論文 / 著書情報
Article / Book Information

Title	Size dependence of exciton-longitudinal-optical-phonon coupling in ZnO/Mg_0.27_Zn_0.73_O quantum wells
Authors	T. Makino,K. Tamura,C. H. Chia,Y. Segawa,M. Kawasaki,A. Ohtomo,H. Koinuma
Citation	Physical Review B, Vol. 66, No. 23,
発行日/Pub. date	2002, 12
公式URL/Journal URL	http://journals.aps.org/prb/
権利情報/Copyright	Copyright (c) 2002 American Physical Society

PHYSICAL REVIEW B **66**, 233305 (2002)

Size dependence of exciton–longitudinal-optical-phonon coupling in $ZnO/Mg_{0.27}Zn_{0.73}O$ quantum wells

T. Makino,[1,*] K. Tamura,[1,2] C. H. Chia,[1,3] Y. Segawa,[1,3] M. Kawasaki,[2,4] A. Ohtomo,[2,4] and H. Koinuma[5,†]
[1]*Photodynamics Research Center, RIKEN (The Institute of Physical and Chemical Research), Aramaki-aza-Aoba 519-1399, Sendai 980-0845, Japan*
[2]*Department of Innovative and Engineered Materials, Tokyo Institute of Technology, Yokohama 226-8502, Japan*
[3]*Department of Physics, Tohoku University, Sendai 980-8578, Japan*
[4]*Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan*
[5]*Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama 226-8503, Japan*

(Received 13 June 2002; published 6 December 2002)

We studied the photoluminescence taken at 5 K from $ZnO/Mg_{0.27}Zn_{0.73}O$ quantum wells on lattice-matched substrates which were grown by laser molecular-beam epitaxy. Well-width dependence of the coupling between localized excitons and longitudinal-optical phonons was estimated experimentally. It is found that the Huang-Rhys factor *S*, which determines the distribution of luminescence intensities between the phonon replicas and the zero-phonon peak, increases significantly when the well width increases. We assign this variation to (i) the fact that electric field present across the well layer by polarization effects tends to push electrons and holes to the opposite side of well layer, and (ii) the localization of the excitons in the plane of the wells due to potential fluctuations that are induced by well width and barrier height fluctuations.

DOI: 10.1103/PhysRevB.66.233305 PACS number(s): 78.55.Et, 81.15.Fg, 71.35.Cc, 72.15.−v

The wide gap wurtzitic semiconductor, ZnO, has received much attention in the past years due to the potential applications for short-wavelength light-emitting devices. This results in a large number of publications devoted to the ZnO epitaxy.[1–3] There is now a fairly good understanding of the properties of ZnO epitaxial layers. On the other hand, it is only recently that the properties of quantum wells (QW's) have been studied in detail.[4]

The interaction between electrons and phonons has a great influence on the optical and electrical properties of semiconductors.[5] One of the important results of exciton-phonon interaction is the temperature-induced broadening of excitonic linewidth in the absorption or reflection spectra.[6,7] In the previous work, we estimated the well-width (L_w) dependence of the exciton-phonon coupling strength.[8] It was found that the coupling strength between excitons and longitudinal-optical (LO) phonons (Γ_{LO}) increases drastically with L_w.

We assigned this variation in Γ_{LO} to the enhancement of the exciton binding energy (EBE) due to the quantum confinement effect. In the case of the bulk ZnO, because the LO-phonon energy of 72 meV is larger than the EBE of 60 meV,[9] there must be many channels for exciton dissociation which gives rise to rather large Γ_{LO}. However, this is no longer the case for ZnO multiple quantum wells (MQW's): the EBE exceeds the LO-phonon energy.[10] Because the dissociation efficiency of the excitons into the continuum states is largely suppressed, Γ_{LO} is reduced. A similar effect was also observed in other QW systems.[7,8]

Another important results of the exciton-phonon interaction is the appearance of phonon replicas of excitons in the luminescence spectra.[5] The intensities of these replicas, relative to the zero-phonon peak, depend strongly on the exciton-phonon coupling strength. Within the Franck-Condon approximation, the distribution of emission intensities between phonon replicas and the main emission peak may be described in terms of the Huang-Rhys factor *S*. In the case of oxide-based low-dimensional heterostructures, the LO phonon replicas have not been studied in detail up to now, although their observation has been reported in the low-temperature photoluminescence (PL) spectra of ZnO/MgZnO MQW's.[10,11] Is the L_w dependence obtained from the former experimental result different from that obtained from the latter experiment? Scattering processes between excitons distributed near the bottom of their dispersion curve and phonons in the anti-Stokes direction contribute to the ''thermo-broadening.'' On the other hand, mechanism of appearance of phonon replicas is related to scattering in the Stokes direction. Here we restrict ourselves to consider the replicas on Stokes side because it is easier to detect experimentally than anti-Stokes replicas. Therefore it is considered that the above-mentioned enhancement in the EBE hardly influences the L_w dependence of the *S* factor. Does this result in the change of the L_w dependence? This question has not been fully clarified yet even in other III-V and II-VI semiconductor low-dimensional systems.

The purpose of this work is to answer the above-mentioned question. In this paper, we present the PL study of a series of ZnO/MgZnO QW samples which were grown by laser molecular-beam epitaxy (MBE) with various L_w. We show that the *S* factor increases significantly when L_w increases. Our attempt of qualitative explanation is based on the fact that electrons and holes are distributed on opposite sides along the *c*-axis direction by the presence of electric field induced by the piezoelectric effect and the effect of spontaneous polarizations.

The ZnO QW samples were grown by laser MBE on $ScAlMgO_4(0001)$ substrates. The structures consist of ten-period MQW's with ZnO wells and 50-Å-thick (Mg,Zn)O barriers. The L_w studied here are 6.9, 9.0, 12.9, 17.5, 23.5,

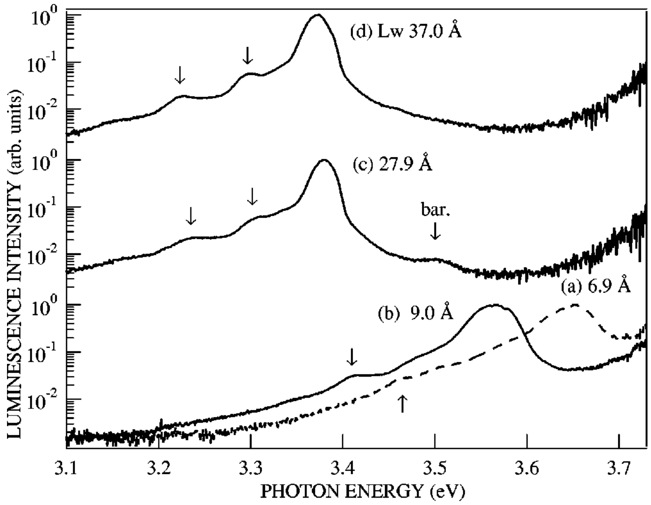

FIG. 1. PL spectra of ZnO QW samples measured at 5 K. Spectra (a)–(d) were measured from four samples with different well widths of the QW samples. A spectrum (a) was drawn by a dashed curve. Well widths are shown in the figure. The LO-phonon replicas are indicated as arrows in the figure. A nomenclature of "bar." means the radiative recombination of excitons distributed in the barrier layers.

27.9, and 37.0 Å, respectively. The exciton Bohr radius of ZnO is ≈ 18 Å. All the samples in our photoluminescence (PL) study were freshly prepared specifically for this study. There is small possibility that the amount of the electric fields applied across well layers is changed very gradually with the time lapse on the scale of months. Such kind of slow changes may be induced by changes of surface states of the samples. Details of the growth procedure and the band-gap energy in $Mg_xZn_{1-x}O$ have been given elsewhere.[12] KrF excimer laser pulses were impinged on ZnO single crystals (99.9999%) or $Mg_xZn_{1-x}O$ ceramic targets (99.999%) located 5 cm away from the substrate surface. The films were grown at 600 °C in 1×10^{-5} Torr of pure oxygen (99.9999%). Energy diagrams of conduction and valence bands are shown in Ref. 4. PL spectra were measured by using apparatuses identical to those used in our previous study.[4]

Figure 1 shows 5-K PL spectra corresponding to four $ZnO/Mg_{0.27}Zn_{0.73}O$ QW samples. The PL spectra are normalized so that the strongest peaks are of the same intensity. The zero-phonon peak of PL measured are (from the low-energy side) at energies of 3.373, 3.380, 3.567, and 3.651 eV, respectively. The zero-phonon emission bands were assigned to the radiative recombination of the localized excitons, as described in our previous paper.[4] This is due to the localization of carriers in regions of larger L_w and/or induced by barrier height fluctuation. Obviously, an increase in L_w from 6.9 to 37.0 Å results in a decrease in PL peak energy. This can be explained by the well-known quantum confinement effect.[4] Probably, a luminescence peak at 3.5 eV [indicated with "bar." in Fig. 1(c)] is related to radiative recombination from localized excitons distributed in the barrier layers.

Here we evaluate the intensity of the LO-phonon replica, relative to the intensity of the zero-phonon peak, as a function of L_w. The 1LO and 2LO phonon replicas are clearly seen for $L_w \geqslant 23.5$ Å. On the other hand, emission of the phonon replicas for the samples with thinner well layers is much weaker. Particularly, one could hardly estimate the S factor for the L_w's of 6.9–17.5 Å. The relative intensity of the replicas increases drastically with the thickness of QW's, i.e., increase of the coupling of electron-hole pairs with phonons. A similar variation was also observed in GaN MQWs and quantum boxes by Kalliokos *et al.*[14] The experimental S factors and L_w thickness are given in Table I, respectively.

TABLE I. Value of experimental Huang-Rhys factor S as a function of well-layer thickness (L_w) obtained in the QW samples. Nomenclature "BL" means "below the estimation limit."

Well layer thickness (Å)	S factor
6.9	BL
9.0	BL
12.9	BL
17.5	BL
23.5	0.053
27.9	0.028
37.0	0.070

Coming to a qualitative interpretation of these results, we note that S generally depends strongly on the spatial distributions of electron and hole charge densities.[5,13,14] The Huang-Rhys factor S becomes larger when the distance between electrons and holes becomes large. It is thus easy to infer that the reduced overlap of these electron and hole charge densities must be somehow responsible for the observed variation of S.[14] The increase of the S factor is due to the separation of electron and hole charges along the c-axis direction by the electric field. It seems that the distance between the electron and holes in this direction is not decided only by Coulomb force. Since ZnO crystallizes in a form of wurtzite, differences in the lattice constant and in a spontaneous polarization coefficient between well and barrier layers give rise to the electric field across well layers. The electric field pushes the electrons and the holes towards opposite sides of the well.

Here we discuss the effect of lateral spreading of excitonic wave functions on the L_w dependence of S factor. According to the model of Kalliokos *et al.*, the S factor does not significantly depend on the L_w as long as the effect of lateral spreading is uniquely taken into account. This is because the lateral extension of excitonic wave functions is mainly determined by the localization length of excitons. As is well known, excitons are localized inside potentials. In-plane pseudo-Bohr radius (λ) reflects the lateral spatial extension. The hydrogenic part of the excitonic envelope function is chosen by the two-dimensional approximation. Generally when increasing the L_w, the electron-hole Coulomb attraction is loosened, resulting in an increase of λ and hence the decrease of S value.[14,15] However, in this case, it is unnecessary to take such effect into account, because the radius of λ is blocked even with the increase in L_w. Therefore L_w dependence of the S factor is determined by the separation of electron and hole charges along the c-axis direction by the electric field, which lead to the increasing variation in S factor.

In summary, we observed the PL bands associated with the localized excitons at 5 K in ZnO/$Mg_{0.27}Zn_{0.73}O$ quantum wells on lattice-matched substrates. The study of the coupling between electron-hole pairs and LO phonons in ZnO QW samples has been conducted. We found that the value of the Huang-Rhys S factor increases monotonically with an increase of the thickness of the QW's. We tried to explain qualitatively this experimental finding by the fact that the distance between charge distribution is not merely controlled by the Coulomb attraction. Probably, electric field present across the well layer by polarization effects tends to push electrons and holes to the opposite side of well layer, which induces the significantly increasing variation in charge distance. The Huang-Rhys factor S is monotonically increasing function of the charge distance, which is compatible with the experimental variation.

---

*Electronic address: tmakino@postman.riken.go.jp

†Also at: Combinatorial Materials Exploration and Technology, Tsukuba 05-004, Japan.

[1] 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).

[2] Y.F. Chen, H.K. Ko, S. Hong, and T. Yao, Appl. Phys. Lett. **76**, 559 (2000).

[3] B. Gil, Phys. Rev. B **64**, 201310(R) (2001).

[4] 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).

[5] C.B. Duke and G.D. Mahan, Phys. Rev. **139**, 1965 (1965).

[6] S. Rudin, T.L. Reinecke, and B. Segall, Phys. Rev. B **42**, 11 218 (1990).

[7] N.T. Pelekanos, J. Ding, M. Hagerott, A.V. Nurmikko, H. Luo, N. Samarth, and J.K. Furdyna, Phys. Rev. B **45**, 6037 (1992).

[8] H.D. Sun, T. Makino, N.T. Tuan, Y. Segawa, M. Kawasaki, A. Ohtomo, K. Tamura, and H. Koinuma, Appl. Phys. Lett. **78**, 2464 (2001).

[9] K. Hümmer, Phys. Status Solidi B **56**, 249 (1973).

[10] H.D. Sun, T. Makino, Y. Segawa, M. Kawasaki, A. Ohtomo, K. Tamura, and H. Koinuma, J. Appl. Phys. **91**, 1993 (2002).

[11] H.D. Sun, Y. Segawa, A. Ohtomo, K. Tamura, M. Kawasaki, and H. Koinuma, J. Appl. Phys. **91**, 6457 (2002).

[12] 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).

[13] A.L. Gurskii and S.V. Voitikov, Solid State Commun. **112**, 339 (1999).

[14] S. Kalliakos, X.B. Zhang, T. Taliercio, P. Lefebvre, B. Gil, N. Grandjean, B. Damilano, and J. Massies, Appl. Phys. Lett. **80**, 428 (2002).

[15] M. Gallart, A. Morel, T. Taliercio, P. Lefebvre, B. Gil, J. Allegre, H. Mathieu, N. Grandjean, M. Leroux, and J. Massies, Phys. Status Solidi B **180**, 127 (2000).