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A series of 10-period ZnO/Zn_{0.9}Mg_{0.1}O multiple quantum wells (MQWs) with well widths varying from 2.2 to 5.6 nm have been grown on r-plane sapphire substrates by pulsed laser deposition. A good periodic structure with clear interfaces was observed by transmission electron microscopy. In a-plane ZnO/Zn_{0.9}Mg_{0.1}O MQWs, the luminescence was dominated by localized exciton emissions at low temperatures, while the free exciton (FE) transition was dominating emissions at temperatures above 100 K. The thermal quenching behavior of exciton emission has been analyzed. A rate equation assuming two nonradiative recombination channels is used to describe the quenching of the transitions observed. Moreover, the FE emission energy in the MQWs shows a systematic blueshift with decreasing well width, which is consistent with a quantum confinement effect. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4767462]

I. INTRODUCTION

ZnO has now gained much attention for its promising applications in short-wavelength optoelectronic devices, because of its wide band gap of 3.37 eV and large exciton binding energy of 60 meV at room temperature.1–3 As demonstrated by light-emitting diodes (LEDs), laser diodes (LDs), and other electronic devices, ZnO-based devices will take the advantage of multiple quantum wells (MQWs) structures such as ZnO/ZnMgO or ZnO/ZnBeO MQWs to optimize the device performance. Recently, much effort has been devoted to the investigation and fabrication of ZnO/ZnMgO MQWs grown along the polar c-axis direction for UV light emitter applications.4–9 However, similar to c-oriented GaN, c-oriented ZnO also suffers the polarization effects. The polarization induced built-in electric fields make negative effects on device properties such as a decrease in the overlapping of the electron and hole wave functions in the quantum well and consequently a decrease of internal quantum efficiency of the emitting devices.10–15 In order to eliminate the polarization effects, the growth of non-polar ZnO-based quantum structures is therefore highly desirable, which has already been demonstrated in GaN-based non-polar quantum structures.14 Recently, much effort has been devoted to the fabrication and investigation of non-polar ZnO/ZnMgO QWs using different orientation A-face16–18 or M-face.19 In those studies, molecular beam epitaxy (MBE) is used as the growth technique. In contrast to MBE, pulsed laser deposition (PLD) is a widely used and versatile technique to prepare ZnO and ZnMgO thin films, which benefits us to monitor the growth by controlling relevant growth parameters such as laser power, pulse frequency, substrate temperature, deposition rate, material composition, etc. However, there have been few reports on the growth of non-polar ZnO/ZnMgO MQWs by PLD method.20

In the present work, we report on the growth of 10-period ZnO/Zn_{0.9}Mg_{0.1}O MQWs on r-plane sapphire substrates by PLD. In addition to an interest in fabricating non-polar ZnO/ZnMgO MQWs, we study the temperature dependence of the excitonic photoluminescence (PL) transitions observed in a-plane ZnO/Zn_{0.9}Mg_{0.1}O MQWs in the temperature range of 13–300 K. A particular emphasis is given to the quenching of these transitions.

II. EXPERIMENTAL DETAILS

Non-polar ZnO/ZnMgO MQWs were grown on r-plane sapphire substrates by the PLD method. Two ceramic targets, i.e., ZnO (4N) and ZnO-MgO (4N) with Mg content of 10 at.%, were used as the source materials. Henceforth, the MQWs grown using these targets will be referred as ZnO/Zn_{0.9}Mg_{0.1}O MQWs. A KrF excimer laser (λ = 248 nm) was employed to ablate the target. The r-plane sapphire substrates were cleaned in successive baths of acetone, ethanol, and deionized water for 30 min at room temperature, respectively. Prior to deposition, the growth chamber was evacuated to a base pressure of 3.0 × 10^{-4}Pa, and then high-purity O_2 (4N) was introduced as working gas. During deposition, the oxygen pressure and substrate temperature were maintained at 1 Pa and 550 °C, respectively. A schematic of the five MQW structures studied is shown in Fig. 1. Each consists of a 150 nm thick Zn_{0.9}Mg_{0.1}O buffer layer followed by a 10-period MQWs of ZnO quantum wells surrounded by 8 nm thick Zn_{0.9}Mg_{0.1}O barriers. The thickness of the ZnO quantum wells was approximately 2.2, 3.1, 4, 4.7, and 5.6 nm in the five MQW structures studied. The layer thickness was controlled by varying the deposition time. Those MQWs are labeled as samples A, B, C, D, and E, respectively.

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The MQW structure was characterized by cross-sectional transmission electron microscopy (TEM). Crystal-line structure of non-polar ZnO/Zn_{0.9}Mg_{0.1}O was analyzed by X-ray diffraction (XRD) with a Cu K\(_\alpha\) radiation source (\(\lambda = 1.54056 \text{ Å}\)). The optical properties were characterized by PL spectra on a FLS 920 fluorescence spectrometer (Edinburgh Instruments) using a He-Cd laser (\(\lambda = 325 \text{ nm}\)) as the excitation source.

III. RESULTS AND DISCUSSION

TEM image in Fig. 2 illustrated the cross section view of ZnO/Zn_{0.9}Mg_{0.1}O MQWs structure (sample B). As can be seen, the well and barrier layers can be clearly identified. The TEM analysis reveals good periodicity and uniformity across the entire structure. In addition, the thickness of well and barrier measured in TEM image is consistent with the nominal value, i.e., well width of \(\sim 3.1 \text{ nm}\) and barrier width of \(\sim 8 \text{ nm}\).

Figure 3 shows a \(\theta-2\theta\) XRD pattern, typical of ZnO/Zn_{0.9}Mg_{0.1}O grown on \(r\)-plane sapphire. In addition to the sapphire (0112) and (0224) peaks, only ZnO/ Zn_{0.9}Mg_{0.1}O (1120) peak appears in XRD pattern, suggesting that ZnO/Zn_{0.9}Mg_{0.1}O grown on \(r\)-plane sapphire has a pure \(a\)-plane orientation. This observation gives us evidence that ZnO/Zn_{0.9}Mg_{0.1}O grown on \(r\)-plane sapphire exactly follows the non-polar single crystal orientation, which is proposed to avoid built-in electric fields along the \(c\)-axis.

FIG. 1. A schematic of the \(a\)-plane ZnO/Zn_{0.9}Mg_{0.1}O MQW structures.

FIG. 2. TEM cross section image of \(a\)-plane ZnO (~3.1 nm)/Zn_{0.9}Mg_{0.1}O (~8 nm) MQWs structure.

FIG. 3. XRD spectrum of \(a\)-plane ZnO/Zn_{0.9}Mg_{0.1}O MQWs in \(\theta-2\theta\) geometry.

FIG. 4. (a) PL spectra at 13 K of a series of non-polar ZnO/Zn_{0.9}Mg_{0.1}O MQWs. (b) Room-temperature PL spectra of the ZnO film and ZnO/ Zn_{0.9}Mg_{0.1}O MQWs with different well layer thicknesses.
Figure 4(a) shows the 13 K PL spectra of the MQWs with different well layer thicknesses. It can be seen that the dominant PL peak shifts monotonously from 3.392 to 3.473 eV as the well layer thickness decreases from 5.6 to 2.2 nm. This blueshift behavior is naturally attributed to the expected quantum confinement effect. Moreover, there are few reports so far on the observations of room-temperature quantum confinement effect in non-polar ZnO/ZnMgO MQWs. Here, we also measure the room-temperature PL spectra of the ZnO film and MQWs with different well layer thicknesses, as shown in Fig. 4(b). It is found that all the MQW structures show a blueshift compared with the free exciton (FX) energy of epitaxial ZnO film, indicating a good interface and crystal quality of the a-plane ZnO/Zn_{0.9}Mg_{0.1}O MQWs. It is noteworthy that the emission from Zn_{0.9}Mg_{0.1}O barrier layer is not observed in our samples, suggesting that the PL emission and carrier confinement in the well regions are highly efficient, which is desirable for LD and LED applications.

The PL peak energies as a function of well layer thicknesses observed from the five MQWs samples are shown in Fig. 5. In comparison, we also deduce the transition energies of the excitons confined in the quantum wells based on the one-dimensional, finite square potential well model. The exciton energy in the quantum wells can be calculated by

\[ E_{\text{ex}}^{\text{QW}} = E_{g}^{\text{ZnO}} + \Delta E_{e} + \Delta E_{h} - E_{b}^{\text{QW}}, \]

(1)

where \( E_{g}^{\text{ZnO}} \) is the band gap energy of ZnO, \( \Delta E_{e} \) and \( \Delta E_{h} \) are the quantization energies of electrons and holes, respectively, and \( E_{b}^{\text{QW}} \) is the exciton binding energy in MQWs. The band gap offset was determined from the experiment results to be 220 meV. The conduction band to valence band offset ratio of 65/35 and the electron and hole masses in the confinement energy of \( m_{e} = 0.24 \) \( m_{0} \) and \( m_{h} = 0.78 \) \( m_{0} \) were used. From Fig. 5, it is worth noting that calculated values are close to the experimental results. With decreasing well layer thickness, a small deviation is observed and might be caused by an enhancement of the exciton binding energy.

To investigate the origin of the dominant PL emission (sample C), the temperature-dependent PL was carried out and the dependence of the peak energies on temperature is plotted in Fig. 6. The data derived from sample C can be described by the Bose-Einstein formula for temperature-induced band gap shrinkage

\[ E_{g}(T) = E_{g}(0) - K / \left[ \exp(\theta/T) - 1 \right], \]

(2)

where \( E_{g}(T) \) is the band gap energy, \( K \) represents the electron-phonon coupling strength, and \( \theta \) is the Einstein temperature. It is seen that the experimental data for temperatures above 100 K can be fitted very well by Eq. (2). However, a notable deviation from the fitted curve appears over the temperature range from 13 to 100 K, which is believed to a characteristic of localized excitons (LEs).

The PL emission redshifts 5 meV over the temperature range from 13 to 100 K. Our explanation for this smaller value of redshift is as follows. The excitons are localized in the potential minima at rather low temperature, which gradually detrap out of the potential minima due to thermal activation with increasing temperature to 100 K. The higher energy side emission is thus increased, and blueshift occurs during this process, which partly compensates for the redshift of band gap. Those competitive processes result in exciton emission showing redshift of 5 meV. As the temperature increases from 100 to 300 K, the continuous redshift of the emission peak is mainly determined by the behavior of the band-gap shrinkage, as the FX emission dominates the PL spectrum and the effect of the excitons localization could be neglected. At temperatures above 100 K, fitting the data to Eq. (2) gives \( K \) value of 0.065 eV and \( \theta \) of 295.7 K. The values are close to those derived from ZnO bulks and films reported by Wang et al.

To better understand the mechanism of excitons in the a-plane ZnO/Zn_{0.9}Mg_{0.1}O MQWs structure, we also deduce the activation energy for quenching of the exciton emission. Figure 7 shows the integrated intensities of the exciton
emission as functions of reciprocal temperature (sample C). In steady state, integrated intensities can be described by the equation

\[ I = I_0 / \left(1 + a_1 \exp(-E_{a1}/kT) + a_2 \exp(-E_{a2}/kT)\right), \tag{3} \]

where \( k \) is Boltzmann’s constant and \( E_a \) denotes the activation energy for the thermal quenching process. Fitting Eq. (3) to the data gives rise to two activation energies of about 8.3 and 29.0 meV, indicating two competitive nonradiative recombination channels, and the results are very similar to the values reported by Chauveau et al. in non-polar ZnO/ZnMgO quantum wells. It should be noted that a low \( E_a \) value of 8.3 meV is of the order of the thermal energy of \( k_B T \) (\( T \approx 95 \) K), suggesting that thermionic emission of the LES out of the localization potentials, which is in good agreement with that derived from Fig. 6. Since the deduced activation energy of 29.0 meV is much smaller than the band offsets as well as the bandgap difference between the ZnO wells and \( \text{Zn}_{0.9}\text{Mg}_{0.1}\text{O} \) barriers, thermal quenching of the exciton emission is not due to the thermal activation of electrons and/or holes from the ZnO wells into the \( \text{Zn}_{0.9}\text{Mg}_{0.1}\text{O} \) barriers. Instead, we give a possible explanation that the dominant mechanism underlying the quenching phenomena of the PL intensity at temperatures above 100 K is attributed to non radiative centers.

IV. CONCLUSIONS

In summary, non-polar ZnO/\( \text{Zn}_{0.9}\text{Mg}_{0.1}\text{O} \) MQWs with different well widths have been prepared on r-plane sapphire substrates by PLD. A good periodicity, uniformity, and abrupt interface have been achieved. In non-polar ZnO/\( \text{Zn}_{0.9}\text{Mg}_{0.1}\text{O} \) MQWs, LE transitions dominate at low temperatures ranging from 13 to 100 K, while FE transitions gradually dominate at temperatures above 100 K. Two competitive nonradiative recombination channels lead to the quenching of the exciton emissions. At room temperature, the FE emission could be tuned in the energy range from 3.33 to 3.416 eV by decreasing well layer thickness from 5.6 to 2.2 nm. The excellent properties of non-polar ZnO/\( \text{Zn}_{0.9}\text{Mg}_{0.1}\text{O} \) MQWs are very promising for ZnO-based optoelectronic devices.

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