<table>
<thead>
<tr>
<th>Title</th>
<th>Radiative recombination of electron-hole pairs spatially separated due to quantum-confined Stark and Franz-Keldish effects in ZnO/Mg$<em>{0.27}$Zn$</em>{0.73}$O quantum wells</th>
</tr>
</thead>
<tbody>
<tr>
<td>Authors</td>
<td>T. Makino, K. Tamura, C. H. Chia, Y. Segawa, M. Kawasaki, A. Ohtomo, H. Koinuma</td>
</tr>
<tr>
<td>Citation</td>
<td>Applied Physics Letters, Vol. 81, No. 13, 2002, 9</td>
</tr>
<tr>
<td>URL</td>
<td><a href="http://scitation.aip.org/content/aip/journal/apl">http://scitation.aip.org/content/aip/journal/apl</a></td>
</tr>
<tr>
<td>Copyright</td>
<td>Copyright (c) 2002 American Institute of Physics</td>
</tr>
</tbody>
</table>
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

T. Makino, a) K. Tamura, b) C. H. Chia, c) and Y. Segawa c)
Photodynamics Research Center, RIKEN (Institute of Physical and Chemical Research), Sendai 980-845, Japan

M. Kawasaki d) and A. Ohtomo
Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

H. Koinuma d)
Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama 226-8503, Japan

(Received 7 May 2002; accepted for publication 24 July 2002)

We studied photoluminescence (PL) properties of eighteen samples of wurtzite ZnO/Mg_{x}Zn_{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 $\sim 40$ meV in energy below the emission band of the localized excitons and $\sim 60$ 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) $L_w \geq 4.23$ 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.

The wide gap wurtzite 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. 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 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_{x}Zn_{1-x}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 $\sim 40$ 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,
The PL spectra are normalized so that the strongest peaks are of the same intensity. The zero-phonon peaks of PL labeled are attributed to the radiative recombination of the localized exciton and the quantum-confined Stark effect. The exciton Bohr radius of ZnO is \( \lambda_x \approx 4 \text{ nm} \). The PL bands are located in the case of small \( L_w \) and are somewhat reduced from 0.7 to 1, while the piezoelectric polarization effect into account. The assignment of the other PL peaks on the lower-energy side is thus determined only by the in-plane Stark effect influenced by these effects, while the arrow with LE corresponds to the radiative recombination process influenced by these effects, while the arrow with LE corresponds to the radiative recombination process.

As shown in Fig. 2, the QCS bands is lower than that of the LE. Nevertheless, in the case of small \( L_w \), the energy difference can be neglected. Therefore, this band is attributed to be due to the radiative recombination from the excitons influenced by the strong internal electric field. In this spectrum although this is possible for some samples the QCS bands is lower than that of the LE. Nevertheless, in the opposite case with \( L_w \) larger. Carrier wave functions drops into these triangle-shaped well regions are spatially separated due to the QCS and QCFK effects. The energy position of the sharp peak structure has not been observed in the experimental absorption spectrum. Therefore, we used the calculations to explain as follows. A band diagram of wurtzitic QWs under the spontaneous polarization shows LO-phonon replicas are indicated as arrows. The energy position of the LO-phonon replicas are indicated as arrows. The energy position of the LO-phonon replicas are indicated as arrows.

The PL spectra taken for the sample with the smaller Mg concentration show 5 K PL spectra corresponding to the PL bands could be confirmed in the PL spectra taken for the sample with the smaller Mg concentration. The magnitude of the electric field present along the growth axis of the system, is caused by the piezoelectric and spontaneous polarizations. It is considered to be easier to observe the QCS bands in the sample with smaller Mg concentration. The assignment of the other PL peaks on the lower-energy side is thus determined only by the in-plane Stark effect influenced by these effects.

It is now well known that the QCS and QCFK effects are not observed in ZnO/Mg\(_{0.27}\)Zn\(_{0.73}\)O QWs. The magnitude of the electric field is varied from 0.7 to 1, and the thickness of the barrier layer was approximately 5 nm, both of which were precisely determined from x-ray diffraction analysis. Magnesium concentrations in the well layer thickness (\( L_w \)) of 4.65 nm, 4.23 nm, and 0.9 nm, respectively. The zero-phonon peaks of PL labeled are attributed to the radiative recombination of the localized exciton and the quantum-confined Stark effect. The excitons are localized due to the width of the growth procedure and the difference in the lattice constant between ZnO and Mg\(_{0.27}\)Zn\(_{0.73}\)O have been given.

The localized excitons push the electron and the hole toward opposite sides of the well layer fluctuation. There are two prominent 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. The PL spectra in the case of small \( L_w \) and are somewhat reduced from 0.7 to 1, while the piezoelectric polarization effect into account. The assignment of the other PL peaks on the lower-energy side is thus determined only by the in-plane Stark effect influenced by these effects, while the arrow with LE corresponds to the radiative recombination process influenced by these effects, while the arrow with LE corresponds to the radiative recombination process.

The LO-phonon replicas are indicated as arrows. The energy position of the sharp peak structure has not been observed in the experimental absorption spectrum. Therefore, we used the calculations to explain as follows. A band diagram of wurtzitic QWs under the spontaneous polarization shows the effect of the internal electric field distributed across the well layer. The overall Stokes-type shift of the PL is due to the strong QCS and QCFK effects induced by this strong internal electric field.

It is now well known that the QCS and QCFK effects are not observed in ZnO/Mg\(_{0.27}\)Zn\(_{0.73}\)O QWs. The magnitude of the electric field is varied from 0.7 to 1, and the thickness of the barrier layer was approximately 5 nm, both of which were precisely determined from x-ray diffraction analysis. Magnesium concentrations in the well layer thickness (\( L_w \)) of 4.65 nm, 4.23 nm, and 0.9 nm, respectively. The zero-phonon peaks of PL labeled are attributed to the radiative recombination of the localized exciton and the quantum-confined Stark effect. The excitons are localized due to the width of the growth procedure and the difference in the lattice constant between ZnO and Mg\(_{0.27}\)Zn\(_{0.73}\)O have been given.

The localized excitons push the electron and the hole toward opposite sides of the well layer fluctuation. There are two prominent 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. The PL spectra in the case of small \( L_w \) and are somewhat reduced from 0.7 to 1, while the piezoelectric polarization effect into account. The assignment of the other PL peaks on the lower-energy side is thus determined only by the in-plane Stark effect influenced by these effects, while the arrow with LE corresponds to the radiative recombination process influenced by these effects, while the arrow with LE corresponds to the radiative recombination process.

The LO-phonon replicas are indicated as arrows. The energy position of the sharp peak structure has not been observed in the experimental absorption spectrum. Therefore, we used the calculations to explain as follows. A band diagram of wurtzitic QWs under the spontaneous polarization shows the effect of the internal electric field distributed across the well layer. The overall Stokes-type shift of the PL is due to the strong QCS and QCFK effects induced by this strong internal electric field.

It is now well known that the QCS and QCFK effects are not observed in ZnO/Mg\(_{0.27}\)Zn\(_{0.73}\)O QWs. The magnitude of the electric field is varied from 0.7 to 1, and the thickness of the barrier layer was approximately 5 nm, both of which were precisely determined from x-ray diffraction analysis. Magnesium concentrations in the well layer thickness (\( L_w \)) of 4.65 nm, 4.23 nm, and 0.9 nm, respectively. The zero-phonon peaks of PL labeled are attributed to the radiative recombination of the localized exciton and the quantum-confined Stark effect. The excitons are localized due to the width of the growth procedure and the difference in the lattice constant between ZnO and Mg\(_{0.27}\)Zn\(_{0.73}\)O have been given.

The localized excitons push the electron and the hole toward opposite sides of the well layer fluctuation. There are two prominent 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. The PL spectra in the case of small \( L_w \) and are somewhat reduced from 0.7 to 1, while the piezoelectric polarization effect into account. The assignment of the other PL peaks on the lower-energy side is thus determined only by the in-plane Stark effect influenced by these effects, while the arrow with LE corresponds to the radiative recombination process influenced by these effects, while the arrow with LE corresponds to the radiative recombination process.

The LO-phonon replicas are indicated as arrows. The energy position of the sharp peak structure has not been observed in the experimental absorption spectrum. Therefore, we used the calculations to explain as follows. A band diagram of wurtzitic QWs under the spontaneous polarization shows the effect of the internal electric field distributed across the well layer. The overall Stokes-type shift of the PL is due to the strong QCS and QCFK effects induced by this strong internal electric field.

It is now well known that the QCS and QCFK effects are not observed in ZnO/Mg\(_{0.27}\)Zn\(_{0.73}\)O QWs. The magnitude of the electric field is varied from 0.7 to 1, and the thickness of the barrier layer was approximately 5 nm, both of which were precisely determined from x-ray diffraction analysis. Magnesium concentrations in the well layer thickness (\( L_w \)) of 4.65 nm, 4.23 nm, and 0.9 nm, respectively. The zero-phonon peaks of PL labeled are attributed to the radiative recombination of the localized exciton and the quantum-confined Stark effect. The excitons are localized due to the width of the growth procedure and the difference in the lattice constant between ZnO and Mg\(_{0.27}\)Zn\(_{0.73}\)O have been given.
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., 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 wurtzite 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/MgO\(_{0.27}\)Zn\(_{0.73}\)O quantum wells at 5 K. This PL band is located \( \sim 40 \) meV in energy below the emission band of the localized excitons and \( \sim 60 \) 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 (\( 0.7 \) nm \( \leq L_w \leq 4.65 \) 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.

One of the authors (T.M.) would like to express his sincere gratitude to Le Si Dang and H. Mariette for fruitful discussions.