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Enhancement of exciton binding energies in ZnO/ZnMgO multiquantum wells

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The effect of confinement on the exciton binding energies has been systematically investigated for two series of ZnO/ZnMgO multiquantum wells with various well widths and barrier heights. The exciton binding energies were extracted from the energy difference between the stimulated emission band induced by inelastic exciton–exciton scattering and the free exciton absorption band. The binding energies of excitons are found to be sensitively dependent on the well widths. The experimental results of the well width dependence of binding energies are in good agreement with Coli and Bajaj's theoretical calculations for these structures [G. Coli and K. K. Bajaj, *Appl. Phys. Lett.* **78**, 2861 (2001)]. The remarkable reduction in coupling strength between excitons and longitudinal optical phonons is closely correlated with the enhancement of the exciton binding energy, indicating that the stability of excitons is greatly increased by the enhancement of exciton binding energy in quantum wells. © 2002 American Institute of Physics.
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I. INTRODUCTION

ZnO is an interesting wide band-gap semiconductor, which can be found in a number of widespread applications including varistors, phosphors, surface acoustic wave devices, and transparent conductive thin films. With its direct band gap of about 3.34 eV at room temperature,¹ ZnO has also drawn attention for its promise for applications in short wavelength optoelectronic devices. Compared with other wide band-gap materials, such as ZnSe, GaN, and SiC, etc., ZnO has numerous advantages for device applications including higher chemical and thermal stability, higher radiation hardness, and lower growth temperature. These properties are favorable for the fabrication and long lifetime operation of devices.² Moreover, ZnO has a very large exciton binding energy, which allows efficient excitonic emission at high temperatures. As is well known, the oscillator strength of excitons is much larger than that of direct electron–hole transitions. In addition, the energy distribution of optical gain by excitonic recombination is much narrower than that of band edge free carrier recombination, thus a lasing process based on the excitonic effect is expected to have a higher gain and a lower threshold than that of an electron-hole plasma (EHP).³ This makes it desirable to develop optoelectronic devices based on excitonic effects. However, for most semiconductor materials, the exciton

binding energy is so small that excitonic effects only play a role at low temperatures. To the contrary, ZnO has an exciton binding energy as large as about 60 meV.¹ This feature assures the stability of excitons in ZnO at high temperatures, in view of the thermal activation energy of ~ 25 meV at 300 K. Hence, ZnO is widely recognized as an ideal material for realizing room temperature excitonic devices, and as such has attracted much attention.^{4–6}

With the advances in the epitaxial technology of ZnO and related alloys, quantum well (QW) structures are of considerable practical interest. Due to the quantum confinement effect, quantum well structures may provide larger oscillation strength, enhanced exciton binding energy, and tunability of the operating wavelength. To understand the excitonic optical properties, it is essential to know the effect of quantum confinement on the exciton binding energy (E_{ex}^b) in QWs. This effect has been extensively studied in III–V narrow band-gap semiconductor QWs.⁷ However, very few experimental results about the quantum size effect have been reported for II–VI wide band-gap semiconductor QWs.^{8,9} This is because the exciton radius of a wide band-gap semiconductor is relatively small so that the quantum size effect is pronounced only as its size in the confinement direction becomes very small.

The practical problem with experimentally investigating the quantum size effect is the difficulty in determining E_{ex}^b in QWs precisely.¹⁰ The most common and probably the simplest method is to obtain the difference between the excitonic energy and corresponding continuum edge by the use of pho-

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to current, photoreflectance, or absorption spectroscopy.^{8,11} However, these methods suffer from difficulty in determining the onset of continuum states. More reliable measurements come from low-temperature photoluminescence or magneto-absorption experiments,⁹ where two clearly resolved peaks are identified as $1s$ and $2s$ exciton states. These measurements give the energy difference $|E_{2s} - E_{1s}|$ directly. However, since the ratio of E_{1s}/E_{2s} in a practical QW is not constant, a reliable theory is needed to compare with experimental value of $|E_{2s} - E_{1s}|$ to deduce E_{ex}^b accurately.^{9,10} In this article, we will give the results of an experimental study of effects of confinement on E_{ex}^b in ZnO/ZnMgO multiquantum wells (MQWs). The value of E_{ex}^b is directly extracted from the energy difference between the stimulated emission band induced by exciton–exciton scattering and the free excitonic absorption peak. The binding energies of excitons are found to be dramatically enhanced compared with bulk ZnO and dependent on the well widths. The experimental results of well width dependence of E_{ex}^b are in good agreement with the theoretical calculations made by Coli and Bajaj for these structures.¹² It was observed that the exciton–longitudinal optical (LO)–phonon coupling strength is greatly reduced in MQWs and closely correlated to the exciton binding energy. This result shows that the stability of excitonic states in ZnO/ZnMgO MQWs is greatly enhanced by the enhancement of exciton binding energy.

II. EXPERIMENT

The ZnO/Zn_{1-x}Mg_xO MQWs were grown by the laser-molecular beam epitaxy (MBE) method on ScAlMgO₄ (SCAM) substrates. Details of the preparation process are described elsewhere.¹³ The active regions of the QW structures consisted of alternating ZnO well layers and Zn_{1-x}Mg_xO barrier layers with 10 periods. Several pixels of MQWs with the same composition x in the barrier layers but different well widths were integrated into the same substrate using the combinational masking method.¹⁴ The thickness of the barrier layers was kept at about 5 nm, while that of well layers ranged from 0.69 to 4.65 nm. Since the lattice of ZnO matches that of substrate SCAM well, the strain effect is negligibly small,¹⁵ so the samples provide an ideal model system with which to study the intrinsic excitonic properties.

The samples were mounted on the cold finger of a helium-cooled cryostat that had proper access for optical measurements including spectra of absorption, surface photoluminescence (PL), and stimulated emission (SE). The sample temperature could be continuously varied from 5 K to room temperature. For stimulated emission measurement, the sample was optically pumped in an edge emission geometry using a dye laser (351 nm). The dye laser was pumped by a XeCl excimer laser (308 nm) with a pulse width of ~ 13 ns and a repetition rate of 10 Hz. The excitation laser beam was focused onto the sample surface using a cylindrical lens to form a rectangular stripe with an area of $\sim 800 \times 100 \mu\text{m}^2$. Emission was collected from one edge of the sample and coupled into a 300 mm monochromator with a 1200 line/mm grating, and was detected by a thermal-electric cooled charge coupled device. Surface photoluminescence was measured in

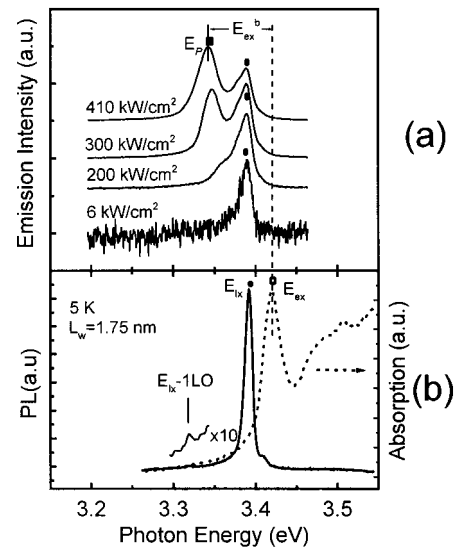


FIG. 1. (a) Evolution of normalized edge emission spectra of ZnO/Zn_{0.88}Mg_{0.12}O MQWs with well width of 17.5 Å as the excitation intensity increases from 6 to 410 kW/cm². (b) Surface photoluminescence spectrum under weak excitation by a cw He–Cd laser (solid line) and an optical absorption spectrum (dotted line) taken at 5 K.

conventional backscattering geometry using a continuous-wave He–Cd laser (325 nm) as the excitation source. Since the SCAM substrate is transparent in the spectral region of interest and no buffer layer was introduced, absorption spectroscopy measurement is quite convenient. Transmittance spectra were measured using a 150 W xenon arc lamp as a light source. The light from the spectral lamp was focused onto the sample with spot size about 1 mm in diameter, and the light transmitted was dispersed and detected by the system mentioned above. The absorption coefficient was determined by comparing the light intensity transmitted from samples with ZnO/Zn_{0.88}Mg_{0.12}O MQWs and those without the MQW epilayer.¹⁶

III. RESULTS AND DISCUSSION

Figure 1(a) shows the evolution of normalized edge emission spectra of a ZnO/Zn_{0.88}Mg_{0.12}O MQW sample with well width (L_w) of 1.75 nm taken at 5 K, where the excitation density varied from 6 to 410 kW/cm². Figure 1(b) shows the absorption and PL spectra plotted for the same sample. The strong excitonic features dominate the low-temperature absorption spectrum. The fundamental excitonic peak can be assigned to the $1s$ exciton resonant peaks of the lowest sub-band transition of MQWs, the peak energy of which is referred to as free exciton energy E_{ex} . The PL band is Stokes shifted with respect to E_{ex} , and is attributed to radiative recombination of localized excitons (E_{Lx}). On the lower energy side of the localized exciton emission band there is a weak emission band. Since the energy difference between this band and the localized exciton emission band is ~ 71 meV, equivalent to the LO-phonon energy $\hbar\omega_{LO}$ of ZnO, this weak emission band can be reasonably assigned as a LO-phonon replica of the localized exciton emission band. At the lowest pumping intensity, only one spontaneous emission

peak (E_{lx}) was observed, and it was located at the same position as the PL peak. With an increase in pumping density, a new peak appeared at the lower energy side of the E_{lx} band. Above a certain threshold, this peak grew superlinearly with respect to the excitation density, indicating stimulated emission. By analyzing the energy position of the SE band relative to the exciton absorption band and their temperature dependence, the SE band shown in Fig. 1 was attributed to excitonic recombination induced by inelastic exciton–exciton scattering (so-called P -band emission).¹⁷ It was confirmed that P -band emission had a much lower threshold than EHP emission and can survive well at room temperature.

In the process of exciton–exciton scattering, an exciton gives some energy to another one and then decays to the ground state, emitting a photon with energy E_P . Generally speaking, exciton–exciton scattering may occur in two ways: one of the excitons may be scattered into an excited state (the excitation process, referred to as P_n -band emission) or it may be scattered into a continuum state (the dissociation process, referred to as P -band emission).^{18,19} Both of these processes contribute to the emission spectrum. At high excitation density, P -band emission becomes dominant, whereas the P_n -band becomes saturated. As a result, the emission peak shifts toward the lower energy side and finally converges at the P band. This process has been well studied in bulk ZnO. For the three-dimensional case, the peak energy of P_n -band emission can be expressed as^{4,18}

$$E_{P_n}^{\max} = E_{ex} - E_{ex}^b (1 - 1/n^2) - 3 \delta k_B T \quad (1a)$$

or for P band

$$E_P = E_{ex} - E_{ex}^b - 3 \delta k_B T, \quad (1b)$$

where E_{ex} is the free exciton energy and E_{ex}^b is the exciton binding energy. The last term in Eqs. (1) represents the kinetic energy, which is very small compared with the exciton binding energy of ZnO and which can be negligible at low temperatures. Thus the exciton binding energy can easily be extracted from Eqs. (1) as $E_{P_n}^{\max}$, and E_{ex} can be readily determined from P_n -band stimulated emission and absorption spectra, respectively. This can be expressed as

$$E_{ex}^b = (E_{ex} - E_{P_n}^{\max}) / (1 - 1/n^2) \quad (2a)$$

or

$$E_{ex}^b = E_{ex} - E_P. \quad (2b)$$

For the quasi two-dimensional (2D) case (as in our quantum wells), the P_n -band energy position is difficult to determine analytically because of difficulty in expressing the excited state energies of excitons. However, it is expected that Eq. (2b) still applies. Therefore, we determined the exciton binding energy from the energy difference between the P line and the excitonic resonance position at low temperature. As an example, the P -band and free excitonic positions (E_{ex}) of the sample shown in Fig. 1 are at 3.334 and 3.420 meV, respectively, so the exciton binding energy is estimated to be

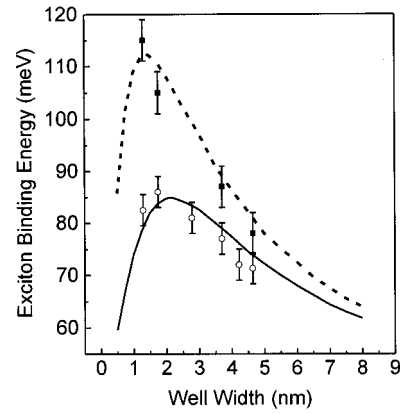


FIG. 2. Variation of the exciton binding energies in ZnO/Zn_{1-x}Mg_xO MQWs as a function of well width. The symbols refer to the experimental values for $x=0.12$ (open circles) and $x=0.27$ (closed squares). Lines refer to the theoretical calculation which takes into account exciton–phonon interaction through the Pollmann–Büttner potential (see Ref. 12).

86 meV. Compared with other methods of determining E_{ex}^b ,^{8,9} our method is more straightforward and therefore should be more reliable.

Shown in Fig. 2 is the well width dependence of exciton binding energies for two series of samples. These two series of samples have the same structure except for the barrier height: the Mg contents of the barrier layers are 0.12 and 0.27, corresponding to barrier heights of 0.2 and 0.5 meV, respectively. As can be clearly seen, the exciton binding energies in MQWs are well width dependent, and significantly higher than those of bulk ZnO. For the series with $x=0.12$, the exciton binding energy increases monotonically up to 86 meV as the well width decreases from 4.65 to 1.75 nm. This tendency is apparently a result of the quantum confinement effect. It is interesting to note that the exciton binding energy decreases to 82 meV as the well width further decreases to 1.29 nm. This feature is reasonable because, in the case of finite well depth, the penetration of electron and hole wave functions into the barrier layer increases as the well width gets smaller, so that for very thin wells the excitons tends toward three-dimensional excitons.⁷ For the series with $x=0.27$, the dependence of the exciton binding energies on well widths exhibits a similar tendency. Due to the large inhomogeneous broadening in thinner wells it is difficult to unambiguously assign the emission band. The corresponding data for well widths thinner than 1.29 nm were not yet available. Thus we have not observed the decrease in exciton binding energy due to wave function penetration. Since the well depth is deeper than for $x=0.12$, it is believed that the turning point for $x=0.27$ MQWs occurs at a narrower well width. As is expected, the quantum confinement effect in the samples with $x=0.27$ is much more pronounced due to the deeper confinement. The highest exciton binding energy is as high as 115 meV, almost double that of bulk ZnO. The remarkable enhancement of exciton binding energies in MQWs should be favorable for the realization of excitonic optoelectronic devices operating at higher temperature.

Coli and Bajaj have calculated both the excitonic transition energies and exciton binding energies for these two se-

ries of MQWs.¹² The results of their calculations for excitonic transition energies as a function of well width agreed well with our experimental data. However, a comparison has not been done for the well width dependence of the exciton binding energy. For such a comparison, we would also give the result of their theoretical calculations which take into account the exciton–phonon interaction through the Pollmann–Büttner potential. The experimental results are in good agreement with the theoretical calculation. It is important to point out that Coli and Bajaj have also calculated the exciton binding energy by describing the electron–hole interaction with a static-screened Coulomb potential but obtained much lower values and exhibited bigger errors (not shown here).¹² They have shown that even including the variation of E_{ex}^b as a function of the well width, calculated assuming a static-screened Coulomb interaction, did not provide a full explanation of the exciton transition energies that were determined by absorption spectra at low temperature. On the other hand, the agreement between their theoretical calculation which takes into account exciton–phonon interaction and the experimental data of both the exciton binding energy and exciton transition energies is much better, demonstrating the importance of LO phonons in ZnO related heterostructures. This is understandable if we keep it in mind that ZnO is a strongly polar compound and thus the coupling between phonons and charged particles should be strong.

It is interesting and important to investigate the correlation between the exciton binding energy and the stability of excitons in MQWs. The latter is reflected by the temperature dependence of excitonic absorption. In fact, lifetime broadening of the excitonic absorption peak is generally interpreted as being due to exciton–phonon interaction. The temperature dependence of the full width at half maximum (FWHM) can approximately be described by the following equation:^{20,21}

$$\Gamma(T) = \Gamma_{\text{inh}} + \gamma_{\text{ph}}T + \Gamma_{\text{LO}} / [\exp(\hbar\omega_{\text{LO}}/k_B T) - 1], \quad (3)$$

where Γ_{inh} , $\hbar\omega_{\text{LO}}$, γ_{ph} , and Γ_{LO} are the inhomogeneous linewidth at 0 K, the LO-phonon energy, the coupling strength of the exciton-acoustic phonon, and the strength of exciton–LO–phonon coupling, respectively. From Eq. (3) it is known that acoustic phonon induced broadening is linear while LO-phonon induced broadening is nonlinear with respect to temperature. Generally, the former process is weak and only dominates at low temperature. Thus the stability of excitons is often represented by the strength of the exciton–LO–phonon coupling Γ_{LO} . The Γ_{LO} values can be extracted by least squares fitting the temperature dependence of excitonic absorption width with Eq. (5) in Ref. 15. We have performed the fitting process for a series of samples ($x = 0.12$) with different well widths, and plotted the well width dependence of Γ_{LO} , shown in Fig. 3. As a comparison, we also include the Γ_{LO} value for a single layer ZnO thin film on the same substrate.²² It can be seen from Fig. 3 that the Γ_{LO} values in the ZnO MQW samples are well width dependent and remarkably reduced compared with those of a ZnO single layer. This means that the stability of excitons in MQWs has been greatly enhanced. Also in Fig. 3, we illustrate the well width dependence of exciton binding energies.

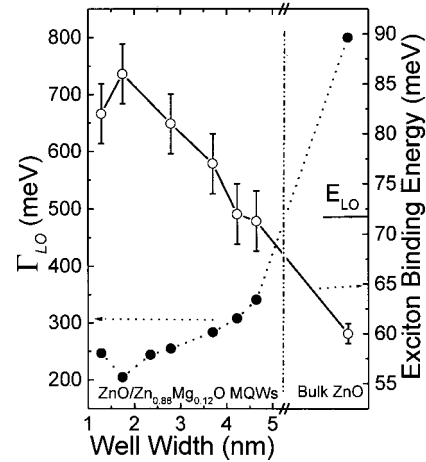


FIG. 3. Coupling strength between the exciton and LO-phonon Γ_{LO} (closed circles) and the exciton binding energies (open circles) in bulk ZnO and ZnO/Zn_{1-x}Mg_xO MQWs ($x = 0.12$) of different well thickness.

It can be clearly seen that the values of Γ_{LO} are closely related to the exciton binding energies. This correlation can be explained well by the following argument.

As is well known, the major processes that contribute to exciton lifetime broadening is that a $1s$ exciton either dissociates into the free electron-hole continuum or scatters within the discrete exciton bands by absorbing one LO phonon via Fröhlich interaction.⁹ Hence the strength of the exciton–LO–phonon coupling Γ_{LO} is dependent on the polarity of the material and the magnitude of the exciton binding energy relative to the LO-phonon energy. For bulk ZnO, the binding energy of a three-dimensional (3D) exciton is about 60 meV and the LO-phonon energy is about 72 meV.¹ Therefore, the probability of exciton dissociation through one LO-phonon scattering is quite high if we account for the strong polarity, which should give rise to rather large Γ_{LO} for ZnO. However, for the MQW samples studied in this work, the QW widths are comparable to or less than the Bohr diameter of 3D exciton (given the Bohr diameter of 3.6 nm for ZnO).¹ This spatial confinement increases the exciton binding energy substantially so that it becomes larger than the LO-phonon energy.²³ In this case, the dissociation efficiency of $1s$ exciton into the continuum states is largely suppressed and Γ_{LO} is effectively reduced. Nevertheless, the transition from $1s$ to other excited exciton states (for example, the $2s$ state) is still possible, but the transition probability depends on the relative ratio of $\hbar\omega_{\text{LO}}$ to E_{ex}^b . This correlation is similar to the theoretical calculations for other II–VI semiconductor quantum well structures.¹⁰

IV. SUMMARY

We have experimentally investigated the well width dependence of exciton binding energies in ZnO/ZnMgO multi-quantum wells. The exciton binding energies in MQWs were determined by the energy difference between the P -band emission and the free exciton absorption peak. The binding energies of excitons in MQWs are found to be much higher than those of bulk ZnO. The experimental results can be

explained well by the quantum size effect, and are in good agreement with the theoretical calculations which took into account exciton–phonon interaction of these structures. It was also found that the coupling strength between the exciton and LO phonon in ZnO/ZnMgO MQWs is largely reduced compared within bulk ZnO. This remarkable reduction is closely correlated with enhancement of the exciton binding energy, indicating that the stability of excitons is greatly increased by the enhancement of exciton binding energy in quantum wells.

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- ¹E. Mollwo, in *Semiconductors: Physics of II–VI and I–VII Compounds, Semimagnetic Semiconductors, Landolt-Börnstein New Series* Vol. 17, edited by O. Madelung, M. Schulz, and H. Weiss (Springer, Berlin, 1982), p. 35.
- ²Y. Chen, D. M. Bagnall, H. Koh, K. Park, K. Hiraga, Z. Zhu, and T. Yao, *J. Appl. Phys.* **84**, 3912 (1998).
- ³B. Hönerlage, R. Levy, J. B. Grun, C. Klingshirn, and K. Bohnert, *Phys. Rep.* **124**, 161 (1985).
- ⁴Y. Segawa, A. Ohtomo, M. Kawasaki, H. Koinuma, Z. K. Tang, P. Yu, and G. K. L. Wong, *Phys. Status Solidi B* **202**, 669 (1997); P. Yu, Z. K. Tang, G. K. L. Wong, M. Kawasaki, A. Ohtomo, H. Koinuma, and Y. Segawa, *Solid State Commun.* **103**, 459 (1997); Z. K. Tang, G. K. L. Wong, P. Yu,

- M. Kawasaki, A. Ohtomo, H. Koinuma, and Y. Segawa, *Appl. Phys. Lett.* **72**, 3270 (1998).
- ⁵D. M. Bagnall, Y. Chen, Z. Zhu, T. Yao, S. Koyama, M. Y. Shen, and T. Goto, *Appl. Phys. Lett.* **70**, 2230 (1997).
- ⁶H. Cao H, Y. G. Zhao, H. C. Ong, S. T. Ho, J. Y. Dai, J. Y. Wu, and R. P. H. Chang, *Appl. Phys. Lett.* **73**, 3656 (1998).
- ⁷S. Schmitt-Rink, D. S. Chemla, and D. A. B. Miller, *Adv. Phys.* **38**, 89 (1989).
- ⁸R. Cingolani *et al.*, *Phys. Rev. B* **51**, 5176 (1995).
- ⁹N. T. Pelekanos, J. Ding, M. Hagerott, A. V. Nurmikko, H. Luo, N. Samarth, and J. K. Furdyna, *Phys. Rev. B* **45**, 6037 (1995).
- ¹⁰R. S. Zheng and M. Matsuura, *Phys. Rev. B* **58**, 10769 (1998).
- ¹¹R. Cingolani *et al.*, *Phys. Rev. B* **50**, 12179 (1994).
- ¹²G. Coli and K. K. Bajaj, *Appl. Phys. Lett.* **78**, 2861 (2001).
- ¹³A. Ohtomo, M. Kawasaki, I. Ohkubo, H. Koinuma, T. Yasuda, and Y. Segawa, *Appl. Phys. Lett.* **75**, 980 (1999).
- ¹⁴Y. Matsumoto, M. Murakami, Z. W. Jin, A. Ohtomo, M. Lippmaa, M. Kawasaki, and H. Koinuma, *Jpn. J. Appl. Phys., Part 2* **38**, L603 (1999).
- ¹⁵H. D. Sun, T. Makino, N. T. Tuan, Y. Segawa, M. Kawasaki, A. Ohtomo, K. Tamura, and H. Koinuma, *Appl. Phys. Lett.* **78**, 2464 (2001).
- ¹⁶W. Stolz, J. C. Maan, M. Altarelli, L. Tapfer, and K. Ploog, *Phys. Rev. B* **36**, 4301 (1987).
- ¹⁷H. D. Sun *et al.*, *Appl. Phys. Lett.* **77**, 4250 (2000).
- ¹⁸C. Klingshirn and H. Haug, *Phys. Rep.* **70**, 315 (1981).
- ¹⁹C. Klingshirn, *Phys. Status Solidi B* **71**, 547 (1975).
- ²⁰R. Hellmann, M. Koch, J. Feldmann, S. T. Lundiff, E. O. Gobel, D. R. Yakovlev, A. Waag, and G. Landwehr, *Phys. Rev. B* **48**, 2847 (1993).
- ²¹M. O'Neill, M. Oestrich, W. W. Ruhle, and D. E. Ashenford, *Phys. Rev. B* **48**, 8980 (1993).
- ²²T. Makino, C. H. Chia, N. T. Tuan, Y. Segawa, M. Kawasaki, A. Ohtomo, K. Tamura, and H. Koinuma, *Appl. Phys. Lett.* **76**, 3549 (2000).
- ²³The LO-phonon energy $\hbar\omega_{LO}$ in our MQWs was determined by observing the LO-phonon sideband shown in Fig. 1. It was found that $\hbar\omega_{LO}$ does not exhibit an obvious change with the well width in the MQWs.