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Temperature dependence of near ultraviolet photoluminescence in ZnO/(Mg, Zn)O multiple quantum wells

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We report on temperature dependence of excitonic photoluminescence (PL) from ZnO/(Mg, Zn)O multiple quantum wells (MQWs). Two kinds of MQWs having different barrier heights grown by laser molecular-beam epitaxy showed significantly different temperature dependences of PL spectra; in ZnO/$Mg_{0.27}Zn_{0.73}O$ MQWs, the PL peak energy at 50–200 K was a monotonically increasing function of temperature, which was opposite to that ascribed by band gap shrinkage. Moreover, spectra taken at 95–200 K encompassed two peaks, both of which originated from recombination of localized excitons. The temperature-induced shift (redshift-blueshift-peak duplication-redshift) at 5–300 K is caused by a change in the exciton dynamics with increasing temperature due to inhomogeneity and the exciton localization effect. On the other hand, the corresponding dependence in ZnO/$Mg_{0.12}Zn_{0.88}O$ MQWs (lower barrier height) was similar to that in bulk II–VI semiconductors. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1357451]

ZnO-based semiconductors have recently attracted much attention due to their potential applications, such as light-emitting devices[1–4] owing to their large binding energy of excitons[5] (59 meV). We previously showed that the mechanism of spontaneous emission in these multiple quantum wells (MQWs) is the radiative recombination of excitons.[6] Excitonic photoluminescence (PL) persisted up to room temperature. Additionally, we observed optically pumped stimulated emission of excitons in ZnO/(Mg, Zn)O MQWs with a low threshold density ($\approx 11\,kW/cm^2$) at room temperature.[7] However, localization, relaxation, and recombination mechanisms of excitons in these MQW structures are not fully understood. In this letter, we describe the temperature dependence of time-integrated PL spectra and the results of time-resolved PL spectra in ZnO/$Mg_{0.27}Zn_{0.73}O$ and ZnO/$Mg_{0.12}Zn_{0.88}O$ MQWs, the well widths of which are 17.5 and 27.9 Å, respectively.

These MQWs were directly grown on lattice-matched $ScAlMgO_4$ substrates by laser molecular-beam epitaxy (LMBE). The structures consist of ten-period MQWs with ZnO wells and 50-Å-thick (Mg, Zn)O barriers. The exciton Bohr radius of ZnO is ≈ 18 Å. Details of the growth procedure and the band gap energy in $Mg_xZn_{1-x}O$ have been given elsewhere.[8] KrF excimer laser pulses were impinged on ZnO single crystals (99.9999%) or $Mg_xZn_{1-x}O$ ceramic targets (99.999%) located 5 cm away from the substrate surface. The films were grown at 600 °C in 1×10^{-5} Torr of pure oxygen (99.9999%). Energy diagrams of conduction and valence bands are shown in Ref. 6. PL and absorption spectra were measured by using apparatuses identical to those used in our previous study.[6] The time-resolved PL measurements were performed with a streak camera in conjunction with a monochromator. Pulsed excitation was provided by the frequency tripled beam of a mode-locked Ti:sapphire laser, which was pumped by an Ar-ion laser. Power of excitation, exciting energy, and overall temporal resolution were $\approx 90\,kW/cm^2$, 4.96 eV, and 30 ps, respectively.

Figure 1(a) shows the evolution of PL (solid line) and absorption (broken line) spectra in ZnO (17.5 Å)/$Mg_{0.27}Zn_{0.73}O$ MQWs over a temperature (T) range from 5 to 300 K. The peak energy of PL spectra (E_{PL}^{pk}) was 3.394 eV at 5 K. No PL band in the barrier layers was observed in this sample.[9] Figure 2(a) shows E_{PL}^{pk} (solid circles and triangles) and the excitonic absorption energy (solid squares) as a functions of temperature. A comparison shows that the dependence of E_{PL}^{pk} is significantly different from that of absorption energy. A Stokes shift between the PL and the absorption peak energies at 5–300 K was confirmed. The absorption peak energies both in ZnO epilayers and in MQWs are monotonically decreasing functions of temperature, as revealed in previous studies.[10,11] This is attributed to the temperature-induced shrinkage of the funda-

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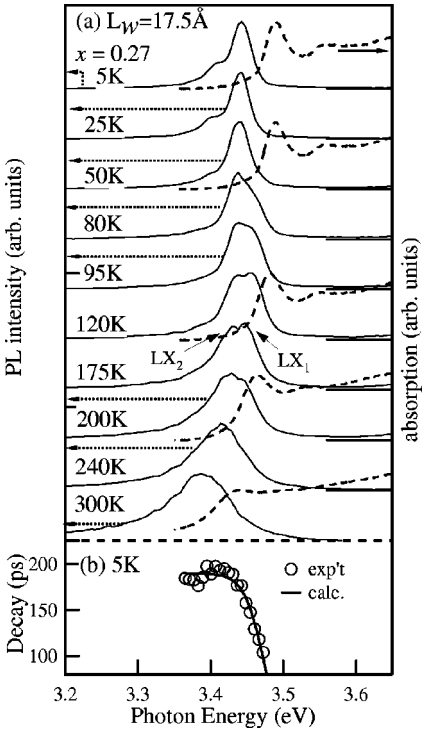

FIG. 1. (a) PL (solid line) and absorption (broken line) spectra in a ZnO (17.5 Å)/$Mg_{0.27}Zn_{0.73}O$ MQW over the temperature range of 5–300 K. All of the spectra have been normalized and shifted in the vertical direction for clarity. (b) PL decay times as a function of monitored photon energy at 5 K in the same MQW. The solid curve is the theoretical one fitted by Eq. (1).

mental energy gap. In general, when a dominant PL peak is assigned to the radiative recombination of localized excitons, its peak energy blueshifts with increasing temperature at low temperatures and redshifts at higher temperatures. The $E_{\mathrm{PL}}^{\mathrm{pk}}$ blueshifts and continuously connects to that of free excitons due to thermal activation of localized excitons. The $E_{\mathrm{PL}}^{\mathrm{pk}}$ of the free-excitonic emission is a monotonically decreasing function of temperature due to the band gap shrinkage. The temperature dependence shown in Fig. 1(a) is, however, different from the abovementioned typical behavior. As the temperature increases from 5 to 50 K, $E_{\mathrm{PL}}^{\mathrm{pk}}$ *redshifts* 3.5 meV. The peak energy of absorption spectra in a ZnO epilayer was almost constant, i.e., band gap shrinkage is negligible over this temperature range. The peak energy of the absorption peak in this MQW redshifts 1 meV over this temperature range. In contrast, the PL peak blueshifts 1.3 meV between 50 and 80 K. By considering the estimated temperature-induced band gap shrinkage of 0.6 meV, the actual blueshift of the PL peak with respect to the band edge is about 1.9 meV over this temperature range. The peak energy of absorption in MQW redshifts 4.5 meV. When the temperature is further increased from 95 to 200 K, a new PL peak arose on the higher-energy side of the main peak, the separation of which was 12–20 meV. It should be noted that the higher PL peak position does not coincide with that of absorption spectra. At a temperature (T) of $T \geqslant 200$ K, the higher PL peak disappeared. The observed redshift in the PL peak energy of 34.0 meV is similar to the band gap shrinkage or redshift in the absorption energy in the MQW.

Figure 1(b) shows PL decay times as a function of monitoring photon energy at 10 K in the ZnO/$Mg_{0.27}Zn_{0.73}O$ MQW. The PL decay time is a monotonically decreasing function of the monitoring photon energy. This behavior is characteristic of localized excitons. This is because the decay of the localized excitons is not only due to radiative recombination but also due to the transfer process to the tail state. If the density of the tail state is approximated as $\exp(E/E_0)$, and if the effective recombination lifetime (τ_{PL}) does not change with emission energy, the observed lifetime $\tau(E)$ can be expressed by the following equation:[12]

$$\tau(E) = \frac{\tau_{\mathrm{PL}}}{\exp[(E - E_{me})/E_0]}, \tag{1}$$

where E_0 shows the degree of the depth in the tail state and E_{me} is the characteristic energy representing the absorption edge. The best fit could be obtained using $\tau_{\mathrm{PL}} = 189.8$ ps, $E_0 = 13.6$ meV, and $E_{me} = 3.6446$ eV.

Figure 2(c) shows the temperature dependence of PL decay times (τ_{PL}) in the ZnO/$Mg_{0.27}Zn_{0.73}O$ MQW with well width of 27.9 Å. The τ_{PL} values increased with elevation in temperature in the range of 5–10 K, while these decreased above 10 K. The decay times were shorter than the temporal resolution of our setup above 120 K. Although the corresponding data in the 17.5-Å-thick MQW were not taken over such a wide temperature range, the temperature dependence of this sample was qualitatively similar.

The recombination mechanism in different temperature ranges can be explained on the basis of Cho's model[13] as follows: (i) For 5 K$<T<$50 K, the relatively long relaxation time of excitons gives the excitons more opportunity to relax down into lower energy tail states caused by the inhomogeneous potential fluctuations before recombining. This is because the radiative recombination processes are dominant compared with nonradiative processes in this temperature

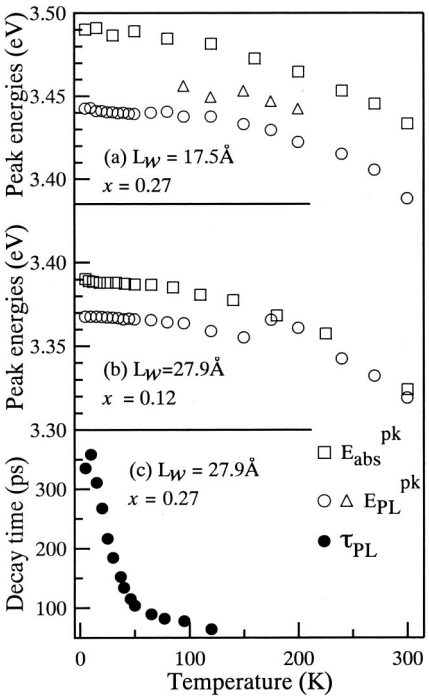

FIG. 2. PL (open circles and triangles) and absorption (open squares) peak positions as a function of temperature in ZnO (17.5 Å)/$Mg_{0.27}Zn_{0.73}O$ (a) and ZnO (27.9 Å)/$Mg_{0.12}Zn_{0.88}O$ (b) MQWs. (c) Temperature dependence of PL decay times, τ_{PL} in ZnO (27.9 Å)/$Mg_{0.27}Zn_{0.73}O$ MQWs at 5–120 K.

range. This behavior produces a redshift in the peak energy position with increasing temperature. (ii) For $50\,\mathrm{K}<T<95\,\mathrm{K}$, the exciton lifetimes decrease with increasing temperature. Thus, these excitons recombine before reaching the lower energy tail states. This behavior enhances a broadening of the higher-energy side emission and leads to a blueshift in the peak energy. (iii) For $95\,\mathrm{K}<T<200\,\mathrm{K}$, further enhancement of high-energy emission components produces a new peak, as seen in Fig. 2(a) (triangles). (iv) Above 200 K, since the excitons are less affected by the temperature-induced rapid change in their lifetime and relaxation rate are increased due to the increased phonon population, blueshift behavior therefore becomes less pronounced. Since the energy of blueshift is smaller than the temperature-induced band gap shrinkage, the peak position again exhibits a redshift behavior. As mentioned earlier, the features for excitonic spontaneous emission in the well layers are significantly affected by the dynamics of excitonic recombination, which vary with temperature, because of band-tail (localized exciton) states arising from layer thickness variations, and/or well-depth fluctuations in the MQWs.

We also examined, for comparison, the temperature dependence of PL peak energy in a MQW having a lower barrier height: a $ZnO/Mg_{0.12}Zn_{0.88}O$ MQW with a well width of 27.9 Å. Figure 2(b) shows the peak energies of PL (circles) and absorption (squares) spectra in this sample. The relevant temperature dependence is also different from the typical (blueshift-redshift) or the earlier-mentioned (redshift–blueshift–peak duplication–redshift) behavior. Temperature-dependent behavior of PL spectra in this case was rather similar to that seen in typical bulk semiconductors or ZnO epilayers.[1,14] In the temperature range of 5–50 K, one dominant peak resulting from a localized exciton recombination was observed. The redshift in the temperature range of 5–150 K is ascribed to band gap shrinkage. This may be because the energy distribution of the localized excitons that can participate the radiative recombination is narrow. With elevation in temperature ($\geqslant 65\,\mathrm{K}$), a new emission band having a free-excitonic origin arises on the higher-energy side and becomes pronounced. This is due to thermal release of localized excitons. The intensity of a free exciton finally overwhelms that of localized excitons at $T\geqslant 175\,\mathrm{K}$.

Two kinds of MQWs having different barrier heights exhibited different exciton dynamics. This is due to the presence or absence of well-depth fluctuation. Since $x=0.27$ (x denoting Mg content) is above the solubility limit,[15] microscopic composition fluctuation is much larger than that in the barrier with $x=0.12$. The inhomogeneity of the band gap energies in the barrier layers induces depth fluctuation and enhancement of the exciton localization energy.[6] These two PL bands (LX_1 and LX_2) observed at 95–200 K are attributed to the radiative recombination of different kinds of localized excitons. The LX_1 (LX_2) band is probably from the excitons localized at the potentials predominantly induced by the well-thickness (well-depth) fluctuation. The temperature dependence of the Stokes shift in the MQW with $x=0.27$ above 200 K may be due to the fact that the localization energy exceeds thermal energy of room temperature ($\approx 25\,\mathrm{meV}$). MQWs of (In, Ga)N/GaN, localization energy of which is much larger than 25 meV, exhibited the similar temperature dependence of the Stokes shift.[16] It should be noted that the Stokes shifts of 47.7 meV in the $x=0.27$ MQW at 5 K is smaller than the binding energy of exciton (81–85 meV), the latter of which is enhanced from the bulk value due to the quantum confinement effect.[17]

In summary, we investigated temperature dependences of time-integrated and time-resolved PL spectra in LMBE-grown ZnO/(Mg, Zn)O MQWs. The peak energy of the excitonic emission exhibited unusual behavior (redshift–blueshift–peak duplication–redshift) with increasing temperature in a $ZnO/Mg_{0.27}Zn_{0.73}O$ MQW. Radiative recombination of excitons in the wells exhibits a significant spectral distribution of times. This distribution is interpreted in terms of localization of excitons by potential fluctuations due to well width and depth variations. The temperature dependence of peak energy is caused by a change in the exciton dynamics due to inhomogeneity and exciton localization, while that in $ZnO/Mg_{0.12}Zn_{0.88}O$ MQW could be interpreted analogously to that in bulk II–VI semiconductors.

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[1] P. Yu, Z. K. Tang, G. K. L. Wong, M. Kawasaki, A. Ohtomo, H. Koinuma, and Y. Segawa, in *Proc. of 23rd International Conf. on Physics of Semicond., Berlin*, edited by M. Scheffler and R. Zimmermann (World Scientific, Singapore, 1996), Vol. 2, p. 1453.
[2] P. Yu, Z. K. Tang, G. K. L. Wong, M. Kawasaki, A. Ohtomo, H. Koinuma, and Y. Segawa, Solid State Commun. **103**, 459 (1997).
[3] Z. K. Tang, G. K. L. Wong, P. Yu, M. Kawasaki, A. Ohtomo, H. Koinuma, and Y. Segawa, Appl. Phys. Lett. **72**, 3270 (1998).
[4] D. M. Bagnall, Y. F. Chen, Z. Zhu, T. Yao, S. Koyama, M. Y. Shen, and T. Goto, Appl. Phys. Lett. **70**, 2230 (1997).
[5] K. Hümmer, Phys. Status Solidi B **56**, 249 (1973).
[6] T. Makino, N. T. Tuan, H. D. Sun, C. H. Chia, Y. Segawa, M. Kawasaki, A. Ohtomo, K. Tamura, and H. Koinuma, Appl. Phys. Lett. **77**, 975 (2000).
[7] A. Ohtomo, K. Tamura, M. Kawasaki, T. Makino, Y. Segawa, Z. K. Tang, G. Wong, Y. Matsumoto, and H. Koinuma, Appl. Phys. Lett. **77**, 2204 (2000).
[8] Y. Matsumoto, M. Murakami, Z. W. Jin, A. Ohtomo, M. Lippmaa, M. Kawasaki, and H. Koinuma, Jpn. J. Appl. Phys., Part 2 **38**, L603 (1999).
[9] Photoluminescence from the barrier layers was observed in ZnO/(Mg, Zn)O single quantum wells.
[10] T. Makino, C. H. Chia, N. T. Tuan, Y. Segawa, M. Kawasaki, A. Ohtomo, K. Tamura, and H. Koinuma, Appl. Phys. Lett. **76**, 3549 (2000).
[11] H. D. Sun, T. Makino, N. T. Tuan, Y. Segawa, M. Kawasaki, A. Ohtomo, K. Tamura, and H. Koinuma, Appl. Phys. Lett. (submitted).
[12] C. Gourdon and P. Lavallard, Phys. Status Solidi B **153**, 641 (1989).
[13] C. Yong-Hoon, B. D. Little, G. H. Gainer, J. J. Song, S. Keller, U. K. Mishra, and S. P. DenBaars, MRS Internet J. Nitride Semicond. Res. **4S1**, G2.4 (1999).
[14] T. Makino, G. Isoya, Y. Segawa, C. H. Chia, T. Yasuda, M. Kawasaki, A. Ohtomo, K. Tamura, and H. Koinuma, J. Cryst. Growth **214/215**, 289 (2000).
[15] A. Ohtomo, R. Shiroki, I. Ohkubo, H. Koinuma, and M. Kawasaki, Appl. Phys. Lett. **75**, 4088 (1999).
[16] S. Nakamura, S. Pearton, and G. Fasol, *The Blue Laser Diode* (Springer, Berlin, 2000).
[17] H. D. Sun, T. Makino, N. T. Tuan, Y. Segawa, Z. K. Tang, G. K. L. Wong, M. Kawasaki, A. Ohtomo, K. Tamura, and H. Koinuma, Appl. Phys. Lett. **77**, 4250 (2000).