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Radiative recombination of electron–hole pairs spatially separated due to quantum-confined Stark and Franz–Keldish effects in ZnO/$Mg_{0.27}Zn_{0.73}O$ quantum wells

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We studied photoluminescence (PL) properties of eighteen samples of wurtzite ZnO/$Mg_xZn_{1-x}O$ multiple quantum wells ($x=0.12$ and 0.27) with various well widths (L_w) of 0.7–4.65 nm. Radiative recombination of the electron–hole pairs that are spatially separated due to the quantum-confined Stark (QCS) and Franz–Keldish (QCFK) effects was observed in two thicker samples at 5 K. This PL band is located ≈ 40 meV in energy below the emission band of the localized excitons and ≈ 60 meV below the absorption energy of the free exciton transition. One can not observe such kind of luminescence unless both of the following conditions are accomplished: (1) higher Mg concentration ($x=0.27$) and (2) $L_w \geqslant 4.23$ nm. These experimental findings do not contradict the following two characteristic features for the QCS and QCFK effects; the magnitude of the electric field due to spontaneous and piezoelectric polarizations and the depth of the triangle-shaped potential wells are the monotonically increasing functions of Mg concentration and the L_w, respectively. The coupling strength with longitudinal-optical phonons, which is determined from the relative luminescence intensities of the phonon replicas, is significantly larger than that between the localized excitons and phonons. It is considered that the strong electric field increases the distance between electron and hole charge distributions from that determined by the Coulomb force and leads to the enhancement in the phonon interaction. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1507606]

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. There are several analogous features with the other famous wide-gap semiconductor, GaN, e.g., band gap energy and the crystal structure. In biaxially strained nitride heterolayers grown in the wurtzite structure with the *c* axis parallel to the growth direction, giant piezoelectric and spontaneous polarization effects are present as a consequence of the noncentrosymmetry of the wurtzite structure.[1–6] The piezoelectric fields for fully strained GaN on AlN are more than an order of magnitude larger than the piezoelectric fields that can be found in zinc blende semiconductors for the same amount of strain. This polarization effect has been extensively investigated in GaN-related heterostructures. As pointed out in our previous study,[7] the piezoelectric fields for ZnO on MgZnO are expected to be much smaller than those for GaN-related system because of the small difference in the lattice constants between ZnO and MgZnO. Although the spontaneous polarization constants (SPC) of MgO or MgZnO alloys have not been reported so far, there exists the possibility of a sizable spontaneous field across the ZnO layers. This is more likely if the large SPC of ZnO (Ref. 1), comparable with that of GaN, is considered. Nevertheless, the observation of the radiative recombination of the electron–hole pairs that are spatially separated due to such quantum-confined Stark (QCS) and Franz–Keldish (QCFK) effects has not been reported so far in ZnO-based quantum wells (QWs). Indeed, in our previous work, we have not taken these two effects into account for the spectral assignment of the photoluminescence (PL) data.

In this letter, we describe the possibility of the presence of spontaneous polarization mismatches at interfaces of ZnO/$Mg_{0.27}Zn_{0.73}O$ heterostructures (higher Mg concentration studied here). This spontaneous polarization effect leads to the observation of the radiative recombination from the electron–hole pairs influenced by the QCS and QCFK effects. As a result, a largely Stokes-shifted PL band located ≈ 40 meV below the localized exciton emission is observed in the PL spectra taken at 5 K.

The ZnO QW samples were grown by laser molecular-beam epitaxy on $ScAlMgO_4$ (0001) substrates. The structures consist of ten-period QWs with ZnO wells and (Mg,

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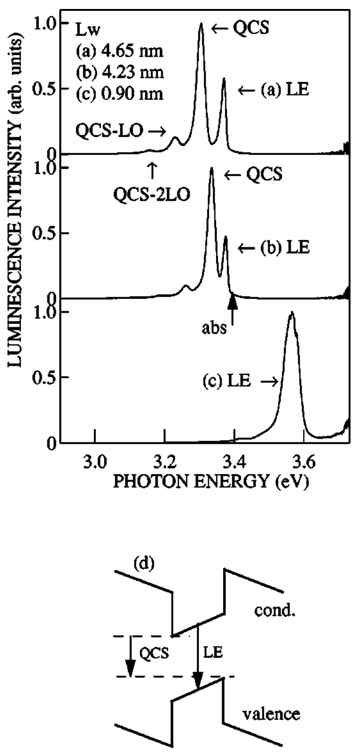

FIG. 1. PL spectra of $ZnO/Mg_{0.27}Zn_{0.73}O$ QW samples measured at 5 K. Spectra (a), (b), and (c) were measured from three samples with different well widths of the QW samples. Nomenclatures of LE and QCS, respectively, mean the localized exciton and the quantum-confined Stark effect. The LO-phonon replicas are indicated as arrows. The energy position of the excitonic absorption [theoretically calculated by Coli and Bajaj (see Ref. 12)] is shown by the arrow with "Abs." (d) Schematic diagram of the conduction and the valence bands of wurtzitic QWs under the spontaneous and piezoelectric polarization field. Electrons and holes distributed in the well regions are spatially separated due to the QCS and QCFK effects. The downward arrow with QCS corresponds to the radiative recombination process influenced by these effects, while the arrow with LE corresponds to that process without their influence.

Zn)O barriers. Well layer thickness (L_w) was varied from 0.7 to 4.65 nm, and the thickness of the barrier layer was approximately 5 nm, both of which were precisely determined from x-ray diffraction analysis. Magnesium concentrations were determined from the absorption edge energy of the reference alloyed epilayers which were grown under the same condition with that of the relevant QWs. Concentration dependence of edge energy has been reported by Matsumoto *et al.*[8] The exciton Bohr radius of ZnO is $\approx$ 1.8 nm. Details of the growth procedure and the difference in the lattice constants between ZnO and $Mg_xZn_{1-x}O$ have been given elsewhere.[7–9] Energy diagrams of conduction and valence bands are shown in Fig. 1 of Ref. 10. The excitation source of the PL measurement was 325-nm-line of the helium–cadmium laser.

Figures 1(a)–1(c) show 5 K PL spectra corresponding to three typical $ZnO/Mg_{0.27}Zn_{0.73}O$ QW samples with well widths (L_w) of 4.65 nm, 4.23 nm, and 0.9 nm, respectively. The PL spectra are normalized so that the strongest peaks are of the same intensity. The zero-phonon peaks of PL labeled with "LE" in Fig. 1 (located at energies of 3.30, 3.38, and 3.56 eV) are attributed to the radiative recombination of the localized excitons.[10] The excitons are localized due to the band gap energy fluctuation in the barrier layer and/or due to the well layer thickness fluctuation. There are two prominent PL peaks in the 4.65- and 4.23-nm-thick QWs. We attributed the higher-energy PL band to be due to the recombination of the localized excitons (LE band). When the PL peak energies were plotted as a function of L_w, smooth L_w dependence could be obtained. A comprehensive peak energy plot was given in Fig. 2 of Ref. 11.

The assignment of the other PL peaks on the lower-energy side (denoted by "QCS") is discussed. These "QCS" bands have larger Stokes shift than that of LE bands and are observed only in the 4.65- and 4.23-nm-thick QWs. These PL bands are located $\approx$ 40 meV in energy below the emission band of the localized excitons and $\approx$ 60 meV below the absorption energy of the free-exciton transition. Absorption energies are shown by arrows in Fig. 1. As shown in Fig. 2, the sharp peak structure has not been observed in the experimental absorption spectrum. Therefore, we used the calculation absorption energy obtained by Coli and Bajaj.[12]

Such kind of emission is not observed in any QW sample with the smaller Mg concentration (x). Only the LE bands could be confirmed in the PL spectra taken for $ZnO/Mg_{0.12}Zn_{0.88}O$ QWs. The magnitude of the electric field in the case of $x=0.27$ is larger than that of $x=0.12$, because of the larger lattice mismatch between ZnO and $ZnO/Mg_{0.27}Zn_{0.73}O$ (cf. Fig. 3 of Ref. 9). This internal field, present along the growth axis of the system, is caused by piezoelectric and spontaneous polarizations. It is considered to be easier to observe the QCS bands in the sample with higher x. Therefore, this band is attributed to be due to the radiative recombination from the excitons influenced by the internal electric field distributed across the well layer. The Stokes-type shift of PL is due to the strong QCS and QCFK effects induced by this strong internal electric field. (We took only the piezoelectric polarization effect into account. The SPC of MgO has not been reported so far. It is beyond our scope to consider the effect of the spontaneous polarization.)

The QCS is not observed in $ZnO/Mg_{0.27}Zn_{0.73}O$ QWs with L_w of 0.7–3.75 nm. This L_w dependence can be explained as follows. A band diagram of wurtzitic QWs under both the piezoelectric and spontaneous polarization fields can be schematically shown in Fig. 1(d). The PL energy of the QCS bands is lower than that of the LE. Nevertheless, in the case of small L_w, the energy difference can be neglected because the depth of triangle-shaped potential well is smaller than the case of larger L_w. Both the electron and hole wave functions are confined in the wells even when the electric field is present. Thus, the overall Stokes-type shift of the PL is thus determined only by the in-plane (lateral) band gap inhomogeneity. We observe the single PL peak (LE band) in this case. On the other hand, in the opposite case (larger $L_w s$), the depth of triangle-shaped potential well becomes larger. Carrier wave functions drops into these triangle-potentials at one side of the well layer. The electric field pushes the electron and the hole toward opposite sides of the well. Thus, the energy difference between QCS and LE becomes unnegligible ($\approx$40 meV in this study).

It is now well known that the QCS and QCFK effects somewhat reduce the excitonic oscillator strength. Figure 2 shows an absorption spectrum in 4.23-nm-thick QW taken at 5 K. One can not confirm here the excitonic peak (e.g., Gaussian) in this spectrum although this is possible for some

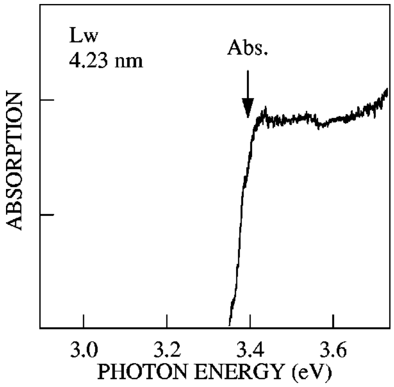

FIG. 2. Absorption spectrum in $ZnO/Mg_{0.27}Zn_{0.73}O$ QW taken at 5 K. The well width is 4.23 nm. The energy position of the excitonic absorption is shown by the arrow with Abs.

thinner QWs (cf. e.g., Fig. 1 of Ref. 13). Such a disappearance may be explained by the oscillator strength quenching.

We give more supporting evidence of our spectral assignment by paying attention to the intensity distribution of longitudinal-optical (LO) phonon replicas in the luminescence spectra. Luminescence band denoted by QCS-LO is radiative recombination of the carriers with simultaneous creation of LO phonon. The energy difference between the QCS and the QCS-LO bands is equal to the energy of the LO phonon of ZnO (72 meV). The 1LO and 2LO phonon replicas of the QCS bands (e.g., QCS-LO) are clearly seen in Figs. 1(a) and 1(b). This is not the case for the localized exciton emission as shown in Fig. 1(c). The intensities of the LO-phonon replicas relative to the intensities of the zero-phonon peaks for 4.23- and 4.65-nm-thick QWs are 0.046 and 0.068, respectively. On the other hand, the corresponding ratio is too small to be deduced in the case of $L_w = 0.9$ nm. Within the Frank–Condon approximation, the distribution of emission intensities between phonon replicas and the main emission peak is related to the coupling strength with the LO phonons. The coupling strength between the electron–hole pairs separated due to QCS and QCFK effects (QCS) and the LO phonons is significantly larger than that between the localized excitons (LE) and the phonons.

Coming to the interpretation of our experimental findings, it should be noted that, as pointed out by Kalliakos *et al.*,[14] the phonon coupling strength (PCS) generally depends strongly on the spatial distributions of electron and hole charge densities and sometimes deviates from the bulk value. This is more characteristic in the cases that the wurtzitic heterostructures are influenced by the strong internal electric field caused by piezoelectric and spontaneous polarizations. Such an electric field pushes the electron and the hole toward opposite sides of the well. The electrons and holes are separated by some distance along the growth axis not only determined by the Coulomb force but also by the electric field. It is thus easy to infer that the reduced overlap of these electron and hole charge densities must be responsible for the observed increase of the PCS. It is known that, in general, the PCS is a growing function of the distance between the electrons and the holes which is speculated from the similar situation observed for the case of donor–acceptor pairs. This results in the difference in the PCS between QCS and LE bands. Conversely, this enhancement supports our spectral assignment concerning the QCS band.

In summary, we observed the photoluminescence of electron–hole pairs which are spatially separated due to the QCS and QCFK effects in 4.23- and 4.65-nm-thick wurtzite. $ZnO/Mg_{0.27}Zn_{0.73}O$ quantum wells at 5 K. This PL band is located $\approx$40 meV in energy below the emission band of the localized excitons and $\approx$60 meV below the absorption energy of the free-exciton transition. As a result of its dependence on the Mg concentration ($x = 0.12$ and 0.27) and the well width ($0.7\ \mathrm{nm} \leqslant L_w \leqslant 4.65\ \mathrm{nm}$), we reached such a spectral assignment. These are similar to the characteristic features typical seen due to the QCS and QCFK effects, e.g., in wurtzite GaN-related heterostructures. It is considered that the strong electric field present along the growth axis of the system increases the distance between electron and hole charge distributions, decreases the overlap between electrons and holes, and leads to the enhancement in their phonon interaction. It is hoped that this work will stimulate some other experimental studies to determine the magnitude of the electric field across the well layers of ZnO QWs.

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