Dependence of photoluminescence of ZnO/Zn$_{0.85}$Mg$_{0.15}$O multi-quantum wells on barrier width

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**Abstract**

Temperature-dependent photoluminescence (PL) from two multi-quantum well (MQW) structures with different barrier widths has been systematically investigated. The PL band in the well layers is dominated by localized excitons (LE), D$_{0X}$, and D$_{0X}$-LO. As the temperature increases, luminescence from the excitons localized in the well layers shows an 'S'-shaped shift in the thin barrier MQW whereas a monotonic redshift is observed from the thick barrier MQW. Quenching of well-related emission is associated with delocalization of the excitons in the potential minima induced by interface fluctuations or alloy disorder. The activation energies correlated with depths of the local potential are deduced to be 7 and 17 meV for the thick and thin barrier MQWs, respectively.

**1. Introduction**

Recently, quasi-two-dimensional (2D) quantum well (QW) or superlattice (SL) structures have been investigated intensively because of applications in light-emitting diodes (LEDs) and laser diodes (LDs). Favorable properties of the structures include the larger oscillation strength, enhanced exciton binding energy, and tunability of the operating wavelengths [1–5]. By taking advantage of the QW structure, more stable and efficient as well as lower threshold UV electroluminescence (EL) can be achieved [6]. As a wide and direct bandgap semiconductor, ZnO is promising candidate in next-generation ultraviolet (UV) LEDs [7–9]. ZnO has very unique properties over GaN, such as large exciton binding energy and the availability of large single-crystal bulk quantities of ZnO for homoepitaxy and there have been many studies on ZnO/ZnMgO or ZnO/ZnBeO quantum wells. Due to the toxicity of Be and related compounds, much effort has been made to investigate ZnO/ZnMgO MQWs in UV light emitter applications. The luminescence properties of the MQWs are known to be determined by the quantum confinement (QC) and quantum confinement Stark (QCS) effects [2,10,11]. The 2D confinement effect also results in the localization of excitons in lateral potential minima at low temperature [10,12–15]. It has been demonstrated that the width of the well plays a critical role in determining both the energy of the excitonic emission and depth of the lateral potential minima where the excitons are localized [11,15]. In fact, the dependence of the PL performance on the well width in ZnO/ZnMgO quantum wells has been investigated but reports on the effects of the barriers (such as thickness, composition, etc.) are still limited. In this work, we report the growth of ZnO/Zn$_{0.85}$Mg$_{0.15}$O MQWs with the barrier widths of 11 nm and 5 nm as well as their corresponding PL properties. The two MQWs show different shift behavior in the LE band in the well layers when the temperature is elevated.

**2. Experimental details**

Two 10-period ZnO/Zn$_{0.85}$Mg$_{0.15}$O MQW structures with barrier widths of 11 nm and 5 nm were grown on Si(111) substrates by pulsed laser deposition (PLD). The well width was about 3 nm in both samples. A KrF excimer laser (248 nm, 5 Hz, 6 ns) was utilized to ablate the sintered ZnO and Zn$_{0.9}$Mg$_{0.1}$O ceramic targets. It was found that the Mg content was about 15 at.% in the obtained films if a target composed of Zn$_{0.9}$Mg$_{0.1}$O and growth temperature of 600 °C were used. The target composition was determined experimentally because of the different vapor pressures of Zn and Mg related species. Prior to deposition, the growth chamber was evac-
Fig. 1. PL spectra acquired from the 11 nm and 5 nm barrier ZnO/Zn0.85Mg0.15O MQWs at 10 K. The band-edge emissions are fitted using four Gaussian functions. The intensities of the well emission are normalized for easy comparison.

3. Results and discussion

It is worth noting that the well related peaks exhibit a redshift of 7–14 meV while the barrier emission shows a blueshift of 13 meV as the barrier width decreases from 11 nm to 5 nm. The shift of the peaks can be ascribed to the change of the bandgap. According to the Burstein–Moss (B–M) effect, the bandgap of a semiconductor depends strongly on the carrier concentration [20]. Herein, it is reasonable that the more carriers move into the quantum wells from the barriers with increasing barrier width due to enhanced quantum confinement. That is to say, the 11 nm barrier MQW shows a higher density of carriers in the well region and lower density of carriers in the barrier region, thereby giving rise to a wider band gap of the ZnO well and narrower band gap of the ZnMgO barrier.

Figs. 2(a) and (b) display the PL spectra of the two MQWs as a function of temperature. It can be observed that the PL intensity decreases with higher temperature, and the emission from the 11 nm barrier MQW decays more rapidly compared to the 5 nm barrier one. Quenching of the emission from the well and barrier is compared in Figs. 3(a) and (b). As shown, the integrated PL intensities as a function of temperature can be described by the Arrhenius formula, i.e. \( I_{PL} \sim I_0/[1 + a \exp(-E_a/kT)] \). The fitting gives rise to activation energies \( E_a \) of 7, 17, and 52 meV, corresponding to the emission from the two samples. The \( E_a \) values obtained from quenching of well related luminescence are 7 meV for the 11 nm barrier MQW and 17 meV for the 5 nm MQW. The \( E_a \) corresponding to the barrier related emission is 52 meV for both samples. It should be noted that these values are much lower than the band offsets as well as the bandgap difference between the wells and barriers. Therefore, the quenching behavior may be induced by thermal detrapping of LEs towards the free excitons (FES) [12,15]. It is known that the excitons are mainly localized in the lateral potential minima (well) at low temperature and the depth correlates with the activation energy. There are many factors affecting \( E_a \), such as the interface roughness, composition fluctuation, or internal electric field. Makino et al. demonstrated that inhomogeneity of the band gap energies in the
Fig. 2. Temperature-dependent PL spectra acquired from the MQWs with barrier widths of (a) 11 nm and (b) 5 nm.

Fig. 3. Temperature quenching behavior of the emission from the (a) ZnO wells and (b) Zn$_{0.85}$Mg$_{0.15}$O barriers of the two MQWs samples. The solid lines correspond to least-squares fits using the Arrhenius relationship. The activation energies are determined to be 7, 17 and 52 meV.

Barrier layers induced depth fluctuation and enhancement of the exciton localization energy [12,14]. They found $E_a$ of 28–29 meV from the LE luminescence quenching in the ZnO/Zn$_{0.73}$Mg$_{0.27}$O MQW and 16–18 meV in the ZnO/Zn$_{0.88}$Mg$_{0.12}$O MQW. In this study, the relatively high $E_a$ value deduced in the 5 nm barrier MQW may be due to the larger composition inhomogeneity in the structure, although the detailed reason needs further study.

Based on the above discussion, the well related emission is composed of the peak of LEs, $D^0X$ and $D^0X$-LO. He et al. revealed that the predominant excitonic emission was attributed to bound excitons and localized excitons for MQWs with well widths of 14 and 3 nm [10]. Zhang et al. observed emissions of $D^0X$ and LE in the QCSE regime when the well width was larger than the exciton Bohr diameter [11]. They believed that the appearance of the peak $D^0X$ was related to the fast formation of excitons, short trapping time of excitons to donor states, and the long lifetime of the peak LE. Thus, it is of interest to study the energy of the LE peak as a function of temperature. Fig. 4(a) shows the dependence of the LE peak energy on temperature in the two MQWs. It is worth noting that the peak position of LE shifts from 3.404 eV at 15 K to 3.329 eV at RT monotonically in the 11 nm barrier MQW due to band gap shrinkage. In contrast, in the 5 nm barrier MQW, an 'S'-shape (red–blue–red) shift is observed. That is, the peak first redshifts to 3.386 eV at 30 K, blueshifts to 3.398 eV at 70 K, and then redshifts again to 3.321 eV at RT. The anomalous blueshift in the range of 30–70 K observed from the 5 nm barrier MQW can be explained by the excitonic localization effect [10,13,15]. With increasing temperature, the carriers have more thermal energy to occupy higher energy levels of the lateral potential minima. However, the 'S' shaped shift is not observed from the 11 nm barrier MQW which has a shallower potential minimum of $\sim$7 meV. The blue-shifted value is so small that it can be compensated by temperature induced band gap shrinkage [21]. Hence, the peak does not exhibit irregular blue shift throughout the range studied (15–250 K). The shift of the barrier emission with increasing temperature is also shown in Fig. 4(b). The 'S' shape shift is found from both samples. The excitons in the barrier emission are also localized in the lateral potential minima induced by alloy disorder. As the temperature increases, the excitons occupy higher energy states of the lateral potential minima, leading to a blueshift. When the temperature reaches 130 K, the localized carriers are detrapped from the potential minima completely and the blueshift ceases. If the temperature is further increased, band gap shrinkage dominates the shift of the peak resulting in a red-shift.
Fig. 4. Dependence of the peak energies of the LE from (a) ZnO wells and (b) Zn_{0.85}Mg_{0.15}O barriers on the temperature for the two MQWs samples.

4. Conclusion

We have experimentally investigated the temperature-dependent PL of ZnO/ZnMgO MQWs with the barrier widths of 5 and 11 nm. It was found that the band edge PL from quantum wells was dominated by LE, D^{0}X and D^{0}X-1LO. The well-related peaks show a minor difference in the energy, which could be explained by the B–M effect. The activation energies for the quenching of the well-related luminescence were deduced to be 7 and 17 meV, for the thick-barrier and thin-barrier MQWs. The peak LE from well layers exhibits a S-shaped shift for thin-barrier MQW while a monotonous redshift for thick-barrier MQW. We hope our work will shed light on the understanding of the dynamic behavior of the excitons in the MQWs.

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