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Phonon replicas in ZnO/ZnMgO multiquantum wells

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The photoluminescence properties of ZnO/ZnMgO multiquantum wells have been investigated by continuous and time-resolved photoluminescence spectra at various temperatures. Strong first-order and second-order longitudinal optical (LO)-phonon replicas were observed in the emission spectra. Both the zero-phonon emission and its LO-phonon replicas can be resolved into two components with different temperature dependence. The observation of LO-phonon replicas provided an additional way to characterize the recombination mechanism in quantum wells. Two kinds of excitons are responsible for the resolved emission components and have different coupling strength with LO phonons: one is donor bound excitons which dominated at low temperatures, the other one is the localized excitons due to the well width fluctuation which took over the dominated emission at high temperatures. © 2002 American Institute of Physics. [DOI: 10.1063/1.1467627]

Phonon assisted photoluminescence (PL) has been observed in many materials. For strongly polar semiconductors, longitudinal optical (LO)-phonon replicas of bound and free exciton emission have been observed in both group III-V and group II-VI bulk materials.¹⁻⁴ It has been shown that investigation of LO-phonon replicas provides a useful means to characterize quantum well samples, although experimental results in this aspect are few.⁵⁻⁷

As a wide band gap semiconductor, ZnO has drawn a great deal of attention for application in short wavelength optoelectronic devices. The large exciton binding energy (~60 meV) in ZnO not only allows for efficient excitonic emission at high temperature but also has attracted interest in fundamental physics.⁸ Recently, the photoluminescence properties associated with excitons have been investigated in ZnO/Zn_{1-x}Mg_xO multiquantum wells (MQWs).⁹ However, LO-phonon assisted emission has never been studied, although it is crucial for elucidating the photoluminescence and lasing mechanism. In this article, we report on the properties of excitonic luminescence and its LO-phonon replicas in ZnO/Zn_{1-x}Mg_xO MQWs investigated by continuous-wave (cw) PL and time-resolved photoluminescence (TRPL) at various temperatures. The observation of LO-phonon replicas provided useful information to characterize the optical properties of ZnO/ZnMgO quantum well structures. It was found that both the zero-phonon PL band and its first-order and second-order LO-phonon replicas consisted of two well-

resolved components, which were attributed to radiative recombination due to excitons localized in boxlike roughness and donor-bound excitons.

The ZnO/Zn_{1-x}Mg_xO MQWs were grown by the laser-molecular beam epitaxy method on a lattice matched ScAlMgO₄ (0001) substrate. The detailed preparation process has been described elsewhere.¹⁰ MQWs were made up of alternating 3.7 nm ZnO well layers and 5 nm Zn_{0.74}Mg_{0.26}O barrier layers with 10 periods. For the PL measurement a cw He-Cd laser (325 nm) was used to excite the sample and the PL signal was dispersed by a 0.3 m grating monochromator and detected by a thermoelectrically cooled charge coupled device in a conventional backscattering geometry. The TRPL signals were taken by a streak camera with a time resolution of ~25 ps in conjunction with a 0.3 m monochromator. The sample was excited by the triply harmonic generation of a Ti-sapphire laser (790 nm, 2 ps, 82 MHz). The excitation density is kept low so that the PL signal changed linearly with excitation density and no new emission bands due to high excitation effects such as emission induced by biexcitons or inelastic exciton-exciton scattering (*P*-band emission) appeared.⁹

Figure 1 shows the PL and absorption spectra at 5 K. The main PL band is apparently associated with QWs and is located at 3.375 meV, which is Stokes shifted ~26 meV with respect to the lowest excitonic absorption peak. At the lower energy side of the main PL band, there are two relatively weaker luminescence bands. One of the bands is located at an energy ~72 meV lower than the main band, and the other one at a further 72 meV lower. As the energy of 72 meV is equal to the LO-phonon energy of ZnO, these two bands can be reasonably attributed to the first-order and second-order LO-phonon replicas of the main band. The Huang-Rhys fac-

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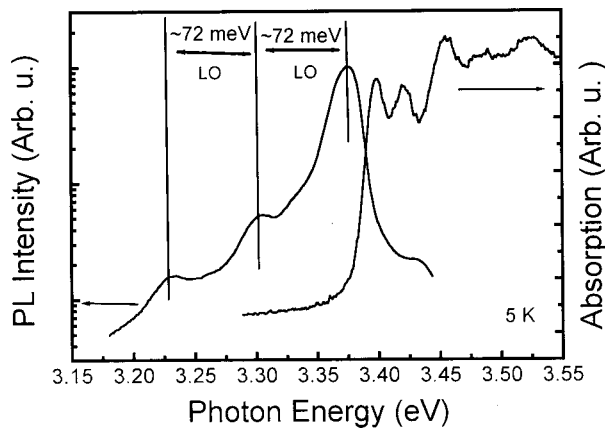


FIG. 1. Photoluminescence and absorption spectra of ZnO/ZnMgO MQWs at 5 K.

tor S , which represents the coupling strength of the radiative transition to LO-phonon polarization field, can be calculated by the relative intensity using $S = 2(I_{2LO}/I_{LO})$.^{6,7} From the measured spectra, the S value associated with this band is estimated to be about 0.35.

The PL spectra of the sample at different temperatures are shown in Fig. 2. One can see that the line shape of the zero-phonon (ZP) band changes sensitively with temperature, and clearly there are two bands (denoted as the BX band and LX band) contributing to the photoluminescence. At 5 K, the BX band is dominated in the ZP band. As the temperature increases, the relative intensity of the LX band to the BX band increases rapidly, and up to about 50 K the LX band has almost the same height as the BX band. At further higher temperatures, the LX band dominated in the spectra and the two peaks are gradually unresolved.

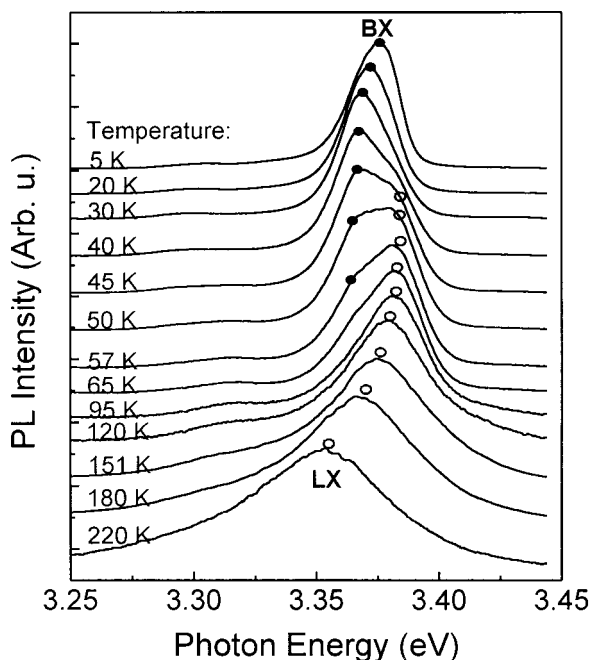


FIG. 2. Normalized spectra of the zero-phonon band at various temperatures. Each curve has been relatively shifted vertically for clearance.

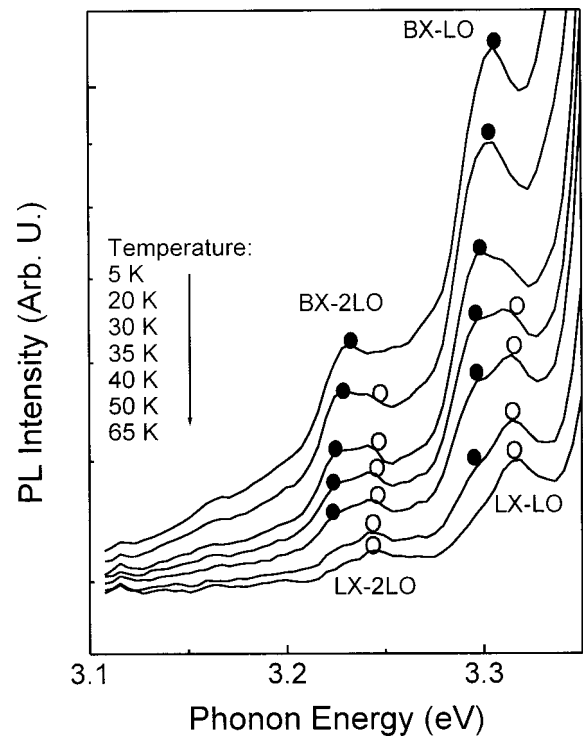


FIG. 3. Temperature dependence of the spectra of LO-phonon replicas of ZnO/ZnMgO MQWs.

The temperature dependence of the phonon replicas is shown in Fig. 3. It is interesting to note that both the first-order and second-order LO-phonon replicas also consist of two well-resolved components. Obviously, the two components in both the 1LO and 2LO-phonon replicas are correlated with the BX and LX bands. Thus we denote the corresponding phonon replicas as BX-1LO, LX-1LO, BX-2LO, and LX-2LO, respectively. It is clearly seen that the temperature dependence of the relative intensity ratio of the two components of the 1LO phonon replica is more sensitive than that of the ZP band, and that of the 2LO replica is even more sensitive. At about 20 K, LX-2LO has almost the same spectral weight as BX-2LO, but BX and BX-1LO still dominate in the corresponding bands. At 50 K, BX and LX bands have about the same peak height while BX-1LO and BX-2LO almost disappear. The S factor associated with the LX band at 50 K was estimated to be ~ 0.42 , higher than that for the BX band at 5 K, which means that the coupling of the LX band to the LO phonon is stronger than that of BX. Thus the BX band and its LO-phonon replicas can be readily attributed to the recombination of bound excitons as in other materials since the bound excitons should have weaker coupling to the LO phonon.^{2,4,8,11} As for the LX band and its LO-phonon replicas, we tentatively ascribe them to the recombination of excitons localized by the interface roughness. One may argue that the two components in the PL spectra could be attributed to the localized excitons and free excitons. If this is true, the peak energy of the LX band should be equal to the lowest excitonic absorption peak energy (Stokes shift ~ 0). However, experimental evidence showed that the Stokes shift remained about 6 meV even at the room temperature, which ruled out such an assumption.¹² Additional

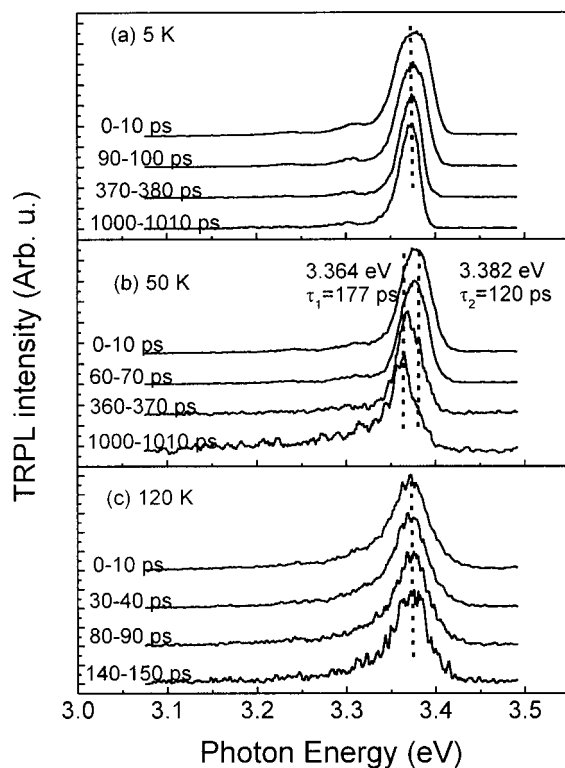


FIG. 4. Time-resolved photoluminescence spectra after various time delays at (a) 5, (b) 50, and (c) 120 K. The dashed lines are guides for the eyes.

confirmation of our assignment is that the LX band was located in the inhomogeneous linewidth of the lowest excitonic absorption peak while the BX band was in the lower energy side and out of the inhomogeneous linewidth.¹²

Further support of the above assignment came from the TRPL measurements at various temperatures. Figure 4 shows the TRPL spectra with various time delays after a pulsed excitation at temperatures of 5, 50, and 120 K, respectively. Each spectrum was recorded for 10 ps duration after a time delay as marked. The longest delay time was much longer than the corresponding effective lifetime. At 5 K, the peak energy and line shape of the ZP band remained the same, indicating that only one PL band (BX) is involved in (or dominated) the PL. The only change was the decrease of width of the emission band with delay time, which can be interpreted as due to the band filling effect. The temporal variation of the PL peak at this temperature shows an exponential decay with an effective lifetime around 660 ps. At 50 K, both the peak energy and line shape change with the delay time. It seems that there are two emission bands with peak energies located at 3.364 and 3.382 eV, respectively, which corresponds to the BX and LX bands as denoted in Fig. 1. From the temporal profile, the effective lifetimes were estimated to be 177 and 120 ps for these two bands at 50 K. The TRPL spectra at 120 K exhibited no observable change with the delay times over the whole lifetime, indicating the disappearance of the BX band. The effective lifetime at the peak energy is decreased to about 59 ps. This behavior is totally consistent with that of temperature dependence of PL. The TRPL spectra, however, provided additional information: (1) the BX band has a much longer lifetime than the LX band.

(2) The temporal profile of the luminescence gradually evolved into an increasingly nonexponential decay with a remarkably decrease of the effective lifetime as the temperature increased. These features further corroborate the involvement of impurity states in the emission process and agree with our assignment.¹³

The luminescence properties can be readily understood by the following description. We do not attempt to describe the PL spectra quantitatively, but discuss our experimental result qualitatively. Photoexcited free excitons will immediately relax into local energy minimum states (localized exciton states) within their lifetime. For binary quantum samples (as in our ZnO/ZnMgO MQWs, the effect of exciton localization results mainly from the interface fluctuation. The localized states can be described as the lowest quantum states of quantum boxes or islandlike structures.^{14,15} Compared with the small Bohr radius of ZnO ($\sim 18 \text{ \AA}$) the lateral size of these islands is assumed to be much larger. As far as the quantum dot concerned, these quantum states are "free excitons." However, compared with the state that extends in the whole well plane, they are still called "localized." It can be visualized that in these "boxes" there are some impurity states which trap the localized excitons efficiently at low temperatures and bound excitons are formed. Therefore, at very low temperatures the main emission is contributed from bound excitons. Actually, it is a common feature that the low-temperature PL of ZnO is dominated by donor-bound exciton emission.¹⁶ As is well known, even undoped ZnO almost always exhibits strong *n*-type conductivity induced by shallow donor impurities, although the origin of the donor level is still controversial.¹⁷⁻¹⁹ With the increase of temperatures, some of the bound excitons are thermally dissociated into the corresponding localized exciton states, and the emission comes from both the bound excitons and localized excitons. At further high temperatures, most of the bound excitons transit to the localized states and the emission from localized excitons dominates in the PL spectra.

In summary, temperature-dependent PL and TRPL spectra have been investigated for ZnO/ZnMgO MQWs. Strong first-order and second-order LO-phonon replicas were observed in PL spectra. Both the zero-phonon photoluminescence and its LO-phonon replicas can be resolved into two components. The observation of LO-phonon replicas provided an additional way to characterize the radiative recombination mechanism in quantum wells. From the correlation of PL bands and their LO-phonon replicas in our ZnO/ZnMgO MQWs, it is clarified that one of the components is due to the bound excitons and the other one is due to the intrinsic excitons localized at the well interfaces.

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