Temperature dependant longitudinal-optical-phonon assisted emission of free excitons in ZnO

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The Segall-Mahan theory is employed to calculate both one and two longitudinal-optical (LO) phonon sidebands of free excitons of zinc oxide (ZnO) in a wide temperature range. The energy spacing from the zero-phonon line to 1 LO and 2 LO phonon sidebands deviates gradually from their characteristic LO phonon energy with increaseing the temperature. The experimental results are good agreement with the theoretical calculation. Only one adjustable parameter is taken into account in this calculation, which determines the range of values of the hole effective mass in ZnO.

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Zinc oxide (ZnO) has received much attention in recent years due to its unique physical properties and its potential technological applications, such as blue and ultraviolet (UV) light emitters and UV detectors[1−5]. Although significant investigation has been conducted on ZnO[6−11], some fundamental problems regarding its optical properties remain unclear. To obtain a proper understanding of its optical properties, the excitonic state must be taken into account. Based on Green's function method, the Segall-Mahan theory considered the effects of exciton-phonon interactions at all orders, including the line broadening, shift, and asymmetry[12−14], and was adopted to calculate phonon-assisted radiative recombination of free excitons in ZnO. In this letter, we study theoretically and experimentally the temperature dependence of the phonon replica of free excitons in ZnO.

The ZnO samples used study were commercial bulk crystals (Commercial Crystal Laboratories). A 325-nm He-Cd laser with approximate 35-mW output was employed to illuminate the Zn-terminated (0001) surface of the sample at a tilted angle of approximate 45°. The signal was collected by an SPEX 750M monochromator and amplified by standard lock-in techniques.

In the Segall-Mahan theory, the absorption coefficient for the process involving one phonon or two phonons can be calculated by[12−14]

$$\alpha_1(\omega) = \frac{4\pi e^2 \beta_{A,1} \omega_l (\varepsilon_\infty^{-1} - \varepsilon_s^{-1})}{4a\hbar c B \sqrt{\varepsilon'}} \left(\frac{E_{A,1}}{E_{A,1} - \omega} \right)^2$$

$$\cdot \left[\frac{M_{||}B}{\mu_\perp \Delta} \right]^{1/2} N(\omega_l) I(\omega),$$

$$\alpha_2(\omega) = \frac{e^2 \varepsilon_s \beta_{A,1} \omega_l^2 (\varepsilon_\infty^{-1} - \varepsilon_s^{-1})^2}{16a\hbar c B^2 \sqrt{\varepsilon'}} \left(\frac{E_{A,1}}{E_{A,1} - \omega} \right)^2$$

$$\cdot \left[\frac{M}{\mu} \right]^3 \left(\frac{\langle E_{A,n'} \rangle - E_{A,1}}{\langle E_{A,n'} \rangle - \omega} \right)^2 N^2(\omega_l) \sum_n I_n(\omega), \quad (1)$$

where a and B are the Bohr radius and the binding energy of exciton, ε_∞ and ε_s are dielectric constants at high and low frequencies, respectively, $4\pi\beta_{A,1}$ denotes the con-

tribution of the $n = 1$ A-exciton state to the polarizability, $E_{A,1}$ is its energy, $M_{||}$ is the total masses of exciton in the c axis, $\mu_\perp$ is the reduced mass in the direction perpendicular to the c axis, $M = m_e + m_h$, $\mu^{-1} = m_e^{-1} + m_h^{-1}$. ε' is the dielectric constant at $E_{A,1}$ in absence of $n = 1$ exciton. $N(\omega_l) = [\exp(\omega_l/k_B T) - 1]^{-1}$ and $I(\omega)$ is the integral given in Segall's paper[12].

The transition probability for emission is related to the absorption:[14]

$$W_{em}(\omega) \propto e^{-\omega/k_B T} \alpha_n(\omega), n = 1, 2. \quad (2)$$

Figure 1 shows the theoretical absorption coefficient (dotted line) and the emission curves (solid line), which are calculated based on the absorption coefficient curves of one or two longitudinal-optical (LO) phonon sidebands (PSB) in ZnO at 146 K. The parameters used are listed in Table 1. The peak positions of 1 LO and 2 LO PSB are at 3.2294 and 3.3065 eV, and the corresponding values of energy spacing are 58.2 and 135.3 meV according to $E_{A,1}$=3.3647 eV, where, $E_{A,1}$ is the peak position of the zero-phonon line in ZnO. They are obviously smaller than one or two units of the standard LO phonon energy, especially for the 1 LO PSB. The line shape of PSB shows obvious asymmetry, which agrees with the observed experimental results.

Figure 2 shows the theoretical emission curve in comparison with measured photoluminescence spectra at three different temperatures of 116, 136, and 146 K. These temperatures were selected to avoid the effect of strong signal of bound exciton at lower temperature and peak overlap due to intensive line shape broadening at higher temperature. In comparison with the theoretical and experimental results, the fitting is found to increase with the increase of the temperature. The bandwidth of the calculated curves at 116 K is quite larger than the measured one, especially for 2 LO PSB. The calculated and measured spectra show great agreement when the temperature increases to 136 and 146 K. An interesting phenomenon is found in the measurement photoluminescence spectra of ZnO at the temperature under 116 K:
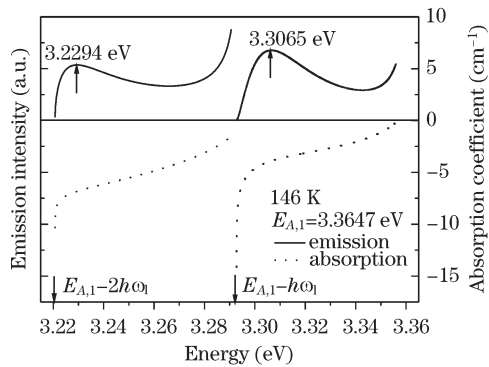
Fig. 1. Solid lines represent the calculated photoluminescence spectra of 1 LO and 2 LO PSB in ZnO at 146 K. Dotted lines represent the calculated absorption coefficient in the corresponding energy range at the same temperature.

Table 1. Parameters Used in the Calculation of the Absorption Coefficient

| Parameters	Symbol	ZnO
Electron Effective Mass (unit of m_0)	m_e	$0.24^{[12]}$
Hole Effective Mass	$m_{h\infty}$	0.8
(unit of m_0)	$m_{h\parallel}$	5
Exciton Binding Energy (meV)	B	$60^{[5]}$
LO phonon Energy (meV)	hw_1	$72^{[12]}$
Statistic Dielectric Constant	$\varepsilon_s = (\varepsilon_\perp \varepsilon_\parallel)^{1/2}$	$7.88^{[12]}$
High-Frequency Dielectric Constant	$\varepsilon_\infty = n_\perp n_\parallel$	$4.0^{[12]}$
Dielectric Constant at E_{A1} in the Absence of $n=1$ Exciton	ε'	$6.2^{[12]}$
Zero-Frequency Polarizability Due to $n=1$ A, B, or C Exciton ($\varepsilon \perp c$)	$4\pi\beta_{A,1}$	$0.0066^{[12]}$
	$4\pi\beta_{B,1}$	$0.0227^{[12]}$
	$4\pi\beta_{C,1}$	$0.0300^{[12]}$
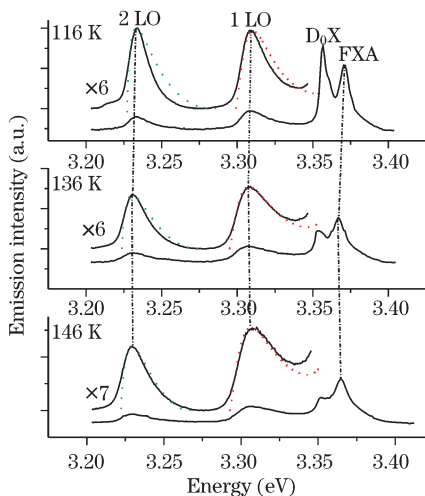
Fig. 2. Solid lines present the measured photoluminescence spectra of ZnO at three different temperatures of 116, 136, and 146 K. The enlarged portion shows the details of the PSB structure. Dotted lines represent the calculated emission spectra of ZnO at the same temperature.
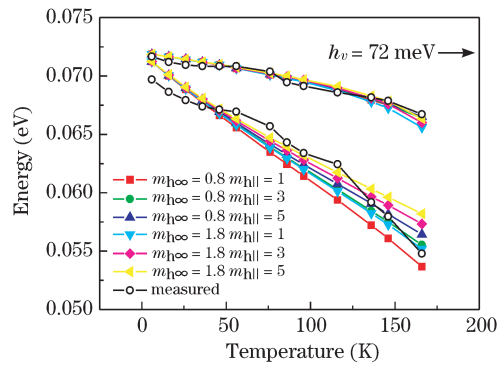

Fig. 3. Measured (open circles) and calculated (solid symbols) energy spacing from the sidebands from the 1 LO or 2 LO to the zero-phonon line against temperature.

the intensity of 2 LO PSB is obviously higher than that of 1 LO PSB. It is assumed that the enhanced intensity and unfitting of the line shape at low temperature are due to the strong exciton-phonon interaction between the bound exciton of ZnO and LO phonons, since the intensity of the emission peak of the bound exciton is stronger than the free exciton under 116 K, The observed energy spacing from zero-phonon line to 1 LO or 2 LO PSB is not exactly equal to one or two units of the standard LO phonon energy of ZnO. In fact, both energy spacings are found to shrink as the temperature increases. The results of theoretical calculation follow this rule and show good agreement with experimental results. Both theoretical and measurement energy spacings between 1 LO PSB or 2 LO PSB and zero-phonon line of free excitons is plotted in Fig. 3.

The hole effective mass in ZnO, as an adjustable parameter, was involved in the calculation. Figure 3 shows curves for energy spacing calculated with a series of $m_{h\infty}$ and $m_{h\parallel}$ values. The theoretical results using the parameters $m_{h\infty}=0.8m_0$ or $1.8m_0$ and $m_{h\parallel}=3m_0$ or $5m_0$ provide relatively satisfactory fitting of the measurements data over the temperature range of 6–150 K. This indicates that the $m_{h\parallel}$ of ZnO should be larger than m_0, which shows agreement with some results reported by Fan *el al.*[15]. All the energy values of $E_{A,1}$ at different temperatures used in the calculation were taken from the measurement results.

In conclusion, we investigat the temperature dependence of photoluminescence in PSB in ZnO due to the interaction of the free excitons with LO phonons and with acoustic phonons in ZnO by experimental and theoretical methods. The Segall-Mahan theory is employed to calculate the sidebands of 1 LO and 2 LO phonons for free excitons in a wide temperature range. The theoretical results show good agreement with the experimental results. The energy spacing between the LO PSB and the zero-phonon line appears to continuouly shrink with the increase of the temperature. Since the effective mass of holes in ZnO is taken into account as an adjustable parameter in calculation, a reasonable range of value of effective mass is determined from the calculation.

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