論文 / 著書情報
Article / Book Information

Title	Photoexcitation screening of the built-in electric field in ZnO single quantum wells
Authors	T. Makino,Y. Segawa,A. Tsukazaki,A. Ohtomo,M. Kawasaki
Citation	Applied Physics Letters, Vol. 93, No. 12,
Pub. date	2008, 9
URL	http://scitation.aip.org/content/aip/journal/apl
Copyright	Copyright (c) 2008 American Institute of Physics

Photoexcitation screening of the built-in electric field in ZnO single quantum wells

T. Makino,[1,a)] Y. Segawa,[2] A. Tsukazaki,[3] A. Ohtomo,[3] and M. Kawasaki[1,2,3,4]
[1]*WPI-Advanced Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan*
[2]*Cross-Correlated Materials Research Group (CMRG), Advanced Science Institute (ASI), RIKEN, Wako 351-0198, Japan*
[3]*Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan*
[4]*CREST, Japan Science and Technology Agency (JST), Tokyo 102-0075, Japan*

(Received 12 July 2008; accepted 20 August 2008; published online 23 September 2008)

$ZnO/Mg_{0.22}Zn_{0.78}O$ quantum wells were studied by excitation-intensity-dependent luminescence at 10 K. The samples were grown by laser molecular-beam epitaxy on $ScAlMgO_4$ substrates to evaluate the well width dependence (1 to 10 nm) of exciton transition energies. Under weak excitation, the photoluminescence shows a quantum-confined Stark effect for the wide wells. The well width dependences of the experimental transition energies are compared with previously reported calculations to evaluate the electric field due to spontaneous and piezoelectric polarizations. The internal electric field is comparable with 650 kV/cm. With an increase in excitation intensity, blueshift of the luminescence was observed, suggesting photoexcitation screening of electric fields. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2981523]

Wide band-gap semiconductors have attracted much attention due to their potential applications for optoelectronic devices operating in the blue and ultraviolet (UV) regions of the spectrum. Recently, ZnO and related oxides have been proposed as promising wide-gap semiconductors for short wavelength applications. The binding energy of ZnO excitons is relatively large[1,2] at 60 meV so that the excitonic recombination could be permitted even at room temperature. Several groups reported the growth of the *p*-type doped ZnO films,[1,2] which is very important for realizing practical application of light-emitting diodes. In addition, introduction of magnesium in ZnO plays a key role in band-gap engineering.[3,4] Growth of $ZnO/Mg_xZn_{1-x}O$ quantum wells (QWs) using various experimental methods has been reported: laser molecular-beam epitaxy (MBE),[4] metal-organic chemical vapor deposition,[5] and MBE.[6,7] In such a system grown along the *c*-axis, its optical properties are affected by both spontaneous and piezoelectric polarization effects. These effects result from the lattice mismatch and wurtzite symmetry. So far, the impact of strain in the ZnO well layer on the electric field has not been extensively studied. Bretagnon *et al.*[8] pointed out the importance of lengthening a barrier layer thickness (L_B) to precisely evaluate the built-in electric field, which is 900 kV/cm for $ZnO/Mg_{0.22}Zn_{0.78}O$ single QWs (SQWs). In this work, we report on optical properties of ZnO QWs and a screening effect of the built-in electric field with photocarriers studied by estimating the excitation intensity dependence of the photoluminescent spectra. The blueshift of the emission is observed under stronger excitation, probably due to the screening of the electric field by the photocarriers.

Our SQW samples were grown by laser MBE on high-temperature annealed MgZnO templates (being 100 nm in thickness) deposited on the *c*-plane of the $ScAlMgO_4$ (SCAM) substrates. The top barrier layer is composed of 50-nm-thick $Mg_xZn_{1-x}O$ ($x=0.22$). Thus, it could be regarded as a ZnO well sandwiched between $Mg_xZn_{1-x}O$ barriers. We have grown samples having a continuously spread variation in the well widths on a substrate using a moving mask during the deposition. The technique was adopted so as to suppress variation in the crystal growth conditions, which is suited for systematic study on the material properties.[9] Details of the growth conditions and experimental setup have been given elsewhere.[2] These samples were characterized by photoluminescence (PL) spectroscopy at temperature of 10 K.[10] Two QW samples, having nominally same specifications, were studied. The well width of the first sample ranges from 1 to 10 nm, while the other one ranges from 2.7 to 8.3 nm. A continuous-wave He–Cd laser (emitting wavelength is 325 nm) was used as an excitation source.

Figure 1(a) shows near-band edge PL spectra in $ZnO/Mg_{0.22}Zn_{0.78}O$ SQWs for eleven different well thicknesses ($2.7\ \mathrm{nm} \leq L_w \leq 8.3\ \mathrm{nm}$). The excitation intensity is $\sim 160\ \mathrm{kW/cm^2}$. For wide well widths ($L_w \gtrsim 3.9$ nm), the QW spectra exhibit PL peaks below the exciton resonance of bulk ZnO (3.37 eV, a vertical dashed line in Fig. 1).

Stronger excitation yielded in different PL features, as shown in Fig. 1(b). The strong excitation condition was performed by the frequency-tripled pulsed beam from a *Q*-switch yttrium aluminum garnet laser (3.49 eV, $\sim 1.6\ \mathrm{kW/cm^2}$). Now, the PL peak energies are higher than or nearly equal to the resonance energy of the bulk. Second, the width of the peak became sharper under such stronger excitation.

Figure 2 shows the emission energy (triangles and squares) as a function of L_w (1–10 nm) under weaker excitation. The PL energies obtained for the two specimens are in reasonable agreement with respect to each other. As expected, the emission from ZnO QWs exhibits strong dependence on L_w. Due to the quantum confinement effect, the blueshift of the emission was observed when L_w is decreased. When $L_w \gtrsim 3.9$ nm, strong redshift observed under weak excitation is a typical phenomenon of the existence of a quantum-confined Stark effect (QCSE), as illustrated in the

a)Electronic mail: tmakino@imr.tohoku.ac.jp.

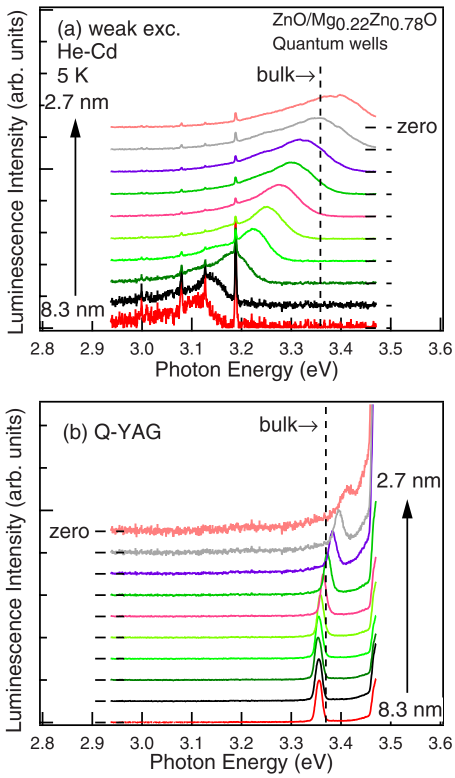

FIG. 1. (Color online) Luminescence spectra in ZnO/(Mg,Zn)O QW samples taken at 10 K: the well widths (L_w) were varied from 2.7 to 8.3 nm. Two sets of experimental spectra are shown under weak (a) and strong (b) excitation conditions. Three sharp lines around 3.1 or 3.2 eV in (a) are artifacts (discharged emissions from an excitation source of a He-Cd laser). Vertical dashed lines indicate the energy of free exciton in bulk ZnO.

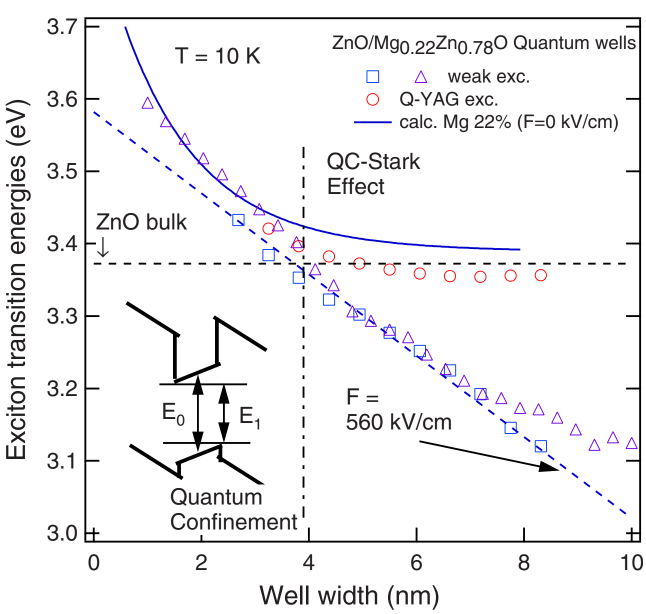

FIG. 2. (Color online) Well width dependences of PL energies for two different excitation intensities in the QWs (open circles, triangles, and squares). Also shown by a solid line are calculated transition energies of excitons neglecting the electric field, which are from Ref. 8. Dashed line corresponds to behavior of the energy shift with the presence of the built-in electric field of 560 kV/cm. The peak shifting behavior (from E_0 to E_1) is schematically depicted in the inset. A horizonatal dashed line indicates the energy of free exciton in bulk ZnO.

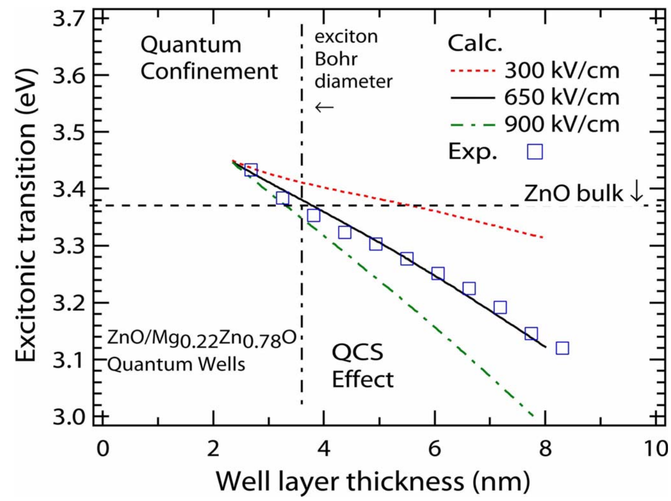

FIG. 3. (Color online) Calculated excitonic transition energies taking effects of the built-in electric field (dashed, solid, and dashed-dotted lines) for three different electric fields into account, cited from Ref. 8. Also shown is the well width dependence of experimental PL energies under weaker excitation (open circles). A horizonatal dashed line indicates the energy of free exciton in bulk ZnO. Also shown by a vertical dashed-dotted line is a value of exciton Bohr *diameter* (i.e., 3.6 nm).

inset of Fig. 2.[11] The electric field pushes the electrons and holes in the well layer to the opposite direction and hence leads to the fundamental transition below the exciton gap of bulk ZnO. Our data exhibited linear relationship between the PL energies and the well thickness, as shown by a dashed line. The linearity is valid as long as the exciton binding energy is independent of the well thickness as later discussed in detail. The slope of the dashed line leads to an internal electric field of ~560 kV/cm.

The experimental data under stronger excitation (~1.6 kW/cm^2) were also plotted against L_w (open circles, L_w=2.7–8.8 nm). It is obvious that the emission energies became close to the calculation result of the excitonic transition energies (blue solid line) neglecting an electric field (F=0 kV/cm) theoretically deduced by Bretagnon *et al.*[8] It can be understood as a result of the screening of the internal electric field caused by the excitation-induced carriers. The energy difference between experiments (open circles) and calculation (solid line), for L_w=6.6 nm, is about 40 meV. This energy difference could correspond to a localization energy of the QW excitons. The localization of excitons occurs due to fluctuations of the well width and/or barrier heights.[12]

Here, we try to evaluate the built-in electric field of our samples. Bretagnon *et al.*[8] calculated the exciton transition energies as a function of Mg composition (x) of the barrier layers including the effects of internal electric field. The quenching of the excitonic binding energies (E_b^{ex}) due to the presence of the field is also taken into account in the calculation. For sufficiently wide wells, where the quantum-confinement effects are negligible, it can be regarded as an impact of electric field (F) on the transition energies. Our experimental results are again plotted in Fig. 3 with the results of calculation abovementioned[8] for F=300, 650, and 900 kV/cm.

As it is understood from the comparison in Fig. 3, the experimental data are in reasonably good agreement with the calculated results for the field of 650 kV/cm. The value is slightly greater than that obtained in Fig. 2 (≃560 kV/cm), neglecting the effect of field-induced instability of excitons. It is reasonable because the E_b^{ex} tends to be a decreasing function of L_w under $F \neq 0$.

Bretagnon and co-workers determined the electric field inherent to a $ZnO/Mg_{0.22}Zn_{0.78}O$ SQWs to be 900 kV/cm, which is slightly greater in magnitude than our value.[8] The magnesium composition of our SQWs is similar to that evaluated in Ref. 8, whereas the barrier layer thickness (L_B=50 nm) is different from that of the latter QWs (L_B=200 nm). The difference in the evaluated electric field can be explained in terms of what is called a "L_B-dependent geometrical effect." The field in the well is approximately proportional to $L_B/(L_w+L_B)$. This may be a possible reason of the difference in the electric field.

We discuss the QCSE quenching at the high-excitation power.[7,13] As the excitation power increases, the PL transition moves to the higher energy side especially for wide enough wells. A self-consistent theoretical approach predicted the screening effect of the built-in polarization[13,14] by photoexcited carriers. The photocreated charged carriers accumulated on the two edges of the well layer compensate the built-in electric field, thus leading to a blueshift of the emission. The photoinduced energy shift is dependent on the L_w. For narrow wells, energy difference is smaller than those at greater L_ws. This tendency on L_w is considered to be consistent with the photoinduced removal of the QCSE. The relevant effect has been verified in GaN and ZnO multiple QWs.[11,14]

In summary, the study of PL energies of excitons as a function of well width (L_w) from 1 to 10 nm was presented for $ZnO/Mg_{0.22}Zn_{0.88}O$ single QWs grown by laser MBE. From the comparison between weakly and strongly photoexcited conditions, a QCSE is revealed. We deduced an internal electric field strength as large as ~650 kV/cm, which is slightly smaller than the previously reported value for the almost same Mg composition.[8] It is explained in terms of the geometrical factor. The photocarrier screening effect of internal electric field on the luminescence energy has been also evidenced by the luminescence blueshift with an increase in excitation intensity.

The authors are thankful to Y. Takagi for helpful discussions. This work was partially supported by JFE 21st Century Foundation, the Asahi Glass Foundation, and the interuniversity cooperative program of the IMR, Tohoku University, Japan.

[1] D. C. Look, D. C. Reynolds, C. W. Litton, R. L. Jones, D. B. Eason, and G. Cantwell, Appl. Phys. Lett. **81**, 1830 (2002).
[2] A. Tsukazaki, A. Ohtomo, T. Onuma, M. Ohtani, T. Makino, M. Sumiya, K. Ohtani, S. F. Chichibu, S. Fuke, Y. Segawa, H. Ohno, H. Koinuma, and M. Kawasaki, Nat. Mater. **4**, 42 (2005).
[3] T. Makino, Y. Segawa, M. Kawasaki, A. Ohtomo, R. Shiroki, K. Tamura, T. Yasuda, and H. Koinuma, Appl. Phys. Lett. **78**, 1237 (2001).
[4] T. Makino, Y. Segawa, M. Kawasaki, and H. Koinuma, Semicond. Sci. Technol. **20**, S78 (2005).
[5] B. P. Zhang, B. L. Liu, J. Z. Yu, Q. M. Wang, C. Y. Liu, Y. C. Liu, and Y. Segawa, Appl. Phys. Lett. **90**, 132113 (2007).
[6] C. Morhain, T. Bretagnon, P. Lefebvre, X. Tang, P. Valvin, T. Guillet, B. Gil, T. Taliercio, M. Teisserire-Doninelli, B. Vinter, and C. Deparis, Phys. Rev. B **72**, 241305 (2005).
[7] T. V. Shubina, A. A. Toropov, O. G. Lublinskaya, P. S. Kop'ev, S. V. Ivanov, A. El-Shaer, M. Al-Suleiman, A. Bakin, A. Waag, A. Voinilovich, E. V. Lutsenko, G. P. Yablonskii, J. P. Bergman, G. Pozina, and B. Monemar, Appl. Phys. Lett. **91**, 201104 (2007).
[8] T. Bretagnon, P. Lefebvre, T. Guillet, T. Taliercio, B. Gil, and C. Morhain, Appl. Phys. Lett. **90**, 201912 (2007).
[9] H. Koinuma and I. Takeuchi, Nat. Mater. **3**, 429 (2004).
[10] T. Makino, C. H. Chia, N. T. Tuan, Y. Segawa, M. Kawasaki, A. Ohtomo, K. Tamura, and H. Koinuma, Appl. Phys. Lett. **76**, 3549 (2000).
[11] T. Makino, A. Ohtomo, C. H. Chia, Y. Segawa, H. Koinuma, and M. Kawasaki, Physica E (Amsterdam) **21**, 671 (2004).
[12] T. Makino, N. T. Tuan, H. D. Sun, C. H. Chia, Y. Segawa, M. Kawasaki, A. Ohtomo, K. Tamura, and H. Koinuma, Appl. Phys. Lett. **77**, 975 (2000).
[13] F. Bernardini and V. Fiorentini, Phys. Rev. B **57**, R9427 (1998).
[14] S. F. Chichibu, T. Sota, K. Wada, S. P. DenBaars, and S. Nakamura, MRS Internet J. Nitride Semicond. Res. **4S1**, G2.7 (1999).