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Temperature quenching of exciton luminescence intensity in ZnO/(Mg,Zn)O multiple quantum wells

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The temperature-dependent behavior of excitonic photoluminescence observed in ZnO/MgZnO multiple quantum wells (MQWs) in the temperature range of 5–300 K is described. In a ZnO/Mg_{0.27}Zn_{0.73}O MQW grown by laser molecular-beam epitaxy, the luminescence was dominated by localized exciton (LE) emission throughout the whole temperature range studied. Luminescence of free excitons (FEs) was not observed. A simple rate equation is used to describe the quenching of LE emission. The activation energy for LE luminescence quenching is of the order of the localization energy of excitons, suggesting that the thermionic emission of the LEs out of the localization potentials leads to nonradiative recombination. In a ZnO/Mg_{0.12}Zn_{0.88}O MQW having lower barriers, the luminescence was dominated by LE emissions at low temperatures, while the FE transition was dominating emissions at temperatures above 175 K. A rate equation assuming one nonradiative recombination channel is used to describe the quenching of the transitions observed. The activation energy for LE luminescence quenching deduced in this sample is also of the order of the localization energy of excitons. The temperature dependences of FE emission intensities are also discussed by using a simple rate equation in which a thermal release effect of LEs toward FEs is taken into account. © 2003 American Institute of Physics. [DOI: 10.1063/1.1563295]

I. INTRODUCTION

ZnO, whose band gap is 3.4 eV at 4.2 K and whose excitonic binding energy is large¹ (59 meV), is the base of a family of compounds (Mg,Zn,Cd)O that has gained much attention recently due to their potential optoelectronic applications in the ultraviolet range. Many optical studies, such as photoluminescence (PL) measurements, have been carried out to try to elucidate the basic properties of ZnO epilayers (see, for example, Refs. 2–11), and much is now known about the basic properties of ZnO epilayers. On the other hand, it is only recently that the basic optical properties of quantum wells (QWs) have begun to be actively investigated. We previously showed that the mechanism of spontaneous emission in multiple quantum wells (MQWs) is a radiative recombination of excitons.¹² Excitonic PL persists up to room temperature. Those excitons are localized in poten-

tial minima due to roughness at the well/barrier interface and/or alloy disorder in the barrier layers. Table I shows the Stokes shift energy (ΔE) between the PL and the absorption peaks and the localization energy of excitons (E_0) in ZnO/Mg_{0.12}Zn_{0.88}O MQWs as a function of the well-layer thickness (L_w). The localization energies have been evaluated from the spectral distribution of the PL decay constants.¹³ Localization, relaxation, and recombination mechanisms of excitons in these MQW structures are, however, not fully understood. In our previous article, we discussed the possible mechanism of unusual “S-shaped”^{14,15} temperature dependence of excitonic PL energies observed in a ZnO/Mg_{0.27}Zn_{0.73}O MQW.¹⁶

In the present work, which is an extension of our previous work,¹⁶ we studied the temperature dependence of the excitonic PL transitions observed in ZnO/Mg_{0.27}Zn_{0.73}O and ZnO/Mg_{0.12}Zn_{0.88}O MQWs in the temperature range of 5–300 K. A particular emphasis was given to the quenching of these transitions, and an explanation in terms of simple rate equations is given in this article. The aim of this study

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TABLE I. Energy difference (ΔE) between absorption peaks and the PL peaks (i.e., Stokes shift)¹² and the localized energy of excitons (E_0)¹³ as a function of well-layer thickness (L_w) obtained in the ZnO/Mg_{0.12}Zn_{0.88}O QW samples and at temperature of 5 K.

Well-layer thickness (Å)	ΔE (meV)	E_0 (meV)
7	40.4	6.5
9	40.2	4.3
13	31.1	3.9
18	26.7	3.3
24	24.9	2.2
28	22.6	2.5
37	22.1	4.4
42	20.7	3.3
47	20.2	3.2

was to obtain a better understanding on the mechanism involved in the temperature-induced reduction of quantum efficiency of these ZnO MQWs. We also deduced the activation energies for quenching of the excitonic emissions.

II. EXPERIMENTAL PROCEDURES

The MQWs were directly grown on lattice-matched ScAlMgO₄ substrates by laser molecular-beam epitaxy (LMBE). The structures consisted of ten-period MQWs with ZnO wells and 50-Å-thick (Mg,Zn)O barriers. Their thicknesses were precisely determined from x-ray diffraction analysis. Magnesium concentrations were determined from the absorption edge energy of the reference alloyed epilayers which were grown under the same condition with that of the relevant QWs. The exciton Bohr radius of ZnO was ≈ 18 Å. Details of the growth procedure and the band-gap energy in Mg_xZn_{1-x}O have been given elsewhere.¹⁷ 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. 12. PL and absorption spectra were measured by using apparatuses identical to those used in our previous study.¹²

III. RESULTS AND DISCUSSION

A. Temperature dependence of PL in ZnO/Mg_{0.27}Zn_{0.73}O MQW

Before discussing luminescence quenching, it would be useful to briefly review temperature-dependent PL spectra in a ZnO/Mg_{0.27}Zn_{0.73}O MQW with a well-layer thickness (L_w) of 18 Å. Temperature dependences of PL and absorption spectra taken for this sample are shown in Fig. 1 of Ref. 16. Figure 2(a) of Ref. 16 also shows their peak energies as a function of temperature taken for the same specimen. The PL spectra were dominated by emission bands resulting from recombination of the localized excitons (LEs) throughout the whole temperature range studied here. An emission band due to a free exciton (FE) recombination was not observed in this sample. Note that the assignment of these bands to LEs and FEs is based on the conclusion made in our previous article.¹⁶ Radiative recombination of the electron-hole pairs

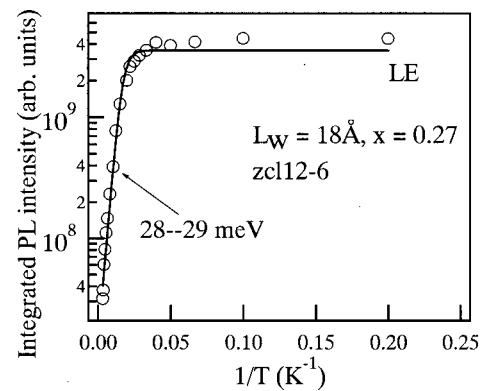


FIG. 1. Temperature dependence of the luminescence intensity of localized exciton bands in a ZnO/Mg_{0.27}Zn_{0.73}O MQW with L_w of 18 Å. Solid lines correspond to least-squares fits using Eq. (2). Activation energy (E_a) obtained from the Arrhenius plot is ≈ 28 meV.

that are spatially separated due to the quantum-confined Stark and Franz-Keldysh effects was observed in ZnO/Mg_{0.27}Zn_{0.73}O MQWs having $L_w \geq 42$ Å at 5 K.¹⁸

Figure 1 is an Arrhenius plot of the integrated intensity of the localized excitonic bands at temperatures of 5–300 K. At temperatures of 5–30 K, intensity of the LE emission remained almost unchanged. At temperatures higher than 40 K, the LE line quenches gradually as shown in Fig. 1. Hereafter, we try to describe the overall behavior of temperature quenching by using the following model because the intensity is described well using a single activation energy.

With the optical injection of excitons, the population governing a certain transition is given by

$$\partial n / \partial t = G - n / \tau_R - n / \tau_{NR}, \quad (1)$$

where n is the density of the photocreated excitons, G is the generation rate, and τ_R and τ_{NR} are radiative and nonradiative lifetimes, respectively. Nonradiative recombination rates are generally thermally activated (regardless of whether they correspond to level depopulation or to the activation of a nonradiative recombination center), i.e., $\tau_{NR} = \tau_0 \exp(E_a/kT)$, where E_a denotes an activation energy.

In a steady state, and since PL intensities are proportional to n/τ_R , the following familiar expression is obtained:

$$I = I_0 / [1 + a \exp(-E_a/kT)], \quad (2)$$

with $a = \tau_R/\tau_0$. Equation (2) will be used in this article. Attention has to be paid when this approximated model is used, which is summarized in Ref. 19. It should also be pointed out that apparent thermal depths are generally lower than optical ones due, for instance, to the existence of excited states, of a crystal field or spin orbit split levels.

The solid line in Fig. 1 is a least-squares fit to its variations using Eq. (2) for the localized exciton intensity. As Fig. 1 shows, the LE intensity is described well using a single activation energy, which amounts to $E_a = 28$ meV for this sample. Here, we compare the activation energy deduced in this study with the Stokes shift of the PL. The energy difference between the PL and absorption peaks is estimated to be 47.7 meV at 5 K. The deduced activation energy is compa-

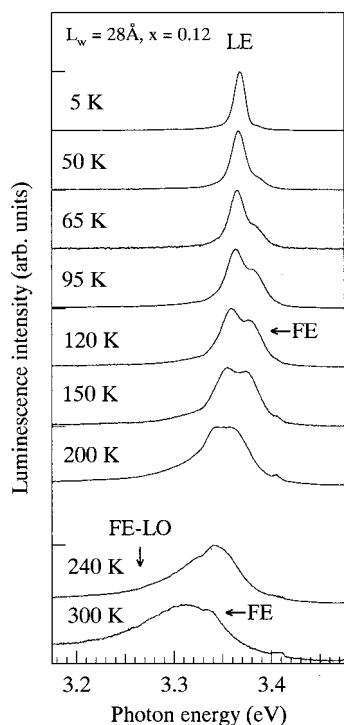


FIG. 2. Temperature dependence of the luminescence spectra of a $\text{ZnO}/\text{Mg}_{0.12}\text{Zn}_{0.88}\text{O}$ MQW with L_w of 28 Å. The spectra have been shifted vertically for clarity. Measured temperatures are shown on the left-hand side. LE and FE denote localized and free excitons, respectively. FE-LO denotes the phonon replica of FE.

rable with or somewhat smaller than the Stokes shift. In general, quenching of the luminescence with temperature can be explained by thermal emission of carriers out of a confining potential with an activation energy correlated with the depth of the confining potential. The observed activation energy is much smaller than the excitonic binding energy (≈ 105 meV), which is somewhat enhanced from the bulk value due to the quantum confinement effect.²⁰ Since the activation energy is also much smaller than the band offsets as well as the band-gap difference between the wells and the barriers, thermal quenching of the excitonic emission is not due to the thermal activation of electrons and/or holes from the ZnO wells into the MgZnO barriers. Instead, it is thought that the dominant mechanism underlying the quenching phenomena of the PL intensity is the thermionic emission of the LEs out of the potential minima caused by potential fluctuations, such as interface fluctuations.^{14,15} Temperature dependence of the PL spectra in a ZnO epilayer grown under similar conditions was described elsewhere.²¹

B. Temperature dependence of PL in $\text{ZnO}/\text{Mg}_{0.12}\text{Zn}_{0.88}\text{O}$ MQW

Figure 2 shows PL spectra of a $\text{ZnO}/\text{Mg}_{0.12}\text{Zn}_{0.88}\text{O}$ MQW with L_w of 28 Å as a function of temperature. At low temperatures, the spectra are dominated by radiative recombination of the localized excitons (LE band). With an increase in temperature, the LE line is progressively quenched to the benefit of the FE band because of thermal detrapping of LEs towards the FEs. Note that the assignment of this

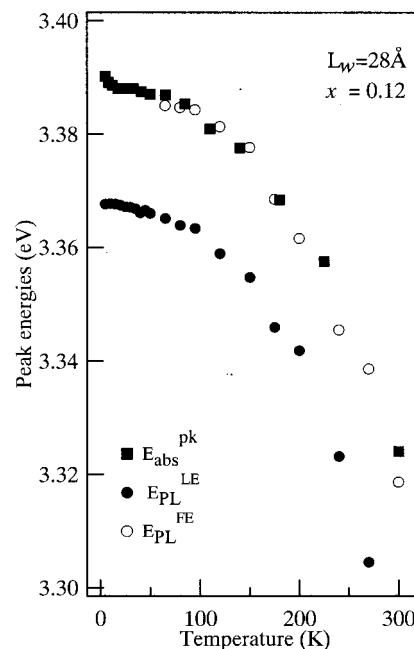


FIG. 3. PL (solid and closed circles) and absorption (solid squares) peak positions as a function of temperature in a $\text{ZnO}(28 \text{ Å})/\text{Mg}_{0.12}\text{Zn}_{0.88}\text{O}$ MQW.

band to FEs is based on the results of temperature-dependent absorption experiments.²² Free exciton emission relatively increases with a rise in temperature. At temperatures above 175 K, the spectra are dominated by free excitons and their longitudinal-optical (LO) phonon replica (FE-LO band).

Figure 3 shows the temperature dependence of PL peak energies for FE and LE bands (open and closed circles) corresponding to Fig. 2 and the excitonic absorption energy (solid squares).²² Figure 3 is therefore a more comprehensive version of Fig. 1(b) of Ref. 16 that includes data on both FE and LE energies. In order to estimate the respective PL intensities, spectra taken at temperatures of 65–175 K were fitted with two Lorentzian functions. Typical fitting results are shown in Fig. 4. Since the LE bands seemed to be ac-

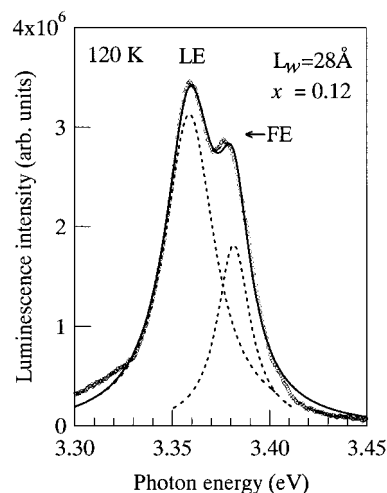


FIG. 4. Photoluminescence spectra in a $\text{ZnO}/\text{Mg}_{0.12}\text{Zn}_{0.88}\text{O}$ MQW with L_w of 28 Å taken at 120 K. Dotted lines correspond to least-squares fits using two Lorentzian functions for decomposition into the LE and FE emission components.

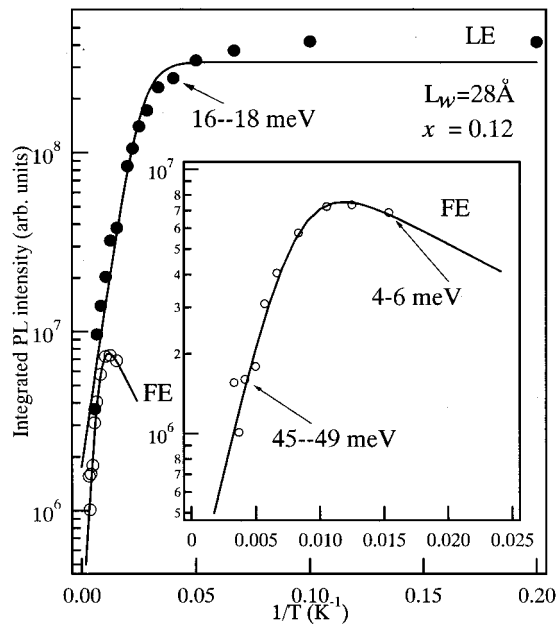


FIG. 5. Temperature dependence of the luminescence intensities of the FE (open circles) and LE (closed circles) bands in a ZnO/Mg_{0.12}Zn_{0.88}O MQWs with L_w of 28 Å. Solid lines correspond to least-square fits using Eqs. (2) and (3). The inset is an expanded view of FE emission intensity.

accompanied by phonon replica of FE-LO at temperatures above 200 K, it was difficult to estimate their emission intensities in this temperature range. The emission intensity of FE at temperatures above 200 K was estimated by fitting these spectra with a single Lorentzian in the emission energy range of 3.3–3.45 eV.

Figure 5 shows Arrhenius plots of the integrated intensities of these two excitonic bands at temperatures of 5–300 K in a ZnO/Mg_{0.12}Zn_{0.88}O MQW with L_w of 28 Å. The intensity of the LE emission bands remained almost unchanged at temperatures of 5–30 K and is then quenched gradually at temperatures above 40 K, as shown in Fig. 5. The overall temperature quenching behavior could be fitted with Eq. (2) assuming one nonradiative recombination channel. The solid line shows the least-squares fit. The activation energy of E_a is estimated to be ≈ 17 meV. Here, we again compare the activation energy with the Stokes shift of ≈ 20 meV. The deduced activation energy is comparable with the Stokes shift. It is also considered here that the mechanism underlying the thermal quenching of the LE-PL is the thermionic emission of the LEs out of the potential minima.

As Fig. 5 shows, the intensity of the FE emission increases at temperatures of 65–95 K, and then decreases at temperatures above 120 K. Temperature dependence of the FE luminescence intensity can be described by the equation

$$I(\text{FE}) = I_1 / [1 + a \exp(-E_a/kT)] \times [\exp(-E_c/kT)], \quad (3)$$

which accounts for both the increase and decrease with temperature of FE intensity, $I(\text{FE})$. Such behavior is induced by thermal detrapping of LEs towards the FEs. Characteristic energy E_c and activation energy E_a amounted to 5–6 and 47 meV, respectively. The estimated characteristic energy is significantly smaller than the localization energy of excitons,

which is equal to the Stokes shift (≈ 20 meV), the reason for which is not clear at this moment. The estimated E_a is much larger than the localization energy but much smaller than the excitonic binding energy (82 meV),²⁰ the reason for which is either unclear at this moment. We believe that in order to precisely estimate the activation energy for FE emission, PL spectra must be measured up to temperatures at which the LE contribution is completely negligible, i.e., temperatures much higher than 300 K. Such measurements are hoped to be carried out in the near future.

In all of the nine ZnO/Mg_{0.12}Zn_{0.88}O MQWs with L_w of 7–47 Å studied in this work, the FE emission bands could be observed at moderate temperatures up to 300 K as seen in the 28-Å-thick MQW (see Fig. 2). On the other hand, this is not the case for the ZnO/Mg_{0.27}Zn_{0.73}O MQWs having the higher barriers. As discussed in Ref. 16, this may be because of the presence or absence of well-depth fluctuation. Since $x = 0.27$ (x denoting Mg content) is above the solubility limit,²³ 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.¹⁶ 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 the thermal energy of room temperature (≈ 25 meV). MQWs of (In,Ga)N/GaN, the localization energy of which is much larger than 25 meV, exhibited temperature dependence of the Stokes shift that is similar to the one obtained in ZnO/Mg_{0.27}Zn_{0.73}O MQWs.²⁴ 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 exciton binding energy.

The PL extinction suggests the presence of nonradiative centers in our ZnO MQWs. As an origin for these nonradiative centers, dislocations are thought to play a role. They are known to be nonradiative centers in GaN at room temperature.¹⁹ In addition, Leroux *et al.*¹⁹ found that the dislocations are partly responsible for temperature-induced PL quenching in GaN epilayers. The dislocations are negatively charged, i.e., attractive for holes.

We have not estimated quantitatively the dislocation density of these MQW grown on lattice-matched substrates studied here. We have recently reported optical properties and the dislocation density of other MQWs grown on *lattice-mismatched* sapphire substrates.²⁴ The dislocation density amounted to $\sim 10^7$ to 10^8 cm⁻². In this case, however, it was impossible to observe the luminescence at room temperature by using the apparatuses identical to those adopted in this study.²⁵ Namely, the excitonic luminescence quenched more rapidly with the temperature rise than the case of the *lattice-matched* MQWs. If we assume that the temperature PL quenching rate is related to the dislocation density, we think that the density is concluded to be significantly smaller than 10^7 cm⁻².

IV. SUMMARY

ZnO/Mg_{0.27}Zn_{0.73}O and ZnO/Mg_{0.12}Zn_{0.88}O MQWs grown using LMBE techniques have been studied by photo-

luminescence as a function of temperature in order to try to elucidate the mechanisms underlying thermal quenching of the excitonic photoluminescences. In the case of a $\text{ZnO}/\text{Mg}_{0.12}\text{Zn}_{0.88}\text{O}$ MQW, the localized exciton band, dominant at all low temperatures, was quenched by thermalization towards the free exciton band. The activation energy of LE luminescence extinction is of the order of the energy of the PL Stokes shift, suggesting that thermionic emission of the LEs out of the localization potentials leads to nonradiative recombination.

In the case of a $\text{ZnO}/\text{Mg}_{0.27}\text{Zn}_{0.73}\text{O}$ MQW, the PL spectra were dominated by LE transitions throughout the whole temperature range studied. The activation energy of LE luminescence extinction is of the order of the energy of the PL Stokes shift, but the activation energy of FE quenching is much smaller than the excitonic binding energy. The reason may be that the temperature range used in this work is insufficient to precisely determine the latter activation energy.

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