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Well-width dependence of radiative and nonradiative recombination times in $ZnO/Mg_{0.12}Zn_{0.88}O$ multiple quantum wells

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A set of $ZnO/Mg_{0.12}Zn_{0.88}O$ multiple quantum wells (MQWs) with well widths, L_w, varying from 6.91 to 46.5 Å has been grown by laser molecular-beam epitaxy. We estimated the L_w dependence of the radiative and nonradiative recombination times of localized excitons at 5 K. Suppression of quantum efficiency can be avoided even in the MQWs having small L_ws studied in this work. Effects of excitonic localization are discussed in order to explain the L_w dependence of radiative recombination time at 5 K. [DOI: 10.1063/1.1396827]

ZnO-based semiconductors are recognized as very promising materials due to the potential application as many optoelectronic devices such as UV light-emitting diodes and laser diodes[1,2] owing to their large binding energy of excitons[3] (59 meV). As demonstrated by the practical light-emitter devices, many semiconductor devices must take advantage of multiple quantum well (MQW) structures for optimized device performance. Many efforts must be devoted toward the understanding, design, and fabrication of ZnO/MgZnO MQWs for light-emitter applications. For the design and fabrication of these MQW structures, one important issue is to maximize the quantum efficiencies (QE), i.e., to maximize the optical emission from the confined states in the well regions and to minimize the optical losses outside the well regions. It has been demonstrated recently that the optical and structural properties of ZnO/MgZnO MQWs were greatly improved by the employment of lattice-matched substrates (room-temperature spontaneous and stimulated emissions of excitons,[4,5] negligible interdiffusion of Mg, and very flat heterointerface.)[6] It is also well known that structural parameters, including both barrier and well widths (L_w) of MQWs, have strong effects on the QE. The mechanisms of L_w dependence of the QE in ZnO/MgZnO MQWs have not yet been investigated. Thus, a systematic study on these MQWs to probe the underlying mechanisms related to the effects of L_w on the QE is needed.

In this study, a set of $ZnO/Mg_{0.12}Zn_{0.88}O$ MQWs with L_w varying from 6.91 to 46.5 Å and a fixed barrier width of 50 Å has been grown by laser molecular-beam epitaxy. Combinatorial-concept aided techniques[7] of our samples suppresses the variations in crystal growth conditions and hence the undesired uncertainty in the deduced spectroscopic results, simply because of the fact that all the nine samples were grown at one time in the same run. Picosecond time-resolved photoluminescence (TRPL) spectroscopy has been employed at 5 K to probe the L_w dependence of the QE. Suppression of the QE can be avoided even in the MQWs with L_w less than 10 Å, indicating the efficient carrier confinement inside the well regions.

The $ZnO/Mg_{0.12}Zn_{0.88}O$ MQW samples with ten periods were directly grown on a 0001-oriented $ScAlMgO_4$ substrate under high vacuum condition, the lattice constant which matches that of ZnO with 0.09%. All the films had a *c*-axis orientation. The well widths of these nine samples were 6.91, 8.95, 12.9, 17.5, 23.5, 27.9, 37.0, 42.3, and 46.5 Å. The well and the barrier layer thicknesses were precisely determined from x-ray diffraction analysis.[5] Excimer laser pulses were impinged to ZnO and $Mg_xZn_{1-x}O$ targets (99.999%).[5] The growth temperature and oxygen pressure were 600 °C and 1×10^{-5} Torr, respectively.

Picosecond TRPL spectroscopy was employed to study the optical properties of these MQWs. A frequency-tripled beam from a mode-locked Ti:Sapphire laser with a repetition rate of 82 MHz, a pulse duration of $\approx$1 ps, and a pumping power of 2–3 μW was used as an excitation source. The excitation energy was 4.946 eV, which is well above the band gap of barrier layers.[5,8] The photoluminescence (PL) was temporally resolved using a streak camera in conjunction with a monochromator. The spectral and temporal resolutions were $\approx$0.3 nm and $\approx$30 ps, respectively.

We confirmed in our previous study[4] that the L_w dependence of the excitonic emission energies in the ZnO well regions (varying from 3.382 to 3.514 eV at 5 K) could be

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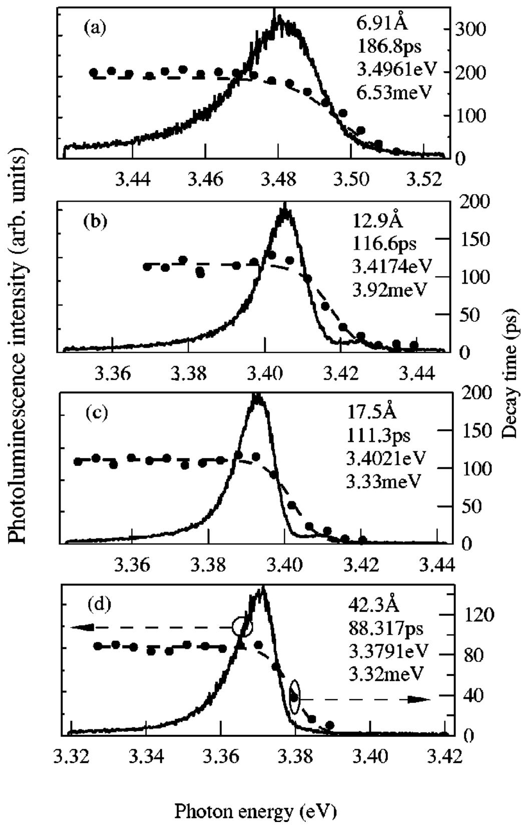

FIG. 1. Time-integrated PL spectra (solid traces) and PL decay time constants as function of emission energies (closed circles) taken at 5 K for four representative MQWs with the L_ws of 6.91 [(a)], 12.9 [(b)], 17.5 [(c)], and 42.3 Å [(d)], respectively are shown. The dashed curves are the theoretical ones fitted by Eq. (1).

interpreted as being due to the quantum confinement effect for the excitons. Spectral distribution of PL decay curves in the nine MQW samples possessing various L_ws were measured at 5 K. Almost all the decay curves could be fitted with a single exponential function.

Figure 1 shows the time-integrated PL spectra (solid traces) and PL decay time constants (closed circles) as a function of monitored photon energies taken at 5 K for four representative MQW samples having the L_ws of 6.91, 12.9, 17.5, and 42.3 Å. Estimated PL decay time is a monotonically decreasing function of the emission energy. 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 lifetime of localized excitons (τ_{PL}) does not change with their emission energy, the observed decay times $\tau(E)$ can be expressed by the following equation:[9]

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

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 fits could be obtained (dashed curves in Fig. 1) using the following parameters; $\tau_{PL}(L_w=6.91\ \text{Å})=187$ ps, $\tau_{PL}(12.9\ \text{Å})=117$ ps, $\tau_{PL}(17.5\ \text{Å})=111$ ps, $\tau_{PL}(42.3\ \text{Å})=88.3$ ps, $E_0(6.91\ \text{Å})=6.5$ meV, $E_0(12.9\ \text{Å})=3.9$ meV, $E_0(17.5\ \text{Å})=3.3$ meV, $E_0(42.3\ \text{Å})=3.3$ meV, $E_{me}(6.91\ \text{Å})=3.496$ meV, $E_{me}(12.9\ \text{Å})=3.417$ meV, $E_{me}(17.5\ \text{Å})=3.402$ meV, and $E_{me}(42.3\ \text{Å})=3.379$ meV, respectively.

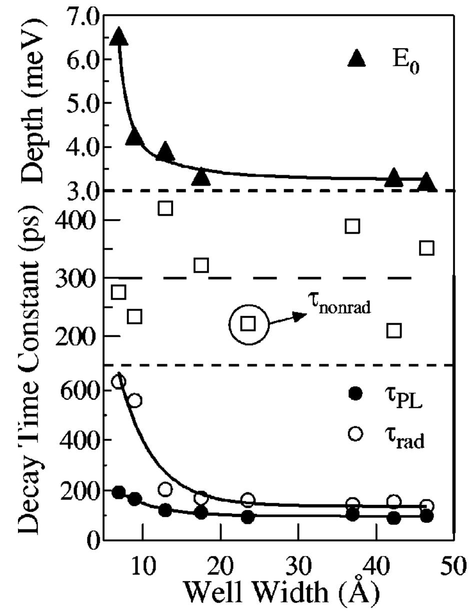

FIG. 2. Well-width dependences of localization depth (E_0, closed triangles) and recombination times, τ_{PL} (closed circles), τ_{rad} (open circles), and τ_{nonrad} (open squares) are shown. The solid curves are the visual guides.

Figure 2 shows the lifetime of localized excitons (τ_{PL}, closed circles) and E_0 (closed triangles) as a function of the L_w. It is found that both the τ_{PL} and E_0 are a monotonically decreasing function of L_w. We tried to deduce the L_w dependence of the radiative (τ_{rad}) and nonradiative (τ_{nonrad}) recombination times. Combined analysis of temperature (T) dependences of PL decay times and of spectrally integrated PL intensity was carried out. Figure 3 shows the temperature variations of the lifetime of localized excitons (τ_{PL}, closed squares) for a typical ZnO MQW ($L_w=8.95$ Å). The PL intensity versus T follows an $\exp(T/T_0)$ law with $T_0\sim 20$ K in this MQW. Since the measured PL decay time is simply given by $\tau_{PL}^{-1}=\tau_{rad}^{-1}+\tau_{nonrad}^{-1}$, we obtain a lower bound to the radiative recombination time $\tau_{rad}=\tau_{PL}/\eta$ by assuming that η equals 1 at $T=0$ K and follows the aforementioned exponential law.

Figure 3 shows T dependence of radiative and nonradiative recombination times (τ_{rad} and τ_{nonrad}) by open circles and squares, respectively. The τ_{rad} values were nearly constant at values of T below 15 K because of the localization of excitons, and the τ_{rad} increases proportionally to T^1 at $40 \leqslant T \leqslant 70$ K. It is likely that excitons are somewhat delocalized and become nearly free two-dimensional (2D) excitons above 40 K because the theoretical calculation for the oscillator strength predicts the relation of $\tau_{rad}\propto T^1$ for 2D excitons.[10] This is also consistent with the fact that the well layer of this MQW is narrower than the excitonic Bohr diameter of 36 Å.

These recombination times were separated with the identical calculation procedures for all the nine MQWs studied in this work. The τ_{rad} and τ_{nonrad} (closed and open circles) obtained at 5 K are plotted against the L_w in Fig. 2. The τ_{rad} is

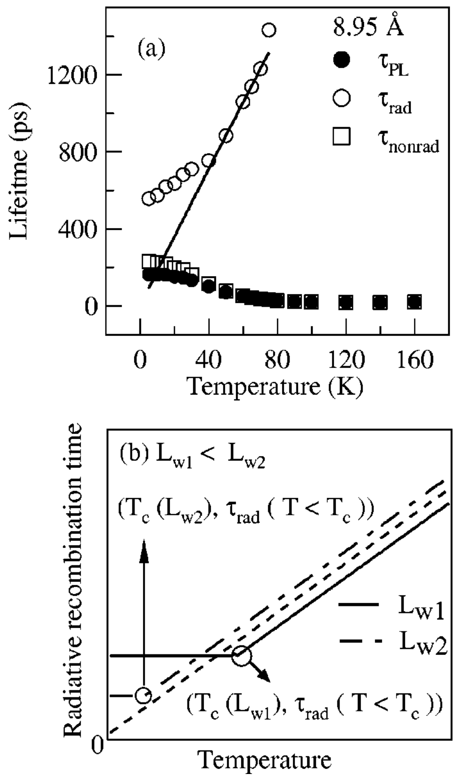

FIG. 3. (a) Temperature dependence of recombination times, τ_{PL} (closed circles), τ_{rad} (open circles), and τ_{nonrad} (open squares) is shown. The solid line is the theoretical one fitted by a linear function of T. Note, the evaluated τ_{rad} and τ_{nonrad} are lower and upper bounds, respectively, due to the assumption of $\eta(T=0\ \mathrm{K})=1$. (b) Schematic of temperature dependence of τ_{rad} in the MQWs with the narrower (L_{w1}, solid line) and the wider (L_{w2}, dashed-dotted line) wells is presented. Dashed line is for the case of a negligible localization effect. The critical temperature (T_c) is defined as a crossing point of linear and stagnant regions.

a monotonically decreasing function of L_w. Because the radiative recombination process is relatively dominant at a low temperature, the values of τ_{nonrad} have relatively large error bars. Nevertheless, it can be said that, as a general trend, the τ_{nonrad} is independent of the L_w.

The L_w dependence of τ_{rad} can be explained as being due to the thermal release effect from the localized to delocalized states of excitons. One can notice that the L_w dependences of the localization depth [E_0 in Eq. (1)] of excitons and the τ_{rad} are similar with respect to each other. Figure 3(b) describes the excitonic localization effect on τ_{rad}. If the localization effect is absent in quantum wells, τ_{rad} is a linearly increasing function of T in the entire range of T (dashed line). Due to the localization effect, τ_{rad} becomes stagnant at low temperatures (solid and dashed-dotted lines).[11] Let us define (1) T_c as a temperature at a crossing point of constant and linear regions, (2) L_{w1} as the smaller L_w, and (3) L_{w2} as the larger one. The solid and dashed lines in Fig. 3(b) schematically represents the T dependence of τ_{rad} in L_{w1} and L_{w2} cases, respectively. The larger the T_c, the larger the localization depth (E_0). The larger the L_w, both the E_0 and T_c become larger, as can be seen in Fig. 2, i.e., $T_c(L_{w1}) > T_c(L_{w2})$. As can be understood from Fig. 3(b), $\tau_{rad}(T \leqslant T_c$ and $L_{w1})$ for smaller L_w (large E_0) is larger than $\tau_{rad}(T \leqslant T_c$ and $L_{w2})$, assuming that the oscillator strength remains unchanged irrespective of L_w. Piezoelectric field effects are unnecessary to be considered due to the negligible strains between the well and the barrier regions.[12] It is necessary to systematically estimate the T dependence of τ_{rad} for MQWs having various L_ws in order to clarify the radiative recombination mechanism in ZnO MQWs. Such experimental studies are under way.

The L_w dependence of τ_{nonrad} is discussed. Usually, the nonradiative recombination (τ_{nonrad}) is shortened in the MQWs with small L_ws because of the degraded film qualities and carrier leakage outside the well region.[13] However, it can be safely concluded that efficient carrier confinement inside the well region could be realized in the entire L_w ranges adopted here.

In summary, a set of ZnO/(Mg,Zn)O MQWs with a well width varying from 6.91 to 46.5 Å has been grown by laser molecular-beam epitaxy. The quantum efficiencies of these MQW samples have been studied by picosecond TRPL spectroscopy. The radiative recombination time, τ_{rad}, was a monotonically decreasing function of L_w, while the nonradiative one, τ_{nonrad}, was nearly independent of the L_w. The former dependence can be explained as being due to the thermal release effect of excitons from localized to delocalized states. Avoidance of the QE suppression even in the case of small L_ws below 10 Å is highly desirable for UV light-emitter device applications.

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