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Confinement-enhanced biexciton binding energy in ZnO/ZnMgO multiple quantum wells

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By employing a nanosecond pump-probe method, biexciton formation process was investigated in ZnO/Zn_{1-x}Mg_xO ($x=0.26$) multiple quantum wells (MQWs) grown on ScAlMgO₄ substrate by laser molecular-beam epitaxy. Bleaching of absorption due to the saturation of excitonic states, and induced absorption related to the exciton–biexciton transition were observed in their spectra. It is demonstrated that the pump-probe method allows us to precisely determine binding energies of exciton complexes even applied to the semiconductor quantum structures where the localization effect are not negligible. This is because a transition from free-excitonic states to free-biexcitonic states is involved in the induced absorption process. The biexciton binding energy is a monotonically decreasing function of well width (L_w). For the MQWs with L_w smaller than 2.5 nm, the biexciton binding energy is larger than 25 meV, comparable to the thermal energy of room temperature. © 2003 American Institute of Physics. [DOI: 10.1063/1.1561158]

Wide-band-gap semiconductors, such as ZnSe, GaN, and ZnS have been studied for many years due to their potential applications, such as blue-emitting devices. Recently, ZnO has also been recognized as a potential candidate for such devices.^{1,2} Since ZnO possesses a larger exciton binding energy³ (59 meV) than those of other wide-band gap semiconductors just mentioned, the possibility of efficient excitonic lasing mechanisms operating at room temperature, in principle, should be higher for ZnO. Formation of electron–hole plasma⁴ and an inelastic exciton–exciton scattering process,⁵ have been shown to be mechanisms leading to stimulated emission in wide-band-gap semiconductors. Biexcitonic transition has also recently been demonstrated to be an important mechanism in stimulated emission.⁶ A biexciton is a quasiparticle created by two excitons. Because of the giant oscillator-strength effects associated with biexcitonic transitions, not only low-threshold but also large differential quantum efficiency can be expected if biexciton-related lasing action is accomplished.

Observation of radiative recombination of biexcitons in ZnO/ZnMgO multiple quantum wells (MQWs) has been reported in our previous study.⁷ However, the optical properties of biexcitons still require further investigation. For instance, biexciton binding energy (E_{xx}^b) has not been precisely determined as yet. For bulk ZnO⁸ and ZnO epitaxial layers,⁹ E_{xx}^b has been reported to be 12 and 15 meV, respectively.

Enhancement of E_{xx}^b is expected when the dimension is reduced from bulk to quasi-two-dimensional structure.¹⁰ Therefore, it is important to study the enhancement of E_{xx}^b in ZnO/ZnMgO MQW structures since an increase in stability of biexcitons can be expected. As pointed out in Ref. 11, localization effects of excitons and of biexcitons, which inevitably exist in MQWs, prevent precise determination of E_{xx}^b from photoluminescence (PL) spectroscopy. This is also true for PL excitation spectroscopy. However, this is not the case for an induced absorption process by which a stepwise two-photon excitation process of biexcitons is studied. Since the density of states of localized excitons is expected to be smaller than that of free excitons, the relevant initial state of an induced absorption process can be free excitonic states under an appropriate intense excitation, and the localization effect on determination of E_{xx}^b can be eliminated.

In this study, we performed nanosecond nondegenerate pump-probe experiments on five ZnO/ZnMgO MQWs with well widths of 4.23, 3.7, 2.79, 2.35, 1.75 nm at 77 K. Induced absorption corresponding to transition from free-excitonic states to free-biexcitonic states was observed. Binding energies of biexcitons in ZnO/ZnMgO MQWs were experimentally determined as a function of well width (L_w). It was found that they are largely enhanced compared with the E_{xx}^b value of bulk ZnO.

The ZnO/ZnMgO MQWs used in this study were grown on lattice-matched ScAlMgO₄ (0001) substrates by the laser-molecular-beam-epitaxy method. Detailed descriptions of the growth and sample characterization were given elsewhere.¹² The MQW structures consist of 10 periods of alternating ZnO well layers and 5-nm-thick Zn_{1-x}Mg_xO ($x=0.26$) barrier layers. The pump source for excitation was XeCl exci-

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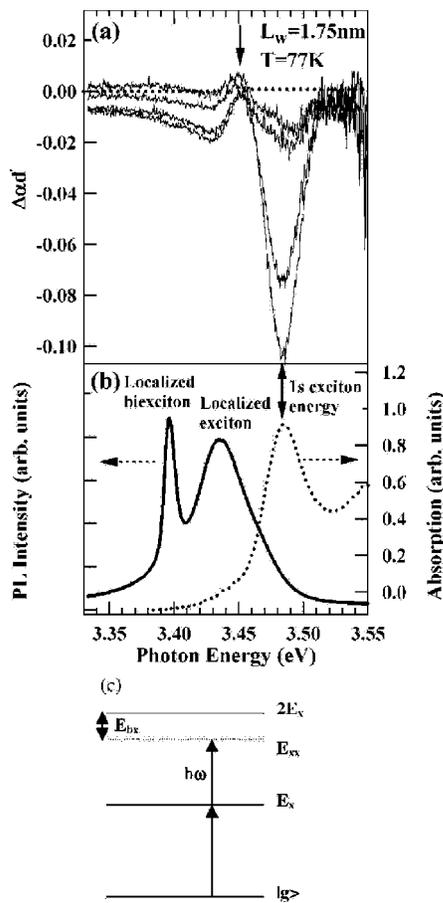


FIG. 1. (a) Evolution of a differential absorption spectrum in a ZnO/ZnMgO MQW ($L_w = 1.75$ nm) with increasing excitation intensity taken at 77 K. (b) PL (solid) and absorption (dashed) spectra for the ZnO/ZnMgO MQW ($L_w = 1.75$ nm). (c) Transition involved in induced absorption from excitonic state (E_x) to biexcitonic state (E_{xx}).

mer laser (308 nm) with a pulse width of 13 ns and with a repetition rate of 10 Hz. A broadband light source covering the whole spectral region of interest was obtained from excimer laser-pumped exalite-351 dye. In view of the hundred-picosecond range of exciton lifetime,¹³ it was considered that a steady-state regime was established in this case. The transmitted light was dispersed by a 30-cm-long monochromator and then detected by a CCD camera. The spatial coincidence of pump and probe beams was carefully checked.

In order to evaluate intense excitation-induced change in the absorption spectra, subtraction of absorption spectra with pump by absorption spectra without pump was performed to obtain differential absorption spectra. Therefore, the positive and negative parts in the differential absorption spectra correspond to the induced and bleaching of absorption, respectively. Figure 1(a) shows the evolution of a differential absorption spectrum under increasing excitation intensity for a ZnO/ZnMgO MQW with L_w of 1.75 nm taken at 77 K. With an increase in excitation intensity, the magnitude of the bleaching band increased. Since the spectral position of the bleaching peak is located at almost the lowest free-excitonic resonance (3.483 eV) estimated from the linear absorption spectrum shown in Fig. 1(b), it is reasonable to conclude that the appearance of the bleaching band is attributed to the saturation effect of the free-excitonic state. An induced-absorption band can be seen below the energy of excitonic

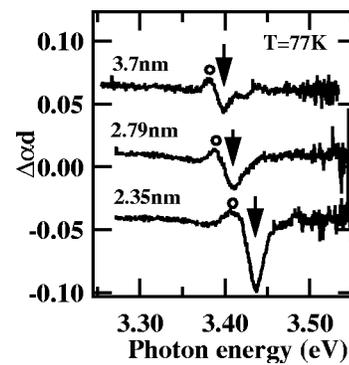


FIG. 2. Differential absorption spectra of ZnO/ZnMgO MQWs as a function of L_w taken at 77 K. Arrows indicate the absorption-bleaching peaks, i.e., 1-s exciton resonance energy. Open circles indicate the induced absorption peaks.

resonance. The assignment of this band will be discussed later. With further increase in the pump intensity, the peak amplitude of induced absorption becomes negative under the influence of the broader bleaching band, but the polarity of this peak still remains positive.

Figure 2 shows differential absorption spectra as a function of L_w . The bleaching peak (arrows), the energy position of which is located at the lowest exciton energy, was blue-shifted as L_w decreased. At the lower energy side of the bleaching peak, induced absorption peak is observed in all of the L_w studied. It should be noted that the energy separation between the lowest exciton resonance (indicated by arrows) and the induced absorption peak (indicated by open circles), increased slightly as L_w decreased. Figure 3 summarizes peak energies of the induced absorption, excitonic absorption, and localized biexciton emission of these ZnO/ZnMgO MQWs.

At the higher-energy side of excitonic resonance, positive peaks were not observed, as shown in Fig. 1(a). The absence of higher positive peaks means that the lower positive peaks are not associated with broadening of the excitonic states accompanied with its excitation-induced saturation.¹⁴ The spectral position of the lower-energy induced absorption band remains constant even when the excitation intensity is varied. Therefore, assignment of induced absorption due to lattice heating¹⁵ or due to renormalization of the band gap can be ruled out within the excitation inten-

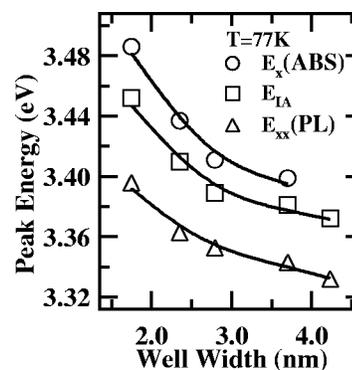


FIG. 3. Peak energies of linear absorption (open circles), induced absorption (open squares), and localized biexciton emission (open triangles) in ZnO/ZnMgO MQWs plotted against L_w . Solid lines were drawn for visual guidance.

sity range adopted in this study. It is well known that induced absorption from excitonic states to biexcitonic states has giant oscillator strength with a moderate exciton density.⁸

In the case of two-dimensional structure, other than free excitons, excitons localized at potential fluctuation might have existed after pumping. However, for high excitation density, at which the exciton bleaching occurred, induced absorption of the transition from free exciton states to free biexciton states should be the main mechanism in this case, considering the larger density state of free excitons than that of localized excitons. If the induced absorption is assigned to the transition from a localized excitonic state to a localized biexcitonic state, the estimated biexciton binding energies are unreasonably large, being comparable to that of bulk excitons (59 meV). Moreover, the discrepancy between the values of E_{xx}^b estimated along this line and those estimated from PL spectroscopy⁷ is unacceptable. Therefore, it is reasonable to consider that the induced absorption occurred is due to the transition from free excitonic states to free biexcitonic states. The biexcitonic emission of this MQW structure, however, as can be seen in Fig. 1(b), is basically due to the radiative recombination of biexcitons localized at the potential variation caused by well width and depth fluctuations. A sketch of the involved transition of induced absorption is shown in Fig. 1(c). For small homogeneous broadening, free biexciton binding energy can be estimated by using the energy separation between the exciton resonance and lower-energy induced absorption peak. This can be seen from the free biexciton energy, as given by $E_{xx} = 2E_x - E_{xx}^b$, with E_x and E_{xx}^b being the free exciton energy, and the free biexciton binding energy and noting that $E_{xx} = \hbar\omega + E_x$, leading to $E_{xx}^b = E_x - \hbar\omega$, where $\hbar\omega$ is the energy of the absorbed photon.

The estimated E_{xx}^b values are plotted against L_w (open triangles) in Fig. 4. For comparison, the dependence of exciton binding energy (E_x^b) on L_w , cited from Ref. 16, is also shown. Both these binding energies are monotonically increasing functions of L_w , due to the quantum confinement effect in the growth direction. The E_{xx}^b values obtained for samples with L_w of 3.7 and 1.75 nm are comparable to the E_{xx}^b values estimated from PL spectroscopy.⁷ The E_{xx}^b value for the widest-well MQW ($L_w = 4.23$ nm) is 17.5 meV. It is enhanced about 30% compared to the E_{xx}^b of bulk ZnO.⁷ For values of L_w smaller than 2.5 nm, E_{xx}^b is greater than 25 meV, comparable to the thermal energy of room temperature. Moreover, E_{xx}^b is enhanced approximately two fold, being as large as the E_{xx}^b value of bulk for the thinnest MQW. In order to clarify the increase in E_{xx}^b when reducing the dimensionality, Hayne's factor E_{xx}^b/E_x^b , was estimated. The L_w dependence of the E_{xx}^b/E_x^b ratio (filled circles) is also shown in Fig. 4. The ratio gradually changed from 0.21 to 0.29 as L_w decreased as a consequence of confinement-enhanced wavefunction overlap between excitons.

In summary, we studied the formation of biexcitons by observing the induced absorption of free excitons to free biexciton states in ZnO/Zn_xMg_{1-x}O ($x = 0.26$) MQW struc-

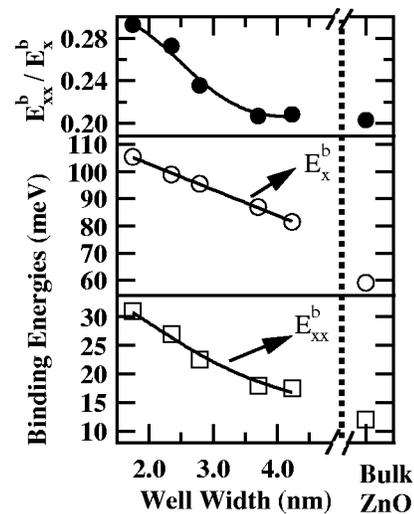


FIG. 4. Well-width dependence of biexciton binding energy (open squares) estimated in ZnO/ZnMgO MQWs. Binding energies of free excitons (open circles), cited from Ref. 16, and the E_{xx}^b/E_x^b ratios (filled circles) as a function of the L_w , are also shown. We plotted the corresponding values of bulk ZnO for comparison at the right part of graph. The E_{xx}^b and E_x^b of bulk ZnO are, respectively, cited from Refs. 8 and 3. Solid lines were drawn for visual guidance.

tures. Biexciton binding energies were determined experimentally, and it was found that they vary from 17.5 to 30.9 meV as L_w decreases.

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