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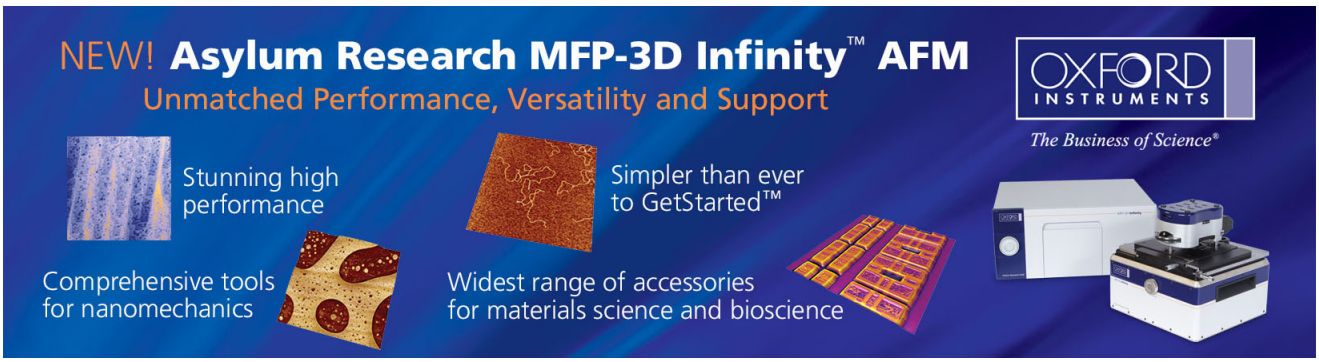

Acoustic and optical phonon assisted formation of biexcitons

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Efficient exciton relaxation is required for bounding two cooled excitons to form biexciton. Acoustic and optical phonon scatterings playing key roles in exciton relaxation are responsible for formation of biexcitons at various temperatures. Using ZnO powders, the authors observed a sublinear dependence on excitation power at low temperature, in which the relaxation process involves only emission of acoustic phonons due to the excitons having kinetic energy lower than those of the optical phonons. However, the exponent comes near theoretical value of 2 for participation of optical phonons when the exciton kinetic energy approaches to the energy of the lowest optical phonon. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2784180]

ZnO is characterized by a large exciton binding energy (~60 meV) that allows stable existence of excitons and efficient excitonic lasing operation at room temperature (RT) or even higher. Since the biexciton binding energy is also large, 12–20 meV,[1–6] in particular, it can be increased to a level comparable to the thermal energy at RT in quantum confined structures. Lasing based on biexcitons has been shown to have much lower threshold than that due to exciton-exciton scattering.[7] Therefore, it is imperative to fully characterize the intrinsic recombination process of excitons in ZnO since not only are excitons a sensitive indicator of material quality but also they play an important role in the stimulated emission and gain processes in real photonic device structures.

Recently, the low temperature photoluminescence (PL) of ZnO materials associated with various exciton transitions, especially biexciton recombination, has been investigated by several research groups.[8–13] For example, Yamamoto *et al.*[9] have observed biexciton emission in ZnO thin films grown by plasma-enhanced molecular-beam epitaxy and indicated that the biexciton intensity is proportional to the 1.5th power of the excitation density (I_{ex}^{α} with $\alpha=1.5$). Kim *et al.*[12] have synthesized ZnO nanowires by metal organic chemical vapor deposition and observed biexciton luminescence with $\alpha=1.34$ at $T=77$ K. The reduction in the exponent was proposed being attributed to the biexcitons are scattered and annihilated by excitons, other biexcitons, and bound excitons.[9,12] Using the temperature- and excitation-power-dependent PL, we present a detailed discussion on the formation of biexciton assisted by acoustic and optical phonon scatterings in ZnO powders prepared by sol-gel method. Surprisingly, other than observed $\alpha=1.86$ at $T=80$ K, we observed significant reduction in the exponent of excitation intensity for biexciton at $T=10$ and 40 K. In addition, the quenching of the biexciton PL intensity may be a result of multiexciton scattering via increasing densities of excitons.

ZnO powders were synthesized using the aqueous sol prepared by stoichiometric zinc acetate dihydrate [99.5% $Zn(OAc)_2 \cdot 2H_2O$] (Riedel-deHaen) and methanol. The concentration of Zn^{2+} was 0.35 mol/l. The sol was annealed in a furnace at 900 °C under air atmosphere for 1 h, and then slowly cooled to RT. Morphology of ZnO powders was characterized by field-emission scanning electron microscopy (JEOL-2100F). The PL measurement was made using a 40 mW He–Cd laser at wavelength of 325 nm and the emission light was dispersed by a TRIAX-320 spectrometer and detected by a UV-sensitive photomultiplier tube. A closed cycle refrigerator was used to set the temperature anywhere between 15 and 300 K.

The scanning electron microscopy image of the ZnO powders (not shown here) presents an average crystallite size of ~1 μm that does not reveal quantum size effect (Bohr radius of exciton in ZnO is ~2.34 nm[14,15]). The near band edge (NBE) emissions of the sample measured at various temperatures are shown in Fig. 1. At $T=15$ K, the most intense PL emission line at 3.363 eV is attributed to the exciton bound to neutral donor (denoted by D^0X). On the high-energy side of the D^0X line, the *A*-free exciton emission (denoted by $FX_A^{n=1}$) is observed at 3.373 eV. There are two weak humps positioned at 3.388 and 3.419 eV to the even higher energy. Based on the reported energy separation of *A*- and *B*-free excitons (~9–15 meV),[16–18] we assigned the emission centered at 3.388 eV to the *B*-exciton transition, which is about 15 meV apart from the *A* exciton, and as-

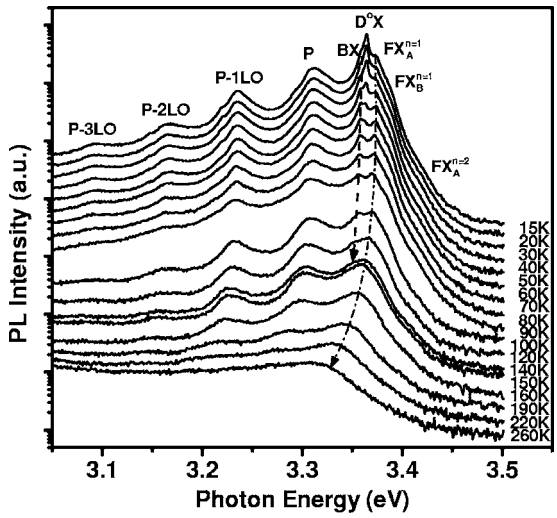

FIG. 1. Temperature dependence of PL spectra in ZnO powders. The dashed line on the right-hand side indicates the predicted energy at RT. The dashed line on the left-hand side guides the biexciton emission up to 140 K.

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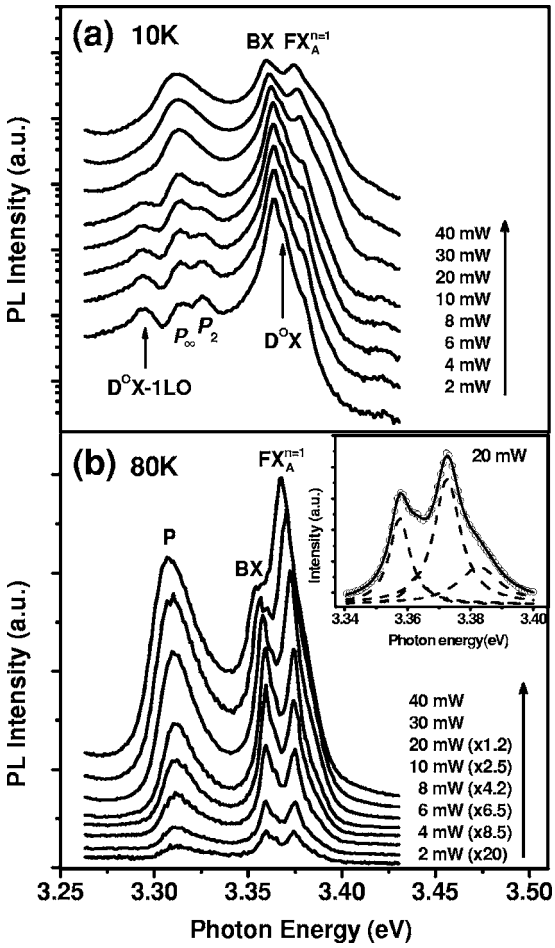

FIG. 2. Dependence of PL spectra on excitation power measured at 10 and 80 K. The inset of Fig. 2(b) shows typically theoretical fit to the PL spectrum for excitation power of 20 mW. Solid lines correspond to the fit and open dots represent the data. The fitted line shapes are also shown separately in dashed lines.

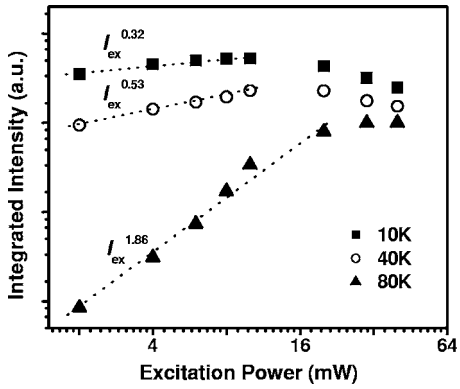

FIG. 3. Integrated emission intensity of biexciton as a function of excitation power under various temperatures. The corresponding power dependencies $I_{BX} \propto I_{ex}^{\alpha}$ are also labeled.

signed the other one hump at 3.419 eV to the first excited state $FX_A^{n=2}$ of *A* exciton (~45 meV to the $FX_A^{n=1}$ state).[19] On the low-energy side of the D^0X line, the peak at 3.358 eV is attributed to biexciton (labeled BX). The energy spacing between BX and $FX_A^{n=1}$ emissions is 15 meV, which is in agreement with the previously reported values.[8–13] Besides the broad line at the lower energy shoulder around 3.308 eV labeled as *P*, we also found several longitudinal-optical (LO)-phonon replicas separated by a constant interval of 71–73 meV. The P line can be resolved into two-electron satellite,[19] donor-to-acceptor pair,[10,11] exciton-exciton scattering,[9] and 1LO-phonon replica of $FX_A^{n=1}$ and D^0X, respectively. With increasing temperature, the intensity of NBE emission decreases, which is partly due to increasing of nonradiative recombination, and the relative intensity of $FX_A^{n=1}$ increases whereas that of D^0X decreases and becomes not detectable for $T>80$ K. Notice that the BX emission can be traced up to ~140 K (12 meV) although *A* exciton, *B* exciton, and *P* line finally merge into a broad peak as further increasing temperature.

Figure 2 shows the dependence of the PL spectra on the excitation power investigated at 10 and 80 K. At $T=10$ K, the lowest curve (2 mW excitation) presents two peaks at the lower energy side of the BX peak which are located within the above-mentioned *P* line, denoted as P_2 and P_∞, which originate from inelastic scattering between excitons.[20] As a result of such scattering, one exciton is scattered into one of the higher states ($n=2,3,4,\ldots,\infty$), while the other exciton loses its kinetic energy to occupy the lower polariton branch, which is roughly located at 3.326 and 3.312 eV for its counterpart exciton being scattered to $n=2$ and $n=\infty$, respectively. In addition, the peak due to 1LO phonon-assisted radiative recombination of D^0X is observed at 3.295 eV denoted by D^0X-1LO. These three bands shift toward the lower energy side and finally merge into a broad *P* line as further increasing the excitation power. For quantitative analysis, the spectral shape of near band edge emission measured at 80 K is decomposed into BX, D^0X, $FX_A^{n=1}$, and $FX_B^{n=1}$ by Lorentzian functions. The typical fitting results are shown in the inset of Fig. 2(b) with dashed lines denoting the various emissions and the solid line corresponding to the sum of the theoretical fits, which shows good agreement with the experimental data denoted as the open dots. It is found that the integrated intensity of the free exciton peak exhibits linear dependence on the excitation power, while that of the biexciton follows a superlinear dependence as $\sim I_{ex}^{1.86}$ (see Fig. 3). The results further support our assignment of $FX_A^{n=1}$ and BX peaks.

In order to further understand the characteristic of the BX line, the PL-integrated intensities of the BX line as a function of excitation power at various temperatures are depicted in Fig. 3. Other than at 80 K, as discussed above, I_{BX} is proportional to I_{ex}^{α} with $\alpha \sim 1.86$ but not an ideal exponent of 2. Its possible causes had been proposed to explain this observation: Phillips *et al.*[21] demonstrated that the reduction in the exponent α is induced in part by the short lifetimes of excitons and biexcitons in direct-band-gap materials. Yamada *et al.*[22] reported that the radiative lifetime of biexcitons is shorter than that of excitons, leading to the absence of any quadratic dependence of biexciton density as a function of exciton density.

However, the key issue is why the exponent α decreases to less than unity ($\alpha \sim$ 0.32 and 0.53) and the integrated intensity exhibits quenching at high excitation power at 10 and 40 K. These phenomena to our best knowledge have not yet been reported, although similar quenching effect had appeared in Fig. 4 of Ref. 23 for GaN/AlN quantum dots. We will discuss shortly that the scattering of acoustic and optical phonons could be responsible for different degrees of reducing α at different measuring temperatures, other than the proposed scattered and annihilated by excitons, other biexcitons, and bound excitons.[9,12]

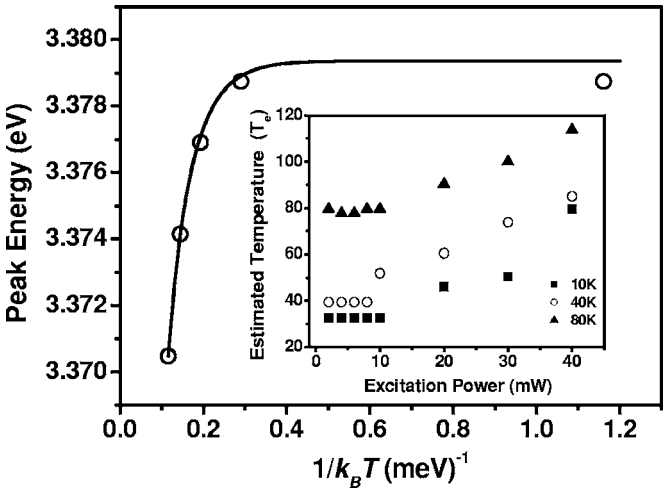

FIG. 4. Experimental (open dots) and calculated (solid lines) exciton energies plotted against inverse temperature. The inset shows the dependence of estimated temperatures (T_e) on the excitation power under various bath temperatures (T_b).

As the excitons having kinetic energy less than those of the optical phonons, the only remaining relaxation process, which lowers the kinetic energy of the excitonic gas, is the emission of acoustic phonons.[24] Due to the small energy quanta of the acoustic phonons, the dissipation of the kinetic energy in the excitonic system is rather slow and requires many scattering events before quasiequilibrium is reached. By elevating the temperature so that the kinetic energy of excitons reaches the energy of the lowest optical phonon, the optical phonon scattering will participate in the exciton relaxation.

We utilized the analysis about emission shift of the free exciton with temperature variation:[25] $E(T)=E(0)-\lambda/[\exp(\hbar\varpi/k_BT_e)-1]$ to evaluate the effective exciton temperature. By fitting the experimental data (open circles) at bath temperature (T_b) of 40–100 K for excitation power of 2 mW as the solid line in Fig. 4, we obtained the fitting parameters: $E(0)=3.379$ eV represents the free exciton emission at $T=0$ K [cf. the reported $E(0)=3.379$ eV at $T=5$ K],[26] $\lambda=24.28$ meV is a proportional coefficient, and $\hbar\varpi=16.08$ meV is the effective phonon energy, which is close to the lowest optical phonon of 12 meV. The inset of Fig. 4 depicts the estimated effective exciton temperature (T_e) as a function of excitation power at various T_b. Notice that the power dependent energy shift corresponds to $T_e=32-80$ K and 40–85 K at $T_b=10$ and 40 K. Under these conditions, the exciton kinetic energy or T_e is inefficient to couple with optical phonons but lowering the kinetic energy of the excitonic gas by emitting acoustic phonons, and the stochastic approach to the population distribution of the excitons in energy space is justified as in the case of the Brownian motion. Consequently, the decrease in α results from the insufficient cooling of excitons by acoustic phonon scattering for bounding exciton pairs to form biexcitons. On the other hand, due to the laser heating, T_e was elevated above T_b from 80 to 114 K at $T_b=80$ K. When the elevated temperature so as the kinetic energy of excitons approaches to the energy of the lowest optical phonon, near 12 meV in this case, the optical phonon will participate in the exciton relaxation process. The inelastic scattering between excitons with assistance of optical phonons ionizes one of the scattered excitons to $n=\infty$ state rather than $n=2$ state and efficiently cools the other exciton to the lower polariton branch so that high P_∞ emission was observed for $T_b=80$ K, as shown in Fig. 2(a). Contrarily, without assistance of optical phonon, high P_2 emission was found at $T_b\leqslant 40$ K.

We therefore conclude that high exciton density does not guarantee bounding exciton pairs to form biexcitons; the acoustic phonon scattering is responsible for exciton relaxation at low temperature while optical phonon scattering will participate in at high temperature. The efficient cooling of exciton with assistance of optical phonon scattering allows effectively bounding exciton pairs to form biexcitons; contrarily, the exciton relaxation only via multiple acoustic phonon scattering may not efficiently enough to dissipate the excess kinetic energy of excitons to form biexcitons in turn to reduce the exponent of excitation. Furthermore, multiexciton scattering via colliding with high density of excitons would result in quenching biexciton luminescence under very high excitation power.

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