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<td>Author(s)</td>
<td>Makino, T.; Tuan, N. T.; Sun, Handong; Chia, C. H.; Segawa, Y.; Kawasaki, M.; Ohtomo, A.; Tamura, K.; Koinuma, H.</td>
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Temperature dependence of near ultraviolet photoluminescence in ZnO/(Mg, Zn)O multiple quantum wells

T. Makino, a) N. T. Tuan, H. D. Sun, C. H. Chia, b) and Y. Segawa
Photodynamics Research Center, RIKEN (Institute of Physical and Chemical Research), Sendai 980-0845, Japan

M. Kawasaki, A. Ohtomo, c) and K. Tamura
Department of Innovative and Engineered Materials, Tokyo Institute of Technology, Yokohama 226-8502, Japan

T. Suemoto, H. Akiyama, M. Baba, S. Saito, and T. Tomita
Institute of Solid State Physics, University of Tokyo, Kashiwa 277-8581, Japan

H. Koinuma d)
Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama 226-8503, Japan

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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/Mg12Zn0.88O 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/Mg12Zn0.88O 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 devices1–4 owing to their large binding energy of excitons5 (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 in ZnO/(Mg, Zn)O MQWs with a low threshold density (≈11 kW/cm2) 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/Mg0.27Zn0.73O and ZnO/Mg0.12Zn0.88O MQWs, the well widths of which are 17.5 and 27.9 Å, respectively.

These MQWs were directly grown on lattice-matched ScAlMgO4 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 Mg1−xZnxO have been given elsewhere.8 KrF excimer laser pulses were impinged on ZnO single crystals (99.999%) or Mg1−xZnxO 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 (99.999%). 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 ≈90 kW/cm2, 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)/Mg0.27Zn0.73O MQWs over a temperature (T) range from 5 to 300 K. The peak energy of PL spectra (EPPL) was 3.394 eV at 5 K. No PL band in the barrier layers was observed in this sample.9 Figure 2(a) shows EPPL (solid circles and triangles) and the excitonic absorption energy (solid squares) as a functions of temperature. A comparison shows that the dependence of EPPL 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-
FIG. 2. PL spectra in a ZnO (17.5 Å)/\textit{Mg}_{0.27}\textit{Zn}_{0.73}\textit{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.

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).

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FIG. 1. (a) PL (solid line) and absorption (broken line) spectra in a ZnO (17.5 Å)/\textit{Mg}_{0.27}\textit{Zn}_{0.73}\textit{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).
range. This behavior produces a redshift in the peak energy position with increasing temperature. (ii) For $50 \, K < T < 95 \, K$, 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 blue-shift in the peak energy. (iii) For $95 \, K < T < 200 \, K$, 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 $\text{ZnO/Mg}_{0.12}\text{Zn}_{0.88}\text{O}$ MQW with a well width of $27.9 \, \text{Å}$. 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.

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 ($\approx 65 \, K$), 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 $T \approx 175 \, K$.

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, microscopical 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. These two PL bands ($L_X^1$ and $L_X^2$) observed at $95–200 \, K$ are attributed to the radiative recombination of different kinds of localized excitons. The $L_X^1$ ($L_X^2$) 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 ($\approx 25 \, \text{meV}$). MQWs of (In,Ga)N/GaN, localization energy of which is much larger than $25 \, \text{meV}$, exhibited the similar temperature dependence of the Stokes shift. It should be noted that the Stokes shifts of $47.7 \, \text{meV}$ in the $x = 0.27$ MQW at $5 \, K$ is smaller than the binding energy of exciton ($81–85 \, \text{meV}$), the latter of which is enhanced from the bulk value due to the quantum confinement effect.

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 $\text{ZnO/Mg}_{0.27}\text{Zn}_{0.73}\text{O}$ 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 $\text{ZnO/Mg}_{0.12}\text{Zn}_{0.88}\text{O}$ MQW could be interpreted analogously to that in bulk II–VI semiconductors.

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