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Optical transition dynamics in ZnO/ZnMgO multiple quantum well structures with different well widths grown on ZnO substrates

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We report the optical properties of ZnO/ZnMgO multiple quantum well (MQW) structures with different well widths grown on ZnO substrates by molecular beam epitaxy. Photoluminescence (PL) spectra show MQW emissions at 3.387 and 3.369 eV for the ZnO/ZnMgO MQW samples with well widths of 2 and 5 nm, respectively, due to the quantum confinement effect. Time-resolved PL results show an efficient photogenerated carrier transfer from the barrier to the MQWs, which leads to an increased intensity ratio of the well to barrier emissions for the ZnO/ZnMgO MQW sample with the wider well width. © *2010 American Institute of Physics*. [doi:10.1063/1.3284959]

I. INTRODUCTION

ZnO is a promising material for the application of high efficiency light emitting diodes with short wavelength region for its large bandgap energy of 3.37 eV, which is similar to GaN (3.39 eV) at room temperature.[1] The large exciton binding energy of 60 meV in ZnO provides higher efficiency of emission for optoelectronic device applications. Several ZnO/ZnMgO multiple quantum well (MQW) structures have been grown on various substrates such as sapphire, GaN, Si, and so on.[2–5] However, the achievement of high quality ZnO/ZnMgO MQW structures has been somehow limited by the use of lattice-mismatched substrates. The lattice-matching $ScAlMgO_4$ or ZnO substrates were also used for the growth of ZnO/ZnMgO MQW structures.[6,7] Beyond disputes, the use of ZnO substrates solves the lattice mismatch problem, providing much better crystal quality of ZnO/ZnMgO MQW structures.[7] However, the detailed optical characteristics and recombination dynamics of ZnO/ZnMgO MQW structures grown on ZnO substrates were not fully understood yet. In this letter, we report the optical properties and carrier dynamics in $ZnO/Zn_{0.9}Mg_{0.1}O$ MQW structures with different well widths grown on ZnO substrates. The characterizations were conducted by high-resolution x-ray diffraction (XRD), photoluminescence (PL), and time-resolved PL spectroscopic techniques.

II. EXPERIMENTS

The $ZnO/Zn_{0.9}Mg_{0.1}O$ MQWs were grown on O-face (0001) ZnO substrates (MAHK Co., Japan) by molecular beam epitaxy (MBE). For better crystalline quality and flatter surface, the bulk ZnO substrates were annealed in O_2 ambient before inserting into the chamber. Prior to the growth, the substrates were heated again in the growth chamber in O_2 plasma in order to eliminate possible contaminations. Ten periods of ZnO/ZnMgO MQWs were sandwiched between 10-nm-thick ZnMgO cap and buffer layers. ZnO well and ZnMgO barrier layers were grown at 600 °C in the chamber. The thicknesses of the well and barrier layers were controlled by the growth time. Details of the growth procedures were reported elsewhere.[7] The thicknesses of well layer (L_w) were set to 2 and 5 nm with a barrier thickness (L_b) of 7 nm for two different samples (which will be denoted by W2 and W5, respectively). For comparison, the optical properties of a ZnO substrate were also investigated. The structural properties were characterized by high-resolution XRD system (PANalytical X'Pert-PRO MRD). PL spectra were measured by a spectrometer using the 325 nm line of a 10 mW continuous wave He–Cd laser as an excitation source. Temperature-dependent PL spectra were acquired using temperature-controlled cryostat in the temperature range from 10 to 300 K. Time-resolved PL experiments were carried out with a frequency-doubled, mode-locked (150 fs) Ti-:sapphire laser system as an excitation source and a time-correlated single photon counting system for detection.

III. RESULTS AND DISCUSSION

Figure 1 shows the (0002) ω-2θ scan XRD patterns of samples W2 and W5 (ZnO/ZnMgO MQWs with well widths of 2 and 5 nm), as well as a reference ZnO sample (ZnO substrate). The strongest peak is due to ZnO substrate, and the full width at half maximum value of symmetric (0002) ω-2θ scan for the ZnO substrate is only 19 arcsec, indicating high crystallinity of the ZnO substrate. Moreover, the appearance of pronounced Pendellösung fringes arising from interference between x-ray waves reflected within the sample structure is an indication of the high crystalline quality of samples W2 and W5, because any interface imperfection or compositional inhomogeneity would decrease the phase co-

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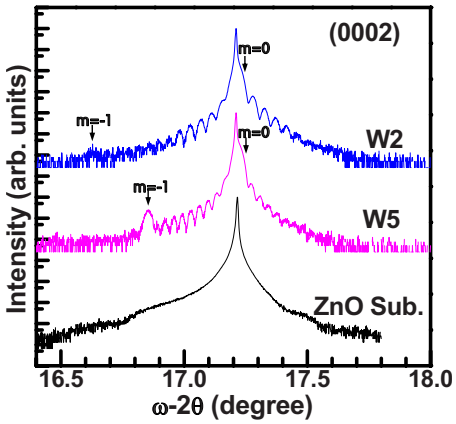

FIG. 1. (Color online) (0002) ω-2θ scan XRD patterns of the ZnO/ZnMgO MQWs with different well widths of 2 and 5 nm (W2 and W5) and a ZnO substrate. XRD patterns have been relatively shifted in the vertical direction for clarity.

herence and eliminate it. From the simulation, the L_w (L_b) value was estimated to be ~1.6(7) nm for W2 and ~5.1(7) nm for W5.

Figure 2 shows PL spectra of samples W2, W5, and a ZnO substrate measured at 10 K. The PL spectrum of the ZnO substrate exhibits very dominant sharp peaks at 3.361 and 3.356 eV due to donor-bound exciton (DBX) transitions. Free excition (FX), two-electron satellite (TES), and acceptor-bound exciton (ABX) transitions can be clearly distinguished at 3.377, 3.334, and 3.323 eV, respectively. Longitudinal optical (LO)-phonon replicas of FX (FX-*n*LO) and LO-phonon replicas of DBX (DBX-*n*LO) can be seen in the oscillatory PL spectrum with an energy periodicity about 72 meV, corresponding to LO-phonon energy of ZnO. All these peaks are observable in samples W2 and W5, except for ZnO FX transition which is overlapped with ZnO MQW emissions. Two additional emissions from ZnO MQWs and ZnMgO barrier layers were observed in samples W2 and W5. The broad weak emissions at about 3.5 eV come from the

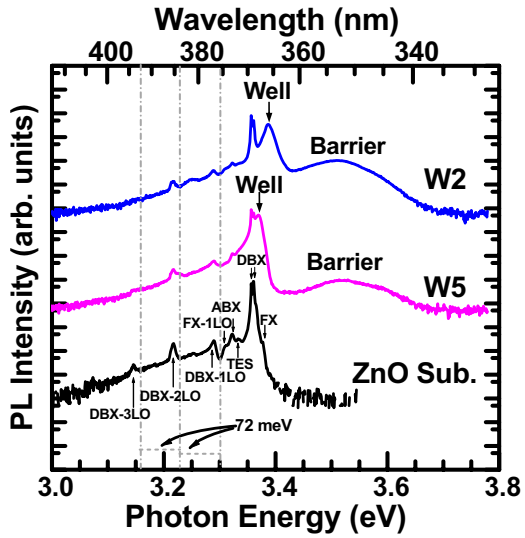

FIG. 2. (Color online) 10 K PL spectra from W2, W5, and a ZnO substrate. PL spectra have been vertically shifted for clarity. "Well" and "Barrier" denote emission from the well and barrier, respectively.

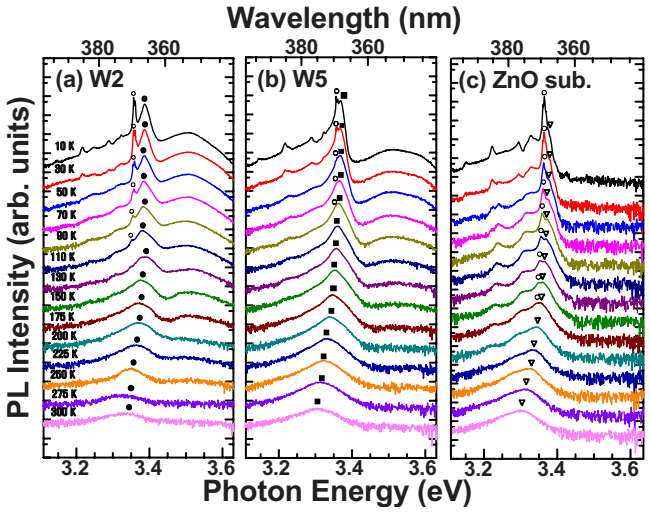

FIG. 3. (Color online) PL spectra of (a) W2, (b) W5, and (c) a ZnO substrate over the temperature range of 10–300 K. MQW emission peaks of W2 and W5 (indicated by closed circle and closed rectangular, respectively), FX (inverted open triangle) and DBX (open circle) of the ZnO substrate. Spectra have been vertically shifted for clarity.

ZnMgO barrier layers, while the strong emission from MQWs in W2 (W5) is blueshifted to 3.387 eV (3.368 eV) compared with bulk ZnO excitonic peak (3.356 eV) due to quantum confinement effect. The energy of well emission of W2 is well consistent with the reported value of $ZnO/Zn_{0.9}Mg_{0.1}O$ ($L_w \sim 1.7$ nm) in other literature.[2] From the PL spectra, we found that the intensity ratio of the well to barrier emissions (defined by $I_{well}/I_{barrier}$) for W5 is nearly 400 which is much larger than that for W2 ($I_{well}/I_{barrier} \sim 25$), indicating more effective carrier transfer from the barriers to the wells for sample W5.

Figure 3 shows temperature-dependent PL spectra of samples W2, W5, and a ZnO substrate. For the reference ZnO sample [Fig. 3(c)], the DBX transition is predominant below 130 K, while the FX transition becomes dominant with temperature higher than 130 K. ABX can be observed up to 50 K and ABX-1LO up to 30 K and then both disappear due to thermal ionization from bound acceptors.[8] TES is negligible with the increase of temperature. DBX-*n*LO transitions can be observed below 90 K and FX-*n*LO transitions become dominant above 110 K. Then FX and FX-*n*LO transitions start to merge together. The narrow linewidth of excitonic transitions indicates the high quality of the ZnO substrate. For samples W2 and W5, the emissions from ZnO substrate are negligible when the temperature is higher than 130 K, as shown in Figs. 3(a) and 3(b). The emission from ZnMgO layer can be resolved for temperature below 200 K in both samples. In Fig. 3(a), the peak energies of the ZnO MQW-related emission indicated by closed circles show the "S-shaped" temperature dependence[9] as the temperature increases from 10 to 300 K, which can be attributed to the exciton localization caused by well-width variations and/or alloy-potential inhomogeneities of ZnO/ZnMgO MQWs[10] The temperature dependent PL spectra of W5 shown in Fig. 3(b) were rather similar to those observed in typical ZnO epilayer. The red-shift behavior in the temperature range of 10–300 K is ascribed to band gap shrinkage effect. These

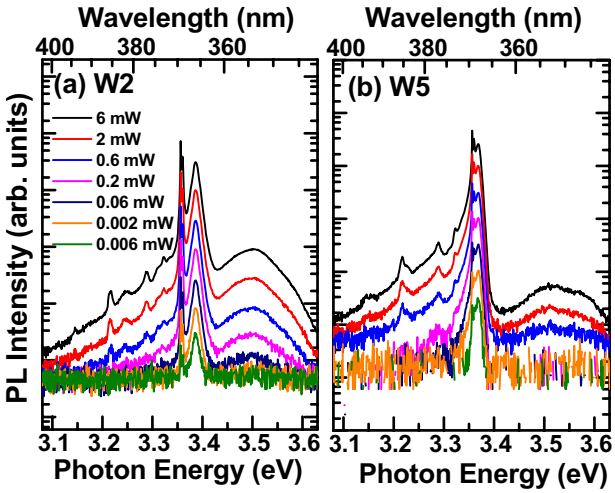

FIG. 4. (Color online) Excitation power-dependent PL spectra of (a) W2 and (b) W5 measured at 10 K.

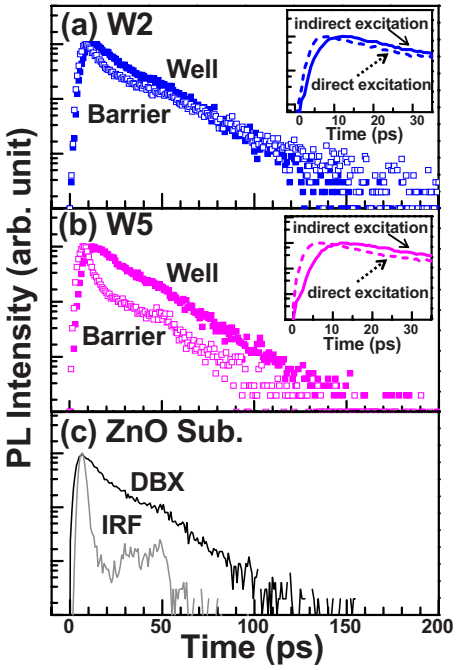

FIG. 5. (Color online) Time-resolved PL decay curves of (a) W2, (b) W5, and (c) a ZnO substrate under the indirect excitation condition (together with IRF). The insets show measured time-resolved PL decay curves from the well emissions of W2 and W5 under the direct excitation condition (dotted lines) and the indirect excitation condition (solid lines).

results indicate that two kinds of MQWs with different well widths exhibited different exciton dynamics due to different well-width (and other potential) fluctuations.

Figures 4(a) and 4(b) show power-dependent PL spectra for samples W2 and W5 at 10 K by varying excitation power over three orders of magnitude. We observed almost no shift in the PL peak energy for both samples W2 and W5. It has been reported that the transition from quantum confinement regime to quantum confined Stark effect regime occurs in $ZnO/Zn_{0.9}Mg_{0.1}O$ MQW grown on Al_2O_3 substrates when the well width is about two times of exciton Bohr radius (~2 nm) of ZnO bulk.[2] The internal electric field is determined from the sum of spontaneous and strain-induced piezoelectric polarizations between the well and the barrier. In case of ZnO/ZnMgO QWs, theoretical studies have shown negligible quantum confined Stark effect when both Mg composition and L_w are small.[3] The negligible internal field effect can be explained by the cancellation of spontaneous and piezoelectric polarizations between the well and the barrier in the ZnO/ZnMgO QW structures.[3] From the power-dependent PL spectra, we observed no PL peak shift of MQW emission in both samples W2 and W5, indicating a negligible built-in electric field effect in the $ZnO/Zn_{0.9}Mg_{0.1}O$ MQWs grown on ZnO substrates by MBE.[10]

Figure 5 shows time-resolved PL decay curves monitored at the well and the barrier emission peaks for samples W2 and W5, together with the decay curve detected at DBX peak of a ZnO substrate and the corresponding instrument response function profile. The decay time of DBX transition from a ZnO substrate is about 180 ps. Insets of Fig. 5 show time-resolved PL decay curves of the well emissions for samples W2 and W5 at the condition of direct excitation (i.e., excitation below the barrier bandgap energy) and indirect excitation (i.e., excitation above the barrier bandgap energy). For both samples, the temporal profiles of the luminescence from the wells exhibit a slower rise time and a longer decay time for indirect excitation compared to direct excitation. Especially for sample W5, we observed a prolonged rise time (~63 ps) and a longer decay time (~169 ps) of the well emission under the indirect excitation condition, as compared to the direct excitation case for which the rise time and the decay time of the well emission were ~38 and ~160 ps, respectively. Furthermore, the higher intensity ratio of the QW to barrier emissions (as shown in Fig. 2) and the faster decay time of the barrier emission (~22 ps) were simultaneously observed for sample W5. These results are suggestive of the efficient carrier transfer process from the barriers to the wells for sample W5. On the other hand, the rise time difference between the indirect and direct excitation conditions for sample W2 is ~13 ps, which is much smaller than the case of sample W5 (~25 ps). Together with the relatively smaller intensity ratio of the QW to barrier emissions of sample W2, we can conclude that the carrier transfer efficiency from the barriers to the wells is smaller for sample W2 compared to W5. We can interpret this in terms of the saturation of the localized states in sample W2 due to smaller density of states in MQWs with narrower well width.[11] Although the different barrier decay time between samples W2 and W5 (~55 and ~22 ps, respectively) may also be partly influenced by different material qualities and small Mg composition discrepancy of ZnMgO alloys, the carrier transfer process would be the dominant reason for the shorter barrier decay time of sample W5. For time-resolved PL analysis, the built-in internal field effect between the well and barrier regions[10] can be almost negligible as shown in power-dependent PL experiments (Fig. 4).

IV. CONCLUSION

We have investigated the optical transitions and carrier dynamics of ZnO/ZnMgO MQW structures with different well widths grown on lattice-matched ZnO substrates. The structural investigation of samples employing XRD technique confirmed good abruptness of MQW interfaces. The temporal profiles of the luminescence from the wells for both samples W2 and W5 exhibited a slower rise time and a longer decay time under indirect excitation condition compared to the direct excitation case. The larger difference of rise time of the well emission under direct and indirect excitation conditions together with the higher intensity ratio of the QW to barrier emissions indicated that the carriers generated in the barrier can be effectively transferred to the MQW region for ZnO/ZnMgO MQWs with the wider well width of 5 nm.

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