Temperature dependence of excitonic absorption spectra in ZnO/Zn0.88Mg0.12O multiquantum wells grown on lattice-matched substrates

Sun, Handong; Makino, T.; Tuan, N. T.; Segawa, Y.; Kawasaki, M.; Ohtomo, A.; Tamura, K.; Koinuma, H.

2001

Sun, H. D., Makino, T., Tuan, N. T., Segawa, Y., Kawasaki, M., Ohtomo, A., et al. (2001). Temperature dependence of excitonic absorption spectra in ZnOÕZn0.88Mg0.12O multiquantum wells grown on lattice-matched substrates. Applied Physics Letters., 78(17), 2464-2466.

https://hdl.handle.net/10356/101293

https://doi.org/10.1063/1.1367300

Temperature dependence of excitonic absorption spectra in $ZnO/Zn_{0.88}Mg_{0.12}O$ multiquantum wells grown on lattice-matched substrates

H. D. Sun,[a] T. Makino, N. T. Tuan, and Y. Segawa
Photodynamics Research Center, Institute of Physical and Chemical Research (RIKEN), Sendai 980-0845, Japan

M. Kawasaki, A. Ohtomo, and K. Tamura
Department of Innovative and Engineered Materials, Tokyo Institute of Technology, Yokohama 226-8502, Japan

H. Koinuma[b]
Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama 226-8503, Japan

(Received 30 June 2000; accepted for publication 22 February 2001)

The excitonic properties of high-quality $ZnO/Zn_{0.88}Mg_{0.12}O$ multiquantum wells grown by laser-molecular-beam epitaxy were investigated using temperature-dependent optical absorption spectra from 5 K to room temperature. The strength of exciton-longitudinal-optical (LO) -phonon coupling was deduced from the temperature dependence of the linewidth of the fundamental excitonic peak. Effective reduction of the exciton-LO-phonon coupling with decreasing the well width was observed, which is consistent with the confinement-induced enhancement of the exciton binding energy. The thermal shift of the lowest excitonic energy is independent of well width, indicating that the strain effect is negligible for this material. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1367300]

ZnO has a large fundamental band gap of ~3.37 eV, which makes it a promising material for use in ultraviolet light-emitting devices and laser diodes. Apart from higher chemical and thermal stability, ZnO has the advantage of a larger exciton binding energy (about 60 meV),[1] which assures more efficient excitonic emission at higher temperatures. Recently, there have been some reports on the observation of stimulated emission in ZnO thin films induced by inelastic exciton–exciton scattering at room temperature,[2,3] which is desirable for the realization of low-threshold semiconductor lasers. From the viewpoint of device applications, it is advantageous to construct low-dimensional structures such as quantum wells (QWs), wires, or dots because such structures may provide larger oscillation strength, enhanced binding energy in the excitonic region, and tunability of operating wavelength.[4] Toward this goal, Ohtomo *et al.* prepared $ZnO/Mg_xZn_{1-x}O$ multiquantum well (MQW) structures on sapphire substrates.[5] Recently, the quality of QW structures has been improved by the employment of lattice-matched $ScAlMgO_4$ (SCAM) as substrates; efficient photoluminescence has been observed at room temperature in these structures.[6] However, the dependence of excitonic properties of this MQW structure on temperature and well width has not been fully studied, although it is crucial to device applications.

In this letter, we report on the excitonic properties of $ZnO/Zn_{0.88}Mg_{0.12}O$ multiquantum wells grown on SCAM substrates using optical absorption measurements. Both the energy position and width of the excitonic absorption peak of MQWs with different well widths were investigated as a function of temperature. The thermal shift of the excitonic energy shows similar behavior for different widths, indicating that the effect of strain in the wells is negligible as a result of very small lattice mismatching between ZnO and the SCAM substrate. The exciton-longitudinal-optical (LO) -phonon coupling strength (Γ_{LO}) decreases with decreasing the well width, which is consistent with the observation of confinement-induced enhancement of exciton binding energy.

$ZnO/Zn_{1-x}Mg_xO$ MQW structures with ten periods were grown by a laser-molecular-beam-epitaxy technique on a SCAM substrate (0001).[6] Since the SCAM substrate is lattice-matched with ZnO (0.08%), no buffer layer was introduced. Nine MQWs with different QW widths were integrated in the same substrate using the combinational masking method reported in Ref. 7. In this study, the Mg content of the barrier layer was chosen to be $x=0.12$, corresponding to a barrier height of about 0.2 eV. The thickness of the barrier layer was kept at about 50 Å, while the thickness of the ZnO QW layers ranged from 0.69 to 4.65 nm. In addition to the merit of lattice matching to ZnO, SCAM is transparent in the spectral region of interest, which makes absorption spectroscopy measurements convenient. The sample was mounted inside a liquid-helium-cooled cryostat, the temperature of which could be varied from 5 K to room temperature. 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 a spot size of about 1 mm in diameter, and the transmitted light was dispersed by a 0.3 m grating monochromator with charge-coupled-device detector. The absorption coefficient was determined by comparing the transmitted light intensity from a sample with

[a]Author to whom correspondence should be addressed; electronic mail: sunhd@postman.riken.go.jp
[b]Also a member of CREST, Japan Science and Technology Corporation.

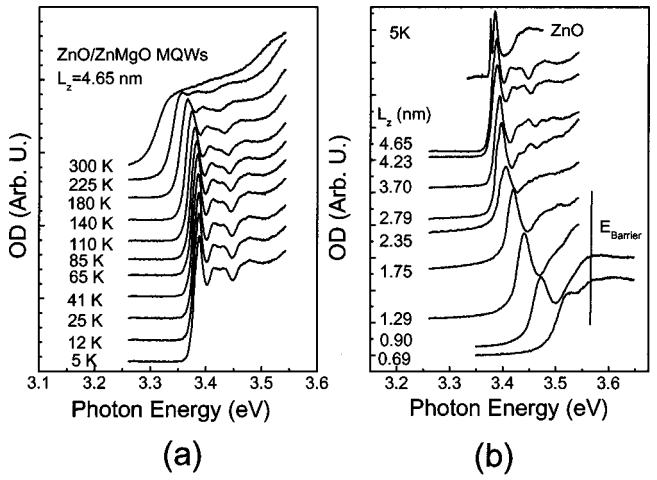

FIG. 1. Optical absorption spectra of a $ZnO/Zn_{0.88}Mg_{0.12}O$ MQW sample with a well width of 4.65 nm at various temperatures (a), and MQW samples with various well widths at 5 K (b), where E_{Barrier} denotes the band-gap energy of the barrier layers. Spectra have been relatively shifted in the vertical direction for clarity.

$ZnO/Zn_{0.88}Mg_{0.12}O$ MQWs and without the MQW epilayer.[8]

In Fig. 1(a), the evolution of the absorption spectra with temperature for a typical MQW sample with a well width of 4.65 nm is shown. The absorption spectra for all nine samples at 5 K are shown in Fig. 1(b). Strong exciton features dominate the low-temperature spectra. The fundamental excitonic peaks can be assigned to the *1S* exciton resonant peaks of $n=1$ subband transitions of MQWs. Quantity n corresponds to the principal quantum number of the subbands. In Fig. 1, the absorption spectrum of a single ZnO epitaxial layer, about 55 nm in thickness, on a SCAM substrate is shown. One can see that the peak energy of the fundamental exciton absorption increases as the well thickness decreases, as a result of the quantum-confinement effect. The dependence of the peak energies on the well thickness is in agreement with the theoretical calculation.[6]

At 5 K, the exciton linewidth Γ_{inh}, of inhomogeneous origin, increases with the decrease of the well width. The inhomogeneous broadening is attributed to two dominant mechanisms: monolayer-type interface roughness and alloy concentration fluctuations. The linewidth of the excitonic peak broadens as the temperature increases.

Thermal broadening of the excitonic absorption peak is generally interpreted as due to an exciton–phonon interaction. The temperature dependence of the full width at half maximum (FWHM) can be approximately described by the following equation:[9,10]

$$\Gamma(T)+\Gamma_{\mathrm{inh}}+\gamma_{\mathrm{ph}}T+\frac{\Gamma_{\mathrm{LO}}}{[\exp(\hbar\omega_{\mathrm{LO}}/k_BT)-1]}, \qquad (1)$$

where Γ_{inh}, $\hbar\omega_{\mathrm{LO}}$, γ_{ph}, and Γ_{LO} are the inhomogeneous linewidth at zero temperature, the LO-phonon energy, the coupling strength of the exciton-acoustic phonon, and the strength of the exciton-LO-phonon coupling, respectively.

Figure 2(a) shows the temperature dependence of the FWHM of the excitonic absorption peak for a typical MQW sample with a QW width of 4.65 nm. The solid line represents the fitted result based on Eq. (1). The best fit is obtained for the parameter values $\Gamma_{\mathrm{inh}}=17$ meV, $\gamma_{\mathrm{ph}}=31$ μeV/K, and $\Gamma_{\mathrm{LO}}=341.5$ meV. Here, we take $\hbar\omega_{\mathrm{LO}}$ to be 72

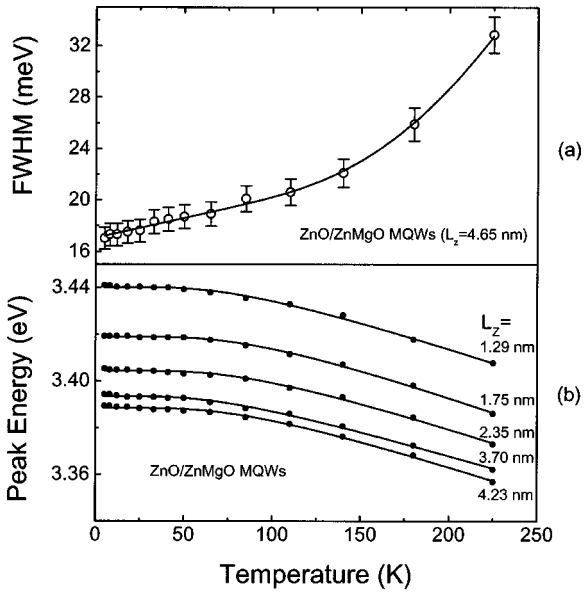

FIG. 2. (a) FWHM of ZnO MQWs with a QW thickness of 4.65 nm as a function of temperature. The solid line represents the fit according to $\Gamma(T)=\Gamma_{\mathrm{inh}}+\gamma_{\mathrm{ph}}T+(\Gamma_{\mathrm{LO}}/[\exp(\hbar\omega_{\mathrm{LO}}/k_BT)-1])$; (b) Temperature dependence of the fundamental absorption peak energy for ZnO MQWs with different well widths L_z. The filled circles are experimental data, and the solid lines are the corresponding fits based on $E(T)=E(0)-(\lambda/[\exp(\beta/T)-1])$.

meV, equal to that of bulk ZnO. It should be pointed out that $\hbar\omega_{\mathrm{LO}}$ does not exhibit an obvious change of well width for the MQWs investigated in this letter, as determined by photoluminescence spectra. We have made the same fitting procedure for other samples and summarize the obtained values of Γ_{LO} for different QW widths in Fig. 3. As a comparison, we also include the Γ_{LO} value for a single-layer ZnO thin film on the same substrate.[11]

It can be seen from Fig. 3 that the Γ_{LO} values in the ZnO MQW samples have been largely reduced compared with the ZnO single layer, and monotonically decrease with decreasing QW widths. This result can be explained by the enhance-

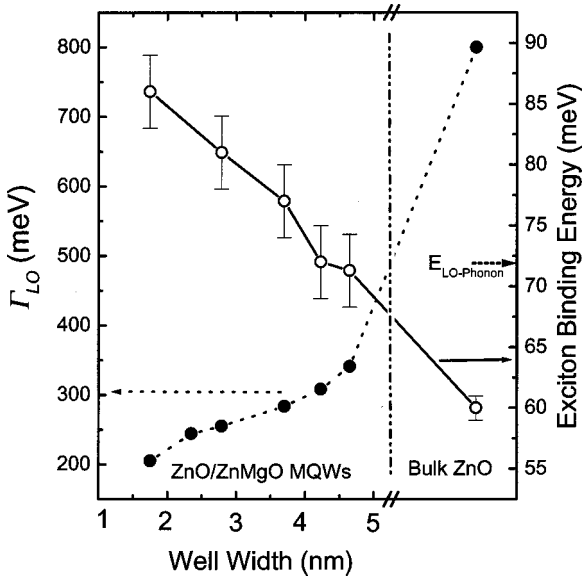

FIG. 3. Coupling strengths between exciton and LO phonons Γ_{LO} (solid circles) and the exciton binding energies (open circles) in bulk ZnO and MQWs of different well thicknesses.

ment of the exciton binding energy (E_b^{ex}) induced by quantum confinement. As is well known, the major process that contributes to exciton linewidth 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 the Fröhlich interaction.[12] Here, Γ_{LO} is dependent on the polarity of the materials 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 72 meV.[1] Therefore, there must be many channels for exciton dissociation, which together with the high polarity, gives rise to rather large Γ_{LO} for ZnO. However, for the QW samples studied in this work, the QW widths are comparable, or less than, the 3D exciton Bohr diameter [given a Bohr diameter of 3.6 nm for ZnO (Ref. 1)]. Because of the space confinement, the excitons show quasi-two-dimensional feature rather than 3D, so that the binding energies of the excitons are more or less enhanced. In Fig. 3, we also illustrate the exciton binding energies for the same set of MQW specimens, which were determined by the difference between the fundamental absorption peak energy and the stimulated emission peak energy induced by exciton–exciton scattering at 5 K.[13] Except for the widest sample, all samples exhibit E_b^{ex} higher than 72 meV. In consideration of the measurement error, we believe that E_b^{ex} in all the samples exceeds $\hbar\omega_{LO}$. Therefore, the dissociation efficiency of the *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, a *2S* state) is still possible. With decreasing of the well width, the exciton binding energy is further enhanced and the energy separation between *1S* and *2S* becomes gradually less accessible. This can explain the further reduction of Γ_{LO} as the QW widths change from 4.65 to 1.75 nm. A similar effect was also observed in other QW systems.[12,14]

Figure 2(b) summarizes another important issue: the temperature dependence of the *1S* exciton absorption peak of ZnO MQW samples with various QW widths. It has been found that all the samples show the same amount of redshift of the fundamental excitonic energy of about 33 ± 2 meV as the temperature increases from 5 to 225 K. The thermal shift of the band gap of the semiconductors is believed to arise from the shift in the relative position of the conduction and valence bands due to temperature-dependent lattice dilation and electron-lattice interaction. The temperature dependence of the characteristic energy can be described by the Varshni formula,[15] or the following Bose–Einstein expression:[16]

$$E(T)=E(0)-\frac{\lambda}{[\exp(\beta/T)-1]}, \tag{2}$$

where λ, β are fitting parameters, and $E(0)$ is the band gap at a temperature of 0 K. By assuming that the exciton binding energy is temperature independent, we fit the fundamental absorption peak according to Eq. (2). It is noted that except for $E(0)$, all the samples have the same fitting parameters with $\lambda=0.070\pm0.005$ eV and $\beta=250\pm10$ K. It is worthwhile noting that the lattice mismatch and the difference in the thermal expansion coefficient between the heterostructures are known to induce strain.[17,18] The strain has an effect on both the band gap and its dependence on temperature, and is sensitive to the thickness.[17,18] The fact that the excitonic energies of the MQW samples with different well widths show the same temperature shift suggests that the strain effect plays a negligible role. This negligible strain effect can be attributed to the very small in-plane lattice mismatch among ZnO well layers, SCAM, and $Mg_{0.12}Zn_{0.88}O$ barrier layers ($<0.12\%$).[5] The quantum-well sample without strain is favorable for device application because it is free from degradation of the luminescence efficiency induced by the piezoelectric field.[6]

In summary, the temperature dependence of optical absorption spectra of $ZnO/Zn_{0.88}Mg_{0.12}O$ MQWs having various QW widths was studied. The effective reduction of the exciton-LO-phonon coupling with decreasing the well width was observed, which could be explained by the confinement-induced enhancement of the exciton binding energy. This property is propitious to the stabilization of excitons at high temperatures. The strain effect plays a negligible role in these MQW samples due to the very small in-plane lattice mismatch among ZnO well layers, SCAM, and $Mg_{0.12}Zn_{0.88}O$ barrier layers.

This work was partially supported by the Proposal Based Program of NEDO (Grant No. 99S12010) and the Special Postdoctoral Research Program of RIKEN, Japan.

[1] E. 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.
[2] Y. 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).
[3] D. M. Bagnall, Y. Chen, Z. Zhu, T. Yao, S. Koyama, M. Y. Shen, and T. Goto, Appl. Phys. Lett. **70**, 2230 (1997).
[4] S. Schmitt-Rink, D. S. Chemla, and D. A. B. Miller, Adv. Phys. **38**, 89 (1989).
[5] A. Ohtomo, M. Kawasaki, I. Ohkubo, H. Koinuma, T. Yasuda, and Y. Segawa, Appl. Phys. Lett. **75**, 980 (1999).
[6] T. Makino, C. H. Chia, N. T. Tuan, H. D. Sun, Y. Segawa, M. Kawasaki, A. Ohtomo, K. Tamura, and H. Koinuma, Appl. Phys. Lett. **77**, 975 (2000).
[7] Y. Matsumoto, M. Murakami, Z. W. Jin, A. Ohtomo, M. Lippmaa, M. Kawasaki, and H. Koinuma, Jpn. J. Appl. Phys., Part 2 **38**, L603 (1999).
[8] W. Stolz, J. C. Maan, M. Altarelli, L. Tapfer, and K. Ploog, Phys. Rev. B **36**, 4301 (1987).
[9] R. Hellmann, M. Koch, J. Feldmann, S. T. Lundiff, E. O. Gobel, D. R. Yakovler, A. Waag, and G. Landwehr, Phys. Rev. B **48**, 2847 (1993).
[10] M. O'Neill, M. Oestriech, W. W. Ruhle, and D. E. Ashenford, Phys. Rev. B **48**, 8980 (1993).
[11] 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).
[12] N. T. Pelekanos, J. Ding, M. Hagerott, A. V. Nurmikko, H. Luo, N. Samarth, and J. K. Furdyna, Phys. Rev. B **45**, 6037 (1992).
[13] H. D. Sun, T. Makino, N. T. Tuan, Y. Segawa, Z. K. Tang, G. K. L. Wong, M. Kawasaki, A. Ohtomo, K. Tamura, and H. Koinuma, Appl. Phys. Lett. **77**, 4250 (2000).
[14] J. S. Wiener, D. S. Chemla, D. A. B. Miller, T. H. Wood, D. Sivco, and A. Y. Cho, Appl. Phys. Lett. **46**, 619 (1985).
[15] Y. P. Varshni, Physica (Utrecht) **34**, 149 (1967).
[16] P. Lautenschlager, M. Garriga, S. Logothetidis, and M. Cardona, Phys. Rev. B **35**, 9174 (1987).
[17] I. A. Buyanova, J. P. Bergman, B. Monemar, H. Amano, and I. Akasaki, Appl. Phys. Lett. **69**, 1255 (1996).
[18] V. Srikant and D. R. Clarke, J. Appl. Phys. **81**, 6357 (1997).