], and silicon [7]. The optical properties have been investigated widely, including quantum confinement effect [5-7], quantum-confined Stark effect (QCSE) [8-10], temperature dependence of excitonic emission [11-13], localized characteristics of excitons [14-16], and so on. Besides, the linewidth of absorption or photoluminescence (PL) is also crucial to understand the fundamental physics and optical properties of semiconductor microstructure. On the one hand, the structural quality of the QW can be characterized by studying the inhomogeneous broadening generally induced by the well width (L_W) fluctuation and alloy disorder. On the other hand, the value of carrier-scattering parameters in semiconductors, such as longitudinal acoustic phonon, longitudinal optical (LO) phonon, and impurity scatterings, can be extracted from the homogeneous broadening [17,18]. In addition, for optoelectronic device applications such as the laser diode, the linewidth has a direct effect on performance and, especially, is directly related to the lasing threshold. Thus, the linewidth measurement is also of critical importance in the performance of optoelectronic device based on QW. Sun et al. [11] investigated the homogenous linewidth broadening of the excitonic absorption peak in ZnO/MgZnO multi-QWs. Effective reduction of the exciton-LO phonon coupling with decreasing L_W was observed. However, more detailed study of the dependence of emission linewidth broadening on L_W was not reported due to the

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difficulty in sample preparation. In this paper, a special ZnO/$Mg_{0.1}Zn_{0.9}O$ single QW sample, in which the L_W was continuously changed from 1.4 to 7.5 nm, was used to evaluate the PL linewidth-broadening mechanisms. It was found that inhomogenous broadening, LO phonon scattering, and impurity scattering contributed to the PL linewidth, and all of them were strongly dependent on the L_W. A detailed analysis of the results was conducted.

Methods

ZnO/$Mg_{0.1}Zn_{0.9}O$ single QW was grown by a metalorganic chemical vapor deposition system. Al_2O_3 $(11\bar{2}0)$ wafers were used as substrates because of the larger critical thickness for ZnO layer-by-layer growth [19]. The sample consists of a three-layer $Mg_{0.1}Zn_{0.9}O$/ZnO/$Mg_{0.1}Zn_{0.9}O$ sandwich structure. The growth temperatures of the $Mg_{0.1}Zn_{0.9}O$ barrier layer and ZnO well layer were 425°C and 475°C, respectively. By introducing a gradient in the growth rate across the sample, a graded layer thickness was obtained. The details of the growth procedure and method to determine the L_W can be found elsewhere [2,9]. In order to mark the sample position, a thin film of Au metal was deposited on the sample surface followed by an opening of hole arrays using standard photolithography and liftoff processes [13]. The holes with a diameter of 5 μm were used for the PL measurements, whereas the area without holes was covered with the Au metal. The sample was then characterized by micro-PL spectroscopy from 5 to 300 K. A continuous He-Cd laser operating at 325 nm was used as the excitation source. A reflective objective lens was applied to focus the laser beam to a diameter of approximately 5 μm into the holes. The luminescence from the sample was collected by the same objective lens, dispersed by a spectrometer, and detected using a charge-coupled device. By conducting the laser beam to different holes, the luminescence from different layer thicknesses was obtained.

Results and discussion

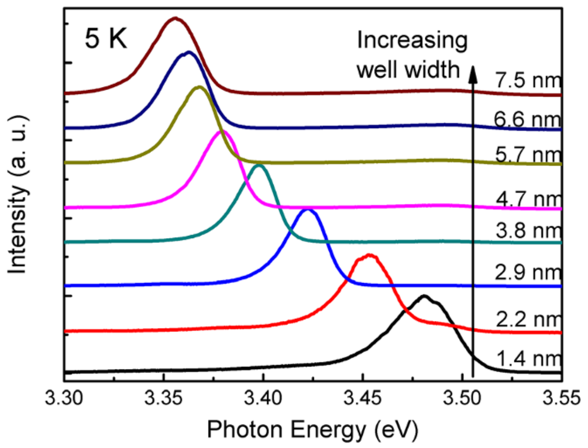

Figure 1 5-K PL spectra of ZnO/$Mg_{0.1}Zn_{0.9}O$ single QWs with different well widths from 1.4 to 7.5 nm. The spectra were normalized and shifted vertically for clarity.

Figure 1 shows the 5-K L_W-dependent PL spectra of the ZnO/$Mg_{0.1}Zn_{0.9}O$ single QWs. All of the spectra are dominated by a strong peak which was assigned to the radiative recombination of the localized excitons, as described in our previous work [13]. The localization is related to the potential variation induced by the L_W fluctuation. Obviously, this emission band shifted to higher energy with decreasing L_W. This can be explained by the well-known quantum confinement effect [5-7]. The emission from the barrier layer located at about 3.61 eV was not observed because of the application of a filter with 350-nm (3.54 eV) cutoff wavelength. It should be also noted that the constant PL peak position (3.61 eV) of the $Mg_{0.1}Zn_{0.9}O$ barrier layers with different layer thicknesses in our previous work is indicative of a negligibly small interdiffusion of chemical species at the ZnO/MgZnO interfaces [13].

The peak energy and full width at half maximum (FWHM) of the excitonic emission spectra are given as a function of L_W in Figure 2, which were extracted from the emission spectra in Figure 1. It is clear that as the L_W increases from 1.4 to 7.5 nm, the emission energy decreases from 3.481 to 3.356 eV. The reason has been explored in our previous work by comparing the measured and calculated QW PL energy [13]. For L_W bellow 3 nm, the reduction of the exciton energy with increasing L_W can be attributed to the weakening of quantum confinement effect. While above 3 nm, the QCSE induces a spatial separation of electrons and holes leading to a further redshift of the PL energy in QW. A good agreement between the measured and calculated PL peak position for the well layer below 3 nm further

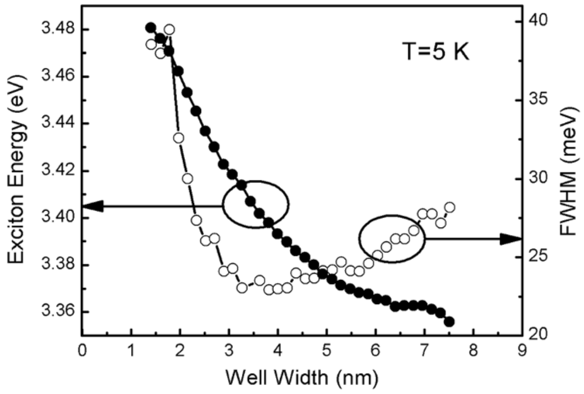

Figure 2 Peak energy and FWHM of exciton emission spectra as a function of well width. The solid and open circles represent the peak energy and FWHM of the exciton emission, respectively.

confirms the negligible interdiffusion of chemical species at the ZnO/MgZnO interfaces. However, the FWHM as a function of L_W behaves differently from peak energy. The FWHM is found to decrease from 1.8 to 3.3 nm and then increase monotonically with increasing L_W. In the small-L_W range, quantum confinement effect is the dominant mechanism. It is known that the confinement potential is sensitive to the L_W, and the same L_W variation may induce larger potential fluctuation in the narrower well so that in this region the FWHM represents an inhomogeneous linewidth broadening mainly induced by L_W fluctuation. Furthermore, as the well thickness increases, the strain in the QW caused by the lattice mismatch between ZnO and $Mg_{0.1}Zn_{0.9}O$ would be relaxed to reduce the accumulated strain energy by generating additional defects. Consequently, a quenching of exciton emission and linewidth broadening occur. Besides, the internal electric field induced by spontaneous and piezoelectric polarizations may play a significant role [20]. It is known that the electrons and holes are separated by a distance along the growth axis by the internal electric field. Therefore, the excitons expand in the QW and can be captured by defects more easily. It is thus easy to infer that the generated defects and spatial redistribution of the electrons and holes must be responsible for the observed increase of FWHM in the large-L_W range.

In order to analyze the homogenous broadening mechanism, temperature-dependent PL measurement was carried out. Figure 3 shows the PL spectra of a typical QW with a L_W of 3.8 nm from 5 to 300 K. The extracted FWHM from the emission spectra in Figure 3 is given as a function of temperature in Figure 4 (solid circles). In agreement with the results reported by Sun et al. [11] and Misra et al. [21], the FWHM grows sublinearly as the temperature increases from 5 to 180 K but rises more sharply as the temperature is raised higher than 180 K. In order to interpret this type of temperature dependence, the experimental FWHM data were fitted using a model that includes three types of broadening mechanisms [17,18]:

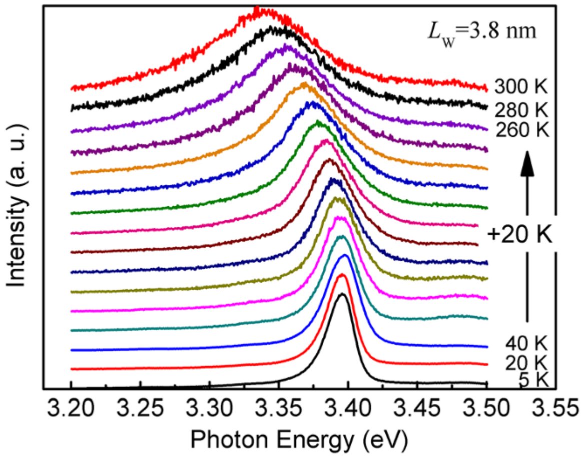

Figure 3 $ZnO/Mg_{0.1}Zn_{0.9}O$ single QW PL spectra with a well width of 3.8 nm at various temperatures. The spectra were normalized and shifted vertically for clarity.

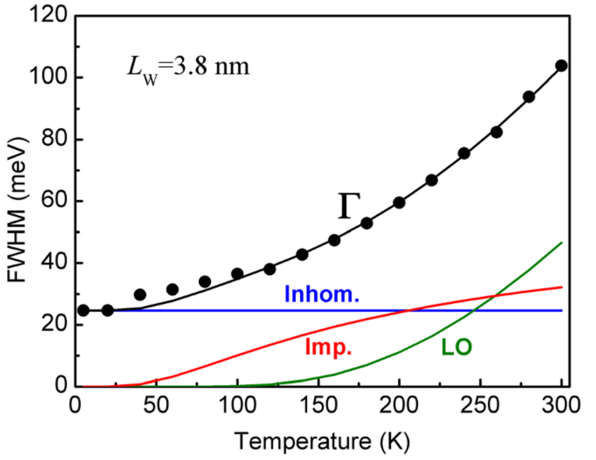

Figure 4 Temperature dependence of experimental and fitted results of FWHM. The solid circles indicate the experimental FWHM extracted from the emission spectra in Figure 3. The solid black line represents the fit according to Equation 1. The colored lines represent the contributions to the FWHM from the inhomogeneous linewidth broadening (Inhom.) and interactions with LO phonons (LO) and impurities (Imp.).

$$\Gamma(T) = \Gamma_{\text{inh}} + \frac{\Gamma_{\text{LO}}}{exp(\hbar\omega_{\text{LO}}/k_B T) - 1} + \Gamma_{\text{imp}}\, exp\left(-\frac{E_B}{k_B T}\right) \tag{1}$$

where Γ_{inh} is the inhomogenous broadening due to the fluctuation of well thickness. Γ_{LO} is the LO phonon scattering coefficient (with a LO phonon energy $\hbar\omega_{\text{LO}}$ = 72 meV), Γ_{imp} is the impurity scattering coefficient, and E_B is the average binding energy of the impurity-exciton complexes. The solid black line in Figure 4 represents the fitted result based on Equation 1. The best fit was obtained for the parameter values Γ_{inh} = 24.6 meV, Γ_{LO} = 708 meV, Γ_{imp} = 57 meV, and E_B = 15 meV. It should be noted that the extracted average binding energy of the impurity-exciton complexes coincides with the donor-exciton localization energy in ZnO [22,23]. Therefore, we speculate that the donors, such as oxygen vacancies [24], zinc interstitials [24], hydrogen [25], etc induced by unintentional n-doping, are the main defects or impurities which broaden the exciton emission spectra.

The individual contributions to the FWHM from inhomogenous broadening and interactions with LO phonon and impurities are presented with colored lines in Figure 4. It is seen that except for inhomogenous broadening, below 250 K, the impurity scattering mainly contributes to the FWHM. As the temperature increases above 250 K, scattering by LO phonons becomes the main temperature-dependent contributor due to the increasing LO phonon population.

We made the same fitting procedure for other QWs and summarized the obtained values of Γ_{LO} and Γ_{imp} for different L_{W}s in Figure 5. It can be seen that there is a monotonic decrease in the Γ_{LO} as the L_{W} is reduced. This result is related to the LO phonon and exciton scattering process via the Fröhlich interaction [26]. We know that 1*s* exciton either is totally ionized into the free electron–hole continuum or scatters within the discrete exciton bands by absorbing one LO phonon with the energy $\hbar\omega_{\mathrm{LO}}$. This process contributes to the exciton linewidth broadening, while the dissociation channel of the excitons into the continuum state by 1-LO phonon absorption is inhibited when the exciton binding energy is larger than the phonon energy. Nevertheless, the transition from 1*s* to other excited exciton states (such as the 2*s* and 2*p* states) is still possible. The exciton binding energy of bulk ZnO is 60 meV, and the LO phonon energy is 72 meV. However, for the ZnO/$\mathrm{Mg_{0.1}Zn_{0.9}O}$ QW, the exciton binding energy will be enhanced as the L_{W} is reduced due to the quantum confinement effect [1]. Therefore, we interpret the strong reduction in the Γ_{LO} as being a manifestation of the fact that with the decrease of L_{W}, the exciton binding energy is enhanced gradually. A similar result has been reported by Sun et al. [11].

On the other hand, different from Γ_{LO}, a monotonic increase in Γ_{imp} is observed with decreasing L_{W}. The coefficient Γ_{imp} is thought to be a measurement for the scattering of shallow donor defects and impurities such as oxygen vacancies, zinc interstitials, hydrogen, etc. Generally, the Γ_{imp} depends on the density of defect and impurity sites. Contrary to the distribution of defects in the ZnO QW with different L_{W}s as indicated in the above analysis, we suppose that defects, impurities, and composition fluctuation in the barrier layers are the dominant scatters. For the narrow QW geometry, the exciton wave function penetrates deeply into the adjacent barrier layers [27], and therefore, the scattering coming from the barrier layers is remarkable. As the well thickness increases, the extension of the exciton wave function into the barrier layers is suppressed; hence, the influence of defect and impurity scattering was sufficiently reduced, leading to a decrease of Γ_{imp} with increasing L_{W}. In addition, in the large-L_{W} range, the defects induced by the strain relaxation in the QW may also contribute to the scattering process, showing a slow decreasing trend in Γ_{imp} with increasing L_{W}.

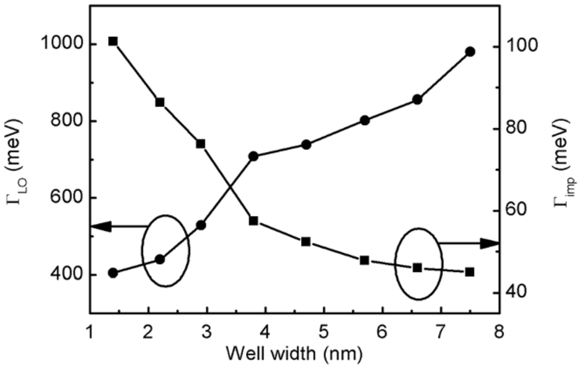

Figure 5 LO phonon scattering coefficient Γ_{LO} and impurity scattering coefficient Γ_{imp} as a function of well width. The solid circles and squares represent Γ_{LO} and Γ_{imp}, respectively.

Conclusions

In conclusion, the broadening mechanisms of the PL excitonic linewidth were investigated in ZnO/$\mathrm{Mg_{0.1}Zn_{0.9}O}$ single QWs with graded thickness. The in homogenous broadening obtained from the 5-K L_{W}-dependent PL spectra decreased first and then increased with increasing L_{W}. This was mainly explained by the reduced potential fluctuation and the generated defects in the QW by strain relaxation, respectively. Furthermore, the homogenous broadening mechanisms including LO phonon scattering and impurity scattering were determined by fitting the temperature-dependent PL linewidth to a theoretical model. The LO phonon scattering coefficient Γ_{LO} and impurity scattering coefficient Γ_{imp} showed different L_{W} dependence. The monotonic decrease in Γ_{LO} with decreasing L_{W} was explained in terms of the confinement-induced enhancement of the exciton binding energy, while the continuous increase in Γ_{imp} with decreasing L_{W} was attributed to the enhanced penetration of the exciton wave function into the barrier layers.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

The work presented here was carried out in collaboration among all authors. XQL and BPZ designed the study. XQL performed the research and prepared the manuscript. BPZ carried out the experiments and analyzed the data. JYZ, LYY, WJL, and XLH analyzed the data and discussed the analysis. ZRQ, SK, and KO participated in the experiments. All authors read and approved the final manuscript.

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