ZnO における励起子発光の温度依存性

クアンティップ・タウィワット[A]、中田博保[A]、吉田一樹[B]、
寺井慶和[B]、藤原康文[B]
[A]大阪教育大学教養学科、[B]大阪大学大学院工学研究学科

Temperature dependence of exciton luminescence in ZnO

T. Khuangthip[A], H. Nakata[A], K. Yoshida[B], Y. Terai[B] and Y. Fujiwara[B]
[A]*Department of Arts and Sciences, Osaka Kyoiku University*
[B]*Graduate School of Engineering, Osaka University*

The photoluminescence (PL) in ZnO bulk crystal was measured at 4 to 40 K. Four exciton lines are observed between 3 and 3.4 eV. The activation energy E^* which is a barrier of energy for nonradiative recombination of excitons at 3.315 eV is estimated to be 4.81 meV. PL intensities of all exciton peaks decrease with increasing temperature.

1. Introduction

Zinc oxide (ZnO) is an attractive semiconductor material especially in optoelectronic applications and is expected as an efficient material for applications in ultraviolet (UV) light emitting diodes, laser diodes and varistors. Compared with the other wide band-gap materials, it has a very large exciton binding energy of ~60 meV, which makes free excitons stable even above room temperature [1]. However, at low temperatures ZnO is more interesting in PL study. A. V. Rodina et al. observed low temperature PL and transmission in magnetic fields of ZnO. They found that nitrogen is the origin of luminescence line I_9 of bound exciton although this had been believed to be related to Na [2]. Most of ZnO applications depend on carrier recombination related to defects and impurities. The effects of crystal defect on UV luminescence behaviors have been investigated extensively [3-6].

In this study, the temperature-dependent PL at low temperatures was studied to understand nonradiative recombination of excitons.

2. Experimental procedure

The ZnO bulk crystal was grown by metal organic chemical vapor deposition (MOCVD) assisted by sputtering. The growth rate was 1.22 nm/min and the thickness was 110 nm. This sample was excited by a He-Cd laser (λ = 325 nm). The photo-luminescence was detected by a photomultiplier attached to a grating monochromator (Nihon bunko C25). Temperature ranged from 4 to 40 K. Temperature dependence of PL intensity was used to determine the recombination of excitons in ZnO bulk crystal.

3. Results and discussion

PL intensities of ZnO bulk crystal depend on temperature of sample. The spectra at various temperatures are shown in Fig. 1-2. PL intensity decreases with increasing temperature. The peak BE at 3.356 eV

is due to acceptor bound exciton (A^0X). At low temperatures, luminescence lines originating from bound exciton (BE) can be seen at the lower energy side of the free exciton (FE) zero phonon line (3.266-3.365 eV) in the bulk crystal [7]. However, the luminescence at 3.315 eV could be determined to a one longitudinal optical (LO) phonon replica of FE [8-9]. A small PL peak BE at 3.356 eV was assigned to an exciton bound to Na. But Rodina et al. concluded from magnetic field mea-surement that is originates in N.

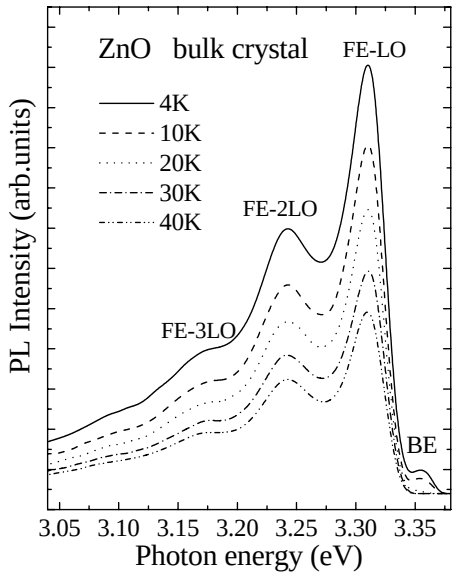

Fig. 1 PL spectra of ZnO bulk crystal.

Figure 3 shows temperature dependence of PL intensity. The analysis of data is done by equation of radiative efficiency which is related to PL intensity depending on temperature.

$$I = \frac{0.93}{1 + 2.39\exp(-55.76/T)} \quad (1)$$

, where I is PL intensity and T is temperature. Equation (1) is related to equation

$$\eta = \frac{1}{1 + C\exp\left(-E^*/kT\right)} \quad (2)$$

where η is radiative efficiency, $C = P_{nr0}/P_r$ is constant, E^* is an activation energy. The term of $C\exp(-E^*/kT)$ is the probability of a nonradiative transition (P_{nr}).

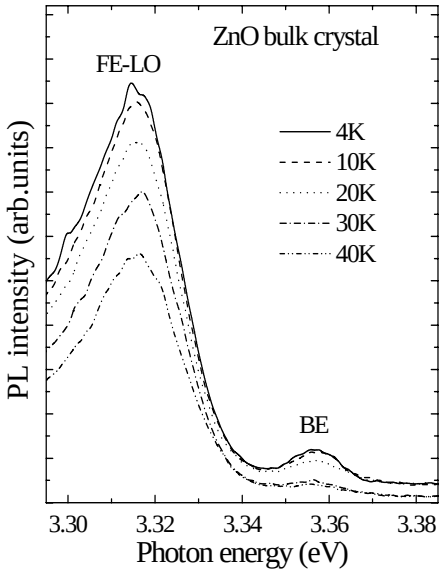

Fig. 2 PL spectra of ZnO at different temperatures.

From equations (1) and (2) concern with FE-LO phonon replica, E^*/k = 55.76 (J/K) then E^* = 4.81 (meV). On the other hand, in the case of BE line, E^*/k = 74.55 (J/K) then E^* = 6.13 (meV). We found that the E^* in the case of BE line is greater than of FE-LO phonon replica it means the free exciton is recombined easier than the

case of bound exciton line. The height of E^* is the energy of barrier that hot carriers overcome ($kT \geq E^*$) to recombine. The increasing of temperature will then increase the nonradiative transitions. Furthermore, equation (2) shows temperature dependence of η related to P_{nr} in semiconductor which reveals exciton recombination and phonon replica in ZnO [10].

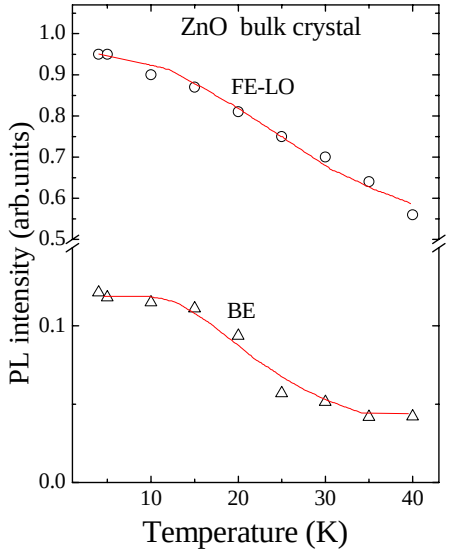

Fig. 3 Temperature dependence peak of bound exciton PL.

Figure 4 shows a configuration diagram with the electron in the excited states at *A*. At low temperature, the excited system has a configuration position r_A. The electron can make a radiative transition $A \rightarrow A'$ and then the system will relax to the ground state equilibrium at *B*. At high temperatures, atomic vibrations can move the atom from a configuration position r_A to position r_C. At *C*, the electron can make a nonradiative transition to the ground state [11].

In this experiment activation energy for nonradiative transition of free exciton energy in bulk crystal is around 4.81 meV. On the other hand, when the system relaxes to position r_B, the exciton is at the lowest energy state without having emitted a photon. When atom relaxation from position r_C to position r_B, many phonons are emitted.

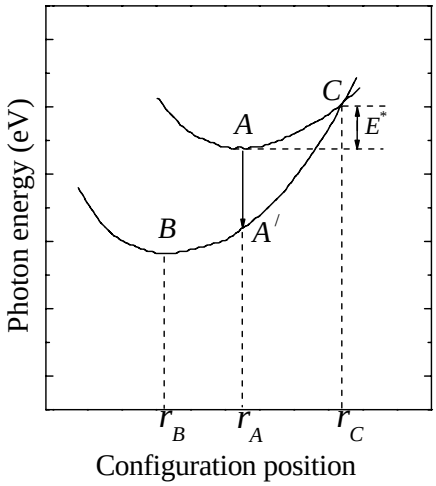

Fig. 4 Configuration diagram showing a radiative transition $A \rightarrow A'$ and a nonradiative transition via *C*.

4. Conclusion

The analysis of data shows that temperature dependence of radiative efficiency η is related to the probability of nonradiative transition P_{nr}. The activation energy E^* of around 4.81 meV for free excitons is a barrier of energy that is only hot carriers with sufficient energy to overcome the barrier ($kT \geq E^*$) can recombine. The increasing of temperature will then increase the nonradiative transitions.

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