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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 $L_w$'s 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. © 2001 American Institute of Physics. [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 owing to their large binding energy of excitons ($59$ 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), negligible interdiffusion of Mg, and very flat heterointerface. 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 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. Excimer laser pulses were impinged to ZnO and Mg$_{0.12}$Zn$_{0.88}$O targets (99.999%). 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 ≈ 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. The photoluminescence (PL) was temporally resolved using a streak camera in conjunction with a monochromator. The spectral and temporal resolutions were ≈ 0.3 nm and ≈ 30 ps, respectively.

We confirmed in our previous study 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...
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 $L_w$ 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 as a function of emission energies (closed circles) taken at 5 K for four representative MQWs with the $L_w$ 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).

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

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: $\tau_{PL}(6.91\,\text{Å})=187$ 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.

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

![FIG. 2. Well-width dependences of localization depth ($E_0$, closed triangles) and recombination times, $\tau_{PL}$ (closed circles), $\tau_{rad}$ (open circles), and $\tau_{nonrad}$ (open squares) are shown. The solid curves are the visual guides.](Image)
define localized states of excitons. One can notice that the thermal release effect from the localized to delocalization effect is absent in quantum wells, due to low temperatures.

The larger the localization effect, the larger the critical temperature ($T_c$) for smaller $L_w$ (large $E_0$) is larger than $\tau_{\text{rad}}(T \lesssim T_c$ and $L_w$). 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. It is necessary to systematically estimate the $T$ dependence of $\tau_{\text{rad}}$ for MQWs having various $L_w$ in order to clarify the radiative recombination mechanism in ZnO MQWs. Such experimental studies are under way.

The $L_w$ dependence of $\tau_{\text{nonrad}}$ is discussed. Usually, the nonradiative recombination ($\tau_{\text{nonrad}}$) is shortened in the MQWs with small $L_w$ because of the degraded film qualities and carrier leakage outside the well region. 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, $\tau_{\text{rad}}$, was a monotonically decreasing function of $L_w$, while the nonradiative one, $\tau_{\text{nonrad}}$, 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 $L_w$ below 10 Å is highly desirable for UV light-emitter device applications.

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