Exciton localization in inhomogeneously broadened ZnO/Mg_xZn_{1-x}O quantum wells

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Exciton localization in ZnO/Mg_xZn_{1-x}O quantum wells (QWs) has been investigated systematically with various ZnO well widths for the fixed Mg_{0.23}Zn_{0.77}O barrier height. A strong exciton confinement is observed with an implicit dependence on the built-in electric field which is calculated to be 0.37 MV/cm. The exciton-phonon coupling strength varied significantly depending upon the degrees of exciton localization with the activation energy of 18–29 meV. The relaxation mechanism in ZnO/Mg_{0.23}Zn_{0.77}O QWs starts to dominate when the exciton localization energy is above the thermal energy, $k_B T$. The band characteristics and strong exciton localization in ZnO/Mg_{0.23}Zn_{0.77}O QWs are attributed to the potential fluctuations associated with the inhomogeneous broadening, represented by the schematics. © 2010 American Institute of Physics. [doi:10.1063/1.3452379]

I. INTRODUCTION

Heterointerface fluctuation due to alloy broadening and interface roughness plays a key role in quantum confinement effects in heterostructures. In particular to ZnO/Mg_xZn_{1-x}O quantum wells (QWs), Mg composition in Mg_xZn_{1-x}O barrier layer fluctuates locally due to shallow solubility limit of rocksalt MgO into wurtzite ZnO lattice matrix by leading to a complex potential profile in ZnO/Mg_xZn_{1-x}O QWs. The built-in electric field induced by the difference in spontaneous and piezoelectric polarizations induced due to the well/barrier heterointerfaces leads to modifications of optical properties of ZnO/Mg_xZn_{1-x}O QWs grows along the (0001) axis.¹ Owing to the small Bohr radius of the exciton, quantum confinement is extremely sensitive to these heterointerface complexities that finally lead to the translational asymmetry and optical disorders in ZnO/Mg_xZn_{1-x}O QWs. With the pioneering work on GaAs/AlGaAs system with the classical square well potential, the role of disorder in excitonic emission has been investigated in InGaAs/GaAs and AlGaSb/GaSb QWs.² Although the systematic studies of these translational asymmetries in the classical square well potential have been demonstrated in zincblende III-V materials, a less attention has been paid to the investigation of exciton localization and disorder in the wurtzite ZnO/Zn_{1-x}Mg_xO QWs.

Figures 1(a) and 1(b) show the schematics with the heterointerface broadening, band characteristics, and exciton localization in their absolute potential minima. Localization of excitons in disordered QWs is determined by the combination of Coulomb interaction between electrons and holes and electron and hole confinement caused by the fluctuations of the local band edges.³ For narrow QWs, a three-dimensional exciton moving model between the corrugated QW interfaces is represented by a quasi-two-dimensional exciton in a lateral disorder potential wave function $V_i(Z_i)$. For a short-range disorder in interfaces, the exciton averages over the underlying disorder with its relative wave function. These disorders break the in-plane translational symmetry in QWs

by leading to a dramatic change in the physical behavior of excitons by producing multiple scattering and different localization routes. In this letter, we address these issues in ZnO/Mg_{0.23}Zn_{0.77}O QWs deposited on Al₂O₃(0001) substrates. The exciton-phonon coupling strength depends on the degrees of exciton localization and the conduction band discontinuity is a result of heterointerface fluctuations. This heterointerface broadening in ZnO/Mg_xZn_{1-x}O QWs has been interpreted in terms of alloy broadening and interface roughness caused by the different phase contrast in MgO and ZnO materials and accumulation of possible droplets from the ablated plumes on the surface, respectively.

II. EXPERIMENTS

ZnO/Mg_xZn_{1-x}O QWs were fabricated on Al₂O₃(0001) substrates by pulsed laser deposition (PLD). The Al₂O₃ substrates were degreased chemically prior to loading into the PLD chamber. The Al₂O₃ substrates were then cleaned thermally inside the chamber for 30 min at 600 °C and O₂ gas was flown thereafter with the partial pressure of 550 mTorr. After the substrate pretreatment, excimer laser (KrF

FIG. 1. (Color online) Schematics of exciton in a QW with (a) rough interface with the corresponding band structure and (b) the corresponding effective potential $V_i(Z_i)$ for the exciton center of mass. The band structure is sketched with (dashed line)/without (solid line) the heterointerface broadening.

=248 nm) was used to ablate ZnO and MgZnO targets (purity 5 N) for the fabrication of ZnO QWs and $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ barrier layers at the substrate temperature of 500 °C. The laser pulse repetition rate was 2 Hz and 4 Hz for the ZnO and $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ layers, respectively with the constant laser power of 280 ± 4 mJ. The $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ buffer was deposited at 300 °C for the layer thickness of 480 nm and annealed at 550 °C for 20 min under the oxygen ambient prior to deposition of ZnO/ $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ QWs.

ZnO/ $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ QWs are characterized by x-ray diffraction (XRD) and photoluminescence (PL) measurements. PL measurements were conducted at LN_2 temperature by using the He–Cd laser source with the excitation wavelength of 325 nm. Photomultiplier tube was used for detection of ZnO/ $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ QWs luminescence.

III. RESULTS AND DISCUSSION

ZnO/ $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ QWs grow along the c -axis on $\text{Al}_2\text{O}_3(0001)$ substrate, confirmed by XRD measurement. Mg composition in $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ barrier layers is estimated from the XRD and PL measurements to be $23 \pm 2\%$. The lattice constant (a) and band gap energy (E_g) of $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ barriers followed $a = (3.249 - 0.047x)$ Å and $E_g = (3.345 + 4.314x)$ eV, respectively. By keeping $\text{Mg}_{0.23}\text{Zn}_{0.77}\text{O}$ compositions constant, ZnO well width was varied from ~ 6 Å to 63 Å. Figure 2(a) shows the PL spectra of ZnO for the bulk and QWs. This clearly reveals a blueshift of ~ 110 meV with the sharp and intense spectrum of ZnO QW. The tail of PL spectrum in the higher energy region shows the emission energy of barrier layer with a relatively broadband. Figure 2(b) shows the systematic ZnO well-dependent PL spectra. It clearly indicates the exciton energy shift with the decrease in ZnO well width. It is noted that no blueshift was observed in this experiment above the ZnO well width of >53 Å. Our PL system is limited to excite the $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ barrier layer for higher Mg composition as He–Cd laser is used with the excitation wavelength of 325 nm. The inset of Fig. 2(b) shows the temperature-dependent PL linewidth for the selected ZnO well widths as a function of inverse temperature and Fig. 2(c) shows the temperature-dependent PL peak energy position as a function of temperature.

Figure 3(a) shows the exciton energy of ZnO/ $\text{Mg}_{0.23}\text{Zn}_{0.77}\text{O}$ QWs as a function of ZnO well width (L_w). For instance, Makino *et al.*⁴ data is reproduced and plotted here together with our data. The PL peak energy is shifted from 3.345 to 3.653 eV for the corresponding L_w of 63 Å to 6 Å. This energy increment unit (E_g^{QW}/L_w) is estimated to be 5.4 meV/Å. Our experimental data agree well with the reference data. These experimental data have been fitted by considering the electron-hole interaction by means of a static-screened Coulomb potential and the built-in electric field, F . To estimate the magnitude of F across the ZnO/ $\text{Mg}_{0.23}\text{Zn}_{0.77}\text{O}$ QWs induced due to the difference of polarizations, the emission energy in a modified QW can be expressed by⁵

FIG. 2. (Color online) (a) PL spectra of bulk ZnO and ZnO/ $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ QW (ZnO well width is ~ 1.31 nm), (b) ZnO well-dependent PL spectra with their temperature-dependent linewidth (inset), and (c) temperature-dependent PL peak energy position for the different ZnO well widths. Mg-ZnO alloy peak is cut as we used the He–Cd laser with the excitation wavelength of 325 nm.

$$E_g^{\text{QW}} = E_g + \Delta E_c + \Delta E_v - E_b^{\text{ex}} - qL_w F, \quad (1)$$

where q is the elementary electron charge. In this fitting, the corresponding electron and hole masses of $0.28m_0$ and $0.78m_0$ are considered.⁴ Theoretical investigation showed that the experimental data are well fitted thoroughly (solid line) except at the ZnO well widths of 3–4 nm; around the ZnO exciton Bohr diameter (a_B) of 3.6 nm. Taking into account of exciton-phonon interaction, we fitted the exciton emission energies by considering the $\Delta E_c/\Delta E_v$ ratio of 42/56. In this theoretical fitting, it was found that the confinement energy has an implicit dependence on the F in ZnO/ $\text{Mg}_{0.23}\text{Zn}_{0.77}\text{O}$ QWs, which is calculated to be 0.37 MV/cm. It is noteworthy to mention that Makino *et al.*⁴ has

FIG. 3. (Color online) (a) PL peak energy position and (b) localization energy as a function of ZnO well width are plotted. Exciton Bohr diameter of ZnO is marked with a line for 3.6 nm. Taking into account of exciton-phonon interaction, the exciton emission energies have been fitted by considering the $\Delta E_c/\Delta E_v$ ratio of 42/56.

reported the F in ZnO/Mg_xZn_{1-x}O QWs in the range of 0.1–1.0 MV/cm.

In the intermediate area of L_W for $L_W > 4$ nm with constant L_B , the transition energy falls below the ZnO band gap energy of 3.36 eV at LN₂ temperature. It has been demonstrated that there is a quantum confined Stark effect in ZnO/Mg_xZn_{1-x}O QWs which basically shrinks the exciton emission energy.^{1,4} This observation is a quantitative understanding of the relation between the growth-induced defects and structural complexities in ZnO/Mg_{0.23}Zn_{0.77}O QWs. It is clear from Fig. 3(a) that with the increase in E_g^{QW} due to decrease in L_W , the energy increment (E_g^{QW}/L_W) unit is non-linear. It is expected that the physical origin of these difficulties lies in the significantly increased stability of excitons by localization. The exciton localization energy in ZnO/Mg_xZn_{1-x}O QWs can be extracted based on the band-tail model by

$$E_T^{QW} = E_g(T) - \frac{\alpha T^2}{T + \beta} - \frac{\sigma^2}{k_B T}, \quad (2)$$

where α and β are known as the fitting parameters. In principle, $\sigma^2/k_B T$ refers to the localization effect, in which σ indicates the degree of localization effect; namely a large value of σ means a strong localization effect.^{4,6}

Figure 2(c) shows the photon energy of ZnO wells as a function of temperature. For the individual QW, the extracted data of σ in ZnO/Mg_{0.23}Zn_{0.77}O QWs have been plotted as a function of L_W in Fig. 3(b). It shows that σ increases from 18 to 29 meV with the corresponding decrease in L_W of 40 Å to 6 Å. For $L_W > 34$ Å, σ is almost constant with the minimum localization energy of ~18 meV. It is noteworthy to mention that Makino *et al.* have reported the value of σ in ZnO/Mg_{0.24}Zn_{0.76}O QWs of 25 meV.⁴ The excitons are localized in ZnO/Mg_xZn_{1-x}O QWs due to the heterointerface

FIG. 4. (Color online) (a) Γ_0 , Γ_{LO} , and γ_{ph} properties in ZnO/Mg_xZn_{1-x}O QWs are plotted as function of (a) ΔE and (b) photon energy versus PL intensity for the MQWs. Solid lines are the polynomial curve fitting.

broadening as the excitons are in rest at their local minima, sketched in Fig. 1(b). This means that the carrier lifetime is very short in ZnO/Mg_xZn_{1-x}O QWs. It is noteworthy to mention that the time-resolved PL measurements (not shown) of ZnO/Mg_xZn_{1-x}O QWs indicated the carrier lifetime to be a few picoseconds.

In the strongly confined QWs, the size and shape of the localizing potential determines the spatial extension and anisotropy of electron-hole wave function and/or electron-hole overlapping. This has a significant influence on the exciton-phonon interaction, i.e., the excitons are locally distorted for the narrower L_W for sizes that are comparable to the exciton Bohr diameter.⁷ This overall distortion contributes to the PL linewidth broadening that can be accounted by $\Gamma_T = \Gamma_0 + \gamma_{ph}T + \Gamma_{LO}/[\exp(\hbar\omega_{LO}/k_B T) - 1]$, where Γ_0 , γ_{ph} , and Γ_{LO} are the linewidth at zero temperature, the coupling strength of the exciton-acoustic phonon and the strength of the exciton-longitudinal-optical (LO) phonon coupling, respectively. For each ZnO well width, temperature-dependent PL measurements were performed and fitted. All the fitted data for the each individual QW have been plotted as a function of ΔE in Fig. 4(a). The ΔE is defined as the energy difference between the corresponding well peak energy position and the peak energy of 1 LO for the ZnO material. The parameters Γ_0 and Γ_{LO} of the localized excitons obtained here are strongly dependent on ΔE in the range of 0–0.15 eV. Experimentally, Γ_0 is recorded in the range of 23–71 meV, while Γ_{LO} values are in the range of 120–760 meV. The gap between Γ_0 and Γ_{LO} decreases with the increase in ΔE and became more or less constant for $\Delta E \geq 0.15$ eV. While ΔE matches well with the LO-phonon energy of 72 meV in ZnO/Mg_{0.23}Zn_{0.77}O QWs, a strong exciton-phonon coupling

takes place. In this experiment, the Γ_{LO} is obtained in the range of 120–760 meV by indicating a strong exciton-LO phonon coupling in ZnO/Mg_{0.23}Zn_{0.77}O QWs. For example, Γ_{LO} values for ZnSe (Ref. 8) and GaN (Ref. 9) are 81 meV and 375–525 meV, respectively. It is clear that Γ_{LO} in ZnO/Mg_{0.23}Zn_{0.77}O QWs is larger than the ZnSe material but more or less similar to the GaN material.

On the contrary, γ_{ph} represents the acoustic-phonon coupling strength, mainly caused by the deformation potential coupling. A totally different behavior is observed in γ_{ph} (compared to Γ_0 and Γ_{LO}) that varied in the range of 6–18 meV/k without any obvious systematic dependence on ΔE , as shown in Fig. 4(a). The γ_{ph} curve starts from below the bulk value and crosses over the bulk value of ZnO for the well widths of 6 Å to 63 Å. This result suggests a reduction in exciton-acoustic-phonon interaction by localization. In quantum wires, such a reduction has been demonstrated by direct comparison of free and localized excitons.¹⁰ The weaker acoustic-phonon interaction has also been demonstrated in the II-VI materials system.⁷ Therefore, this observation implies that the interaction between exciton and acoustic-phonon is steadily reduced by increasing the exciton localization in ZnO/Mg_xZn_{1-x}O QWs. In principle, when the localization is strong, the energy level space is larger than the thermal energy $k_B T$ ($\Delta E \geq k_B T$), a further increase in the localization does not further reduce the coupling between exciton and acoustic-phonon as the level space has already been large enough for this bottleneck effect. In this regime, additional effects, like lattice relaxation mechanics takes place that influences the dependence of the exciton-acoustic-phonon interaction in the well widths.

Figure 4(b) shows the PL intensity of ZnO/Mg_{0.23}Zn_{0.77}O multiquantum wells (MQWs) as a function of photon energy. For comparison, PL intensity of binary GaAs and ternary AlGaAs MQWs is reproduced and plotted together.¹¹ For ZnO/Mg_{0.23}Zn_{0.77}O MQWs, the PL intensity is almost constant for exciton energy in the range of 3.345 to 3.51 eV and thereafter drops down sharply by broadening the PL line widths. Interestingly the similar tendency is observed in the ternary AlGaAs MQWs rather than in the binary GaAs MQWs.¹¹ This PL intensity decreasing tendency in MQWs can be explained in terms of the band-crossover in the conduction band in which $n=1$ quantum level for Γ electrons come close to or above the $n=1$ for the indirect band electrons. However, the reason for the PL intensity dropping in binary ZnO and GaAs MQWs is different which is not yet clear. It may be related to the problem of the conduction band discontinuity in narrow ZnO/MgZnO QWs where the alloy broadening and interface roughness are dominant, as represented with the schematic.

The PL linewidth in ZnO/Mg_xZn_{1-x}O QWs depends on the Mg_xZn_{1-x}O alloy content, x . This broadening is caused by a statistical occupation of Zn sites by Mg cations, resulting in the potential fluctuations discussed by Bajaj and co-workers.¹² This potential disorder in ZnO/Mg_{0.23}Zn_{0.77}O QWs induces the depth fluctuations and enhances the exciton localization energy. This inhomogeneous broadening in QWs in the presence of alloy disorder and interface roughness is described by a Gaussian function with a standard deviation

of $\Gamma_T^2 = \Gamma_{alloy}^2 + \Gamma_{rough}^2$. The contribution of alloy disorder to the excitonic broadening is given by¹² $\Gamma_{alloy} = 0.41 |dE_g/dx| \sqrt{x(1-x)} V_C/V_{ex}$, where V_C is the volume of the primitive cell (24.51 Å³) and $V_{ex} = 4\pi a_B^3/3$ is the exciton volume. The composition-dependent energy variation in Mg_{0.23}Zn_{0.77}O barrier height is estimated to be $|dE_g/dx| = 4.31$ eV. Using the value of $a_B = 18$ Å for bulk ZnO material, Γ_{alloy} is estimated to be 23.46 meV.

On the other hand, contribution of interface roughness in the inhomogeneous broadening is difficult to calculate because Γ_{rough} is sensitive to the lateral size of the valleys and islands as well as to the correlation between the two interfaces of the QWs. The quality of interface strongly depends on the many parameters, namely growth conditions and growth orientation/mode. In the oxide QWs, an enhancement of the broadening is also expected due to the presence of F that has been calculated to be 0.37 MV/cm. The electric field forces the electron and the hole closer to the two opposite interfaces, and, therefore, the exciton experiences the effect of the roughness more strongly. Assuming an equal density of the valleys and islands in ZnO/MgZnO QWs with lateral dimensions of order of a_B , Γ_{rough} can be calculated by¹³ $\Gamma_{rough} = |dE_{ex}^{QW}/dL_W| \delta L_W$, where $|dE_{ex}^{QW}/dL_W|$ is the variation in the exciton transition energy with the well width 0.054 eV/nm calculated from Fig. 3(a) and δL_W is the standard deviation of the probability distribution of the effective well width (0.185 nm). Then the estimated Γ_{rough} in ZnO/Mg_{0.23}Zn_{0.77}O QWs is to be 9.62 meV.

The full width at half maximum of the emission peak, $\Gamma_0 = \Gamma(8 \ln 2)^{1/2} = 2.35\Gamma$, is found to be 54 meV for a completely screened field and 84 meV for a maximum built-in electric field. Therefore, the experimental linewidth of 23–71 meV clearly indicates that the contribution from the interface roughness is there but not significant in the ZnO/Mg_{0.23}Zn_{0.77}O QWs. In the case of In_{0.15}Ga_{0.85}As/GaAs QWs, inhomogeneous broadening is reported of 2.0–6.8 meV.¹³ Therefore, this higher inhomogeneity in ZnO/Mg_{0.23}Zn_{0.77}O QW is attributed to the complex heterointerface due to the crucial local role of Mg atoms in Mg_xZn_{1-x}O alloys. In addition, the phase contrast in the rocksalt MgO and wurtzite ZnO adds an additional effect in the heterointerface inhomogeneity. It has been demonstrated that Mg atoms in (Zn and Mg) O lattice matrix relaxes asymmetrically under this phase contrast.¹⁴ The conduction band discontinuity is a result of this heterointerface fluctuations especially for the extremely narrow QWs ($L_W \leq 1$ nm), and thereby the sharp falls of PL intensity by broadening the PL line widths.

IV. CONCLUSION

Exciton localization in inhomogeneously broadened ZnO/Mg_{0.23}Zn_{0.77}O QWs has been demonstrated. The best fit for the exciton emission energies as a function of well width is found by using the $\Delta E_c/\Delta E_v$ ratio of 42/56. The activation energy of exciton localization is obtained to be 18–29 meV, while the built-in electric field is found to be 0.37 MV/cm. The alloy broadening and interface roughness that contribute to the inhomogeneous broadening are esti-

mated to be 23.46 meV and 9.62 meV, respectively. In addition, the lattice relaxation mechanics took place above the localization energy of 25 meV and the conduction band discontinuity is dominant below the well width of ≤ 1 nm observed in the ZnO/Mg_{0.23}Zn_{0.77}O QWs.

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