Resonant coupling of bound excitons with LO phonons in ZnO: Excitonic polaron states and Fano interference

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We report on a photoluminescence observation of robust excitonic polarons due to resonant coupling of exciton and longitudinal optical (LO) phonon as well as Fano-type interference in high quality ZnO crystal. At low enough temperatures, resonant coupling of excitons and LO phonons leads to not only traditional Stokes lines (SLs) but also up to second-order anti-Stokes lines (ASLs) besides the zero-phonon line (ZPL). The SLs and ASLs are found to be not mirror symmetric with respect to the ZPL, strongly suggesting that they are from different coupling states of exciton and phonons. Besides these spectral features showing the quasiparticle properties of exciton-phonon coupling system, the first-order SL is found to exhibit characteristic Fano lineshape, caused by quantum interference between the LO components of excitonic polarons and the continuous phonon bath. These findings lead to a new insight into fundamental effects of exciton-phonon interactions. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2140701]

As a II-VI wide-gap polar semiconductor with the wurtzite structure, zinc oxide (ZnO) is of great technological importance. Since the demonstration of lasing from its microcrystalline film,[1] ZnO has attracted renewed interests in recent years.[2–12] ZnO has some unique properties such as large exciton binding energy (~60 meV) and strong exciton longitudinal optical (LO) phonon interaction.[12] While most of the recent efforts have been devoted to understanding such issues as defects,[2–4,11] surface polarity,[6,8] and *p*-type doping,[5,10] etc., few reports were presented to investigate exciton-phonon interactions in ZnO, despite that such interactions were well recognized to be fundamentally important for its optoelectronic properties from both experiments[12] and theories.[13,14] For example, strong exciton-phonon interactions may lead to new exciton-phonon bound states,[13] which causes striking phonon-assisted exciton transitions, referred to as phonon sidebands or replicas, in absorption and emission spectrum. A characteristic spectral feature of the new exciton-phonon bound states is predicted to be that the energy separations of the phonon sidebands with respect to the zero-phonon line in emission and absorption spectra can be quite different. For emission, the energy separation is close to the standard characteristic energy of LO phonons. For absorption, however, the energy separation is significantly smaller. In ZnO, the characteristic energy of the A_1–LO phonon at zone center is about ~72 meV (~574 cm^{-1}).[15] The binding energy of shallow excitons in ZnO may be comparable to the characteristic energy of LO phonons, leading to interesting effects of resonant coupling between exciton and LO phonons.[16] A similar resonant coupling in semiconductor quantum dots has attracted an increasing interest.[17–20] Such resonant mixing between exciton and phonons has been argued to form new quasi-particles, namely excitonic polarons[20] and to produce a new class of nonadiabatic lines in phonon-assisted luminescence of exciton,[19] which are difficult to be interpreted by means of the previous adiabatic theory of multiphonon transitions in deep centers developed by Huang and Rhys.[21,22] At the same time, another resonance phenomenon Fano-type quantum interference[23] has been theoretically predicted to exist in the coupling exciton-phonon systems of semiconductors[14,24–26] in the 1960's. However, to our knowledge, it has not yet been experimentally observed in excitonic luminescence. In this letter, we report the first luminescence evidence of the existence of excitonic polaron states and phonon-mediated Fano-type quantum interference in high-quality ZnO single crystal. Using a new theory model developed by us, almost all the spectral features observed can be naturally accounted for.

The ZnO samples used in the present study are commercial bulk crystals (Commercial Crystal Laboratories). The 325 nm line of a He–Cd laser was employed to illuminate the Zn-terminated ZnO $(000\bar{1})$ surface or O-terminated ZnO sur-

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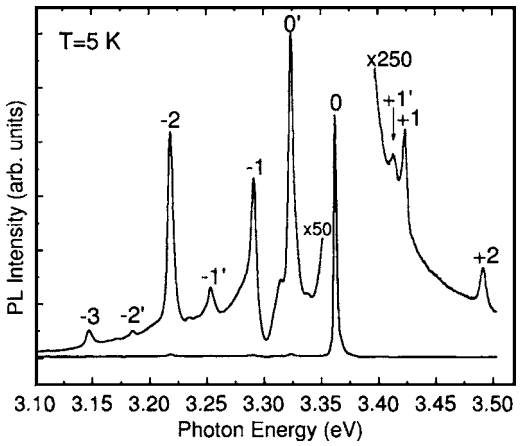

FIG. 1. Representative photoluminescence spectrum of the exciton-phonon coupling system in ZnO measured at 5 K. Various phonon-assisted transitions including anti-Stokes lines and Fano-type interference lineshape are clearly observed.

face at a tilted angle of about 45°. The low-temperature photoluminescence setup employed in the present work was previously described elsewhere.[27]

Figure 1 shows a representative low-temperature emission spectrum of the ZnO sample with Zn-terminated surface. The strongest peak at ~3.361 eV (369 nm), which is marked as 0, is conventionally identified to be the zero-phonon line (ZPL) of the bound excitons (neutral-donor-bound excitons,[28] usually called I_2 line in literature). The direct band gap of ZnO at low temperature is 3.437 eV.[11] The energy difference between the zero-phonon line and ZnO band gap is thus equal to (3.437−3.361) eV=76 meV, which is slightly larger than the characteristic energy (72 meV) of the A_1−LO at zone center. This provides a physical configuration in which the resonant mixing of excitons and LO phonons occurs. As a result, the nonadiabatic lines should be observed in emission spectra of ZnO excitons. From the emission spectrum in Fig. 1, it is obvious that the first, second, and third phonon Stokes lines (SLs) of the bound excitons, which are denoted with −1, −2, and −3, respectively, are all clearly resolved. These lines represent optical processes in which one, two, and three LO phonon creations accompany the corresponding photon generations. The energy separation between any two of the adjacent SLs including the zero-phonon line is ~71 meV, which is almost identical to the characteristic energy (~72 meV) of the A_1–LO of ZnO. Besides these "conventional" SL lines, the anti-Stokes lines (ASLs, marked as +1′, +1, and +2, respectively) are observed at the higher energy side of the ZPL line. Notice that the energy separations between the ASL lines and the ZPL line are noticeably smaller than the corresponding values between the SL lines and the ZPL line. In other words, the ASL and SL lines are not mirror symmetric with respect to the ZPL line. The ASL lines are broader than the SL ones, strongly indicating that the ASL and SL lines are from different coupling exciton-phonon states. Since the thermally excited phonons are negligible at 5 K so that the probability of reabsorbing LO phonons to generate "hot" excitons from "cold" excitons is negligibly small, the observation of ASL lines directly supports the aforementioned argument. A natural explanation for above spectral features is that the resonant coupling between exciton and phonons produces a number of bound states, i.e., excitonic polaron states.[20] As proved by a newly developed theory (briefly described later),[29] these bound states contain different exciton and phonon components and give rise to the ASL, ZPL, and SL lines. The recorded first luminescence observation of the anti-Stokes line was reported for CdS in 1970,[30] but the origin was not identified.

From Fig. 1, it is also seen that there is an additional group of emission lines appearing at the lower energy side of the ZPL at ~3.361 eV (marked as 0). Notice that this new group of lines is very similar to the group of lines 0, −1, −2, −3. We thus temporarily mark them 0′, −1′ and −2′. One distinct spectral feature in Fig. 1 is the specific asymmetric lineshape of the first phonon SL (marked as −1). Moreover, there exists a clear dip at its higher energy side. It is a typical Fano lineshape.[23] Besides its characteristic Fano lineshape, the intensity of the first-phonon SL is unusually weaker than that of the second phonon SL, which is a scarcely seen phenomenon in cases like ZnO whose Huang–Rhys factor is much less than unity. These anomalies suggest that quantum mechanical interference occurred in the radiative recombination processes of excitonic polarons.

The observation of phonon-mediated Fano interference phenomenon in luminescence is quite interesting and challenging for the theoretical treatment of the exciton-phonon interactions. First of all, it is recognized that an accurate calculation of the absorption or emission spectrum of a coupled exciton-phonon system in complicated solid-state environment is extremely difficult. Starting from solving Schrödinger equation of the exciton-phonon coupling system, we attempt to theoretically reveal these novel spectral features observed in the LO phonon-assisted excitonic PL spectra of ZnO. Details of the theoretical model have been published elsewhere.[29] Here we rewrite the major equations of the model. The model Hamiltonian of the exciton-phonon coupling system can be written as

$$H=\sum_{\mathbf{K}}\varepsilon_{\mathbf{K}}a_{\mathbf{K}}^{\dagger}a_{\mathbf{K}}+\sum_{l,\mathbf{q}}\hbar\omega_{l,\mathbf{q}}b_{l,\mathbf{q}}^{\dagger}b_{l,\mathbf{q}}+\sum_{l,\mathbf{K},\mathbf{q}}V_{l,\mathbf{q}}a_{\mathbf{K}-\mathbf{q}}^{\dagger}a_{\mathbf{K}}(b_{l,\mathbf{q}}^{\dagger}+b_{l,-\mathbf{q}}), \quad (1)$$

where $a_{\mathbf{K}}(a_{\mathbf{K}}^{\dagger})$ and $b_{l,\mathbf{q}}(b_{l,\mathbf{q}}^{\dagger})$ are annihilation (creation) operators for exciton with mass-center momentum $\mathbf{K}$ and for phonon in the lth band with momentum $\mathbf{q}$, respectively. $\varepsilon_{\mathbf{K}}$ and $\omega_{l,\mathbf{q}}$ characterize the dispersion relations of excitons and phonons. $V_{l,\mathbf{q}}=[2\pi e^2\hbar\omega_{l,\mathbf{q}}/Vq^2(\kappa_{\infty}^{-1}-\kappa_0^{-1})]^{1/2}$ is the Fröhlich coupling strength of exciton and LO phonon. Here, κ_{∞}, κ_0, and V are the dielectric constants for infinite and zero frequencies and the volume in a cell, respectively. For localized excitons bound at impurities discussed in the present work, we can neglect its dispersion and let $\varepsilon_{\mathbf{K}}\equiv\varepsilon_0$. For Hamiltonian (1), the mth eigenwave functions of excitonic polaron states can be written as

$$\Psi_m = \sum_{nl,\mathbf{q}} c_{m,\{n_{l,\mathbf{q}}\}} a^\dagger \prod_{l,\mathbf{q}} \frac{(b_{l,\mathbf{q}}^\dagger)^{nl,\mathbf{q}}}{\sqrt{n_{l,\mathbf{q}}}}|0\rangle, \tag{2}$$

where $n_{l,\mathbf{q}}$ is the number of phonons of mode $(l,\mathbf{q})$ in the corresponding component, $|0\rangle$ is the exciton vacuum, and the coefficients satisfy the following iteration relations

$$\left[E_m - \left(\varepsilon_0 + \sum_{l,\mathbf{q}} n_{l,\mathbf{q}}\hbar\omega_{l,\mathbf{q}}\right)\right] c_{m,\{n_{l,\mathbf{q}}\}} = \sum_{l',\mathbf{q}'} \sqrt{n_{l',\mathbf{q}'}} V_{l',\mathbf{q}'} c_{m,\{n_{l,\mathbf{q}}\}-(l',\mathbf{q}')} + \sum_{l',\mathbf{q}'} \sqrt{n_{l',\mathbf{q}'}+1} V_{l',\mathbf{q}'} c_{m,\{n_{l,\mathbf{q}}\}+(l',\mathbf{q}')}. \tag{3}$$

When only one exciton is considered, the exciton and phonon parts in the polaron wave functions described by Eq. (2) are still separable. Within the adiabatic scheme, the eigenenergies of polaron states can be derived as

$$E_m = \varepsilon_0 + m\hbar\omega_{l,\mathbf{q}} - \Delta_{l,\mathbf{q}}, \tag{4}$$

where $\Delta_{l,\mathbf{q}} \equiv V_l^2 \mathrm{q}/\hbar\omega_{l,\mathbf{q}}$ is the binding energy of the excitonic polaron. If we further neglect the dispersion of phonons and assume that there is only one LO mode interacting with exciton, we can omit indices l, $\mathbf{q}$ and rewrite Eqs. (3) and (4) into

$$[(m-n)\hbar\omega_0 - \Delta_0]c_{m,n} = V_0\sqrt{n}c_{m,n-1} + V_0\sqrt{n+1}c_{m,n+1}, \tag{5}$$

and

$$E_m = \varepsilon_0 + m\hbar\omega_0 - \Delta_0. \tag{6}$$

Here V_0 represents the average exciton-phonon coupling strength. From Eq. (5), one can strictly prove that the well-known Huang–Rhys theory[21] deals with only the ground state (GS) of the excitonic polarons for any coupling strength.[29] The eigenenergy of the GS state is lower than the bare exciton energy by $\Delta_0 = V_0^2/\hbar\omega_0$, and the coefficient of its component containing n LO phonons is $c_{0,n} = (-1)^n S^{n/2}/e^{S/2}\sqrt{n!}$ with $S \equiv \Delta_0/\hbar\omega_0$ being the Huang–Rhys factor. $|c_{0,n}|^2$ gives the intensities of phonon sidebands predicted by the Huang–Rhys theory. Furthermore, the excited polaron states $(m>0)$, which are not handled in the Huang–Rhys theory, can produce ASLs by their components with phonon number $n<m$. The energetic positions of these ASLs located at $E_m - n\hbar\omega_0 = \varepsilon_0 + (m-n)\hbar\omega_0 - \Delta_0$. All these lines form the first set of phonon sidebands marked as $0'$, $-1'$, $-2'$, $+1'$, and $+2'$ lines in Fig. 1. Besides the LO mode, however, there are a large number of bath modes. Although these modes are not directly interacting with the exciton, they may have a crucial influence on phonon components in the excitonic polaron states. This effect can be taken into consideration with the mixing Hamiltonian

$$H_1 = \sum_\lambda g_\lambda (b_0^\dagger b_\lambda + \mathrm{H.c.}) + \sum_\lambda \hbar\omega_\lambda \left(b_\lambda^\dagger b_\lambda + \frac{1}{2}\right), \tag{7}$$

where λ is the mode index of phonons, g_λ is the coupling strength between the LO and bath modes, and operator b_0 is for the LO mode investigated above. Although all modes are diagonal in a perfect crystal, coupling may be produced by formation of the exciton polaron states in which the vibrations of the LO phonon components are altered. The dispersion relation ω_λ is assumed to be continuous with a constant density of states in an energy range from 0 to W. The orthogonal phonon modes under Hamiltonian (7) can be rewritten as

$$b_l = \frac{\hbar\omega_l - \hbar\omega}{\sqrt{g_\lambda^2 + (\hbar\omega - \hbar\omega_l)^2}} b_\lambda + \frac{g_\lambda}{\sqrt{g_\lambda^2 + (\hbar\omega - \hbar\omega_l)^2}} b_0, \tag{8}$$

with frequency $\omega_l \sim \omega_\lambda$ as determined by the following equation

$$\hbar\omega_l - \hbar\omega = \sum_\lambda \frac{g_\lambda^2}{\hbar\omega_l - \hbar\omega_\lambda}. \tag{9}$$

The obtained set of modes $\{l\}$ can be used to construct exciton-phonon composites of Eq. (2) and the coupling strength in Eq. (3) is given by

$$V_l = \frac{g_\lambda}{\sqrt{g_\lambda^2 + (\hbar\omega - \hbar\omega_l)^2}} V_0. \tag{10}$$

The mixing introduced by H_1 is coherent and Fano interference between the discrete LO mode and other continuous modes can take place. When the exciton in Ψ_m is annihilated, photon emission occurs. Simultaneously, the components with phonons in mode l will give rise to an accompanied emission of l-mode phonon. Because the l mode is a mixed mode consisting of a LO-mode component and a λ-mode component as illustrated in Eq. (8), an interference between these two components will happen, and the probability of corresponding light emission is proportional to

$$\alpha_l = \frac{(\tilde{\epsilon}+1)^2}{\tilde{\epsilon}^2+1}, \tag{11}$$

with $\tilde{\epsilon} = (\hbar\omega_l - \hbar\omega)/g_\lambda$. Such an interference in the optical transitions can lead to a typical Fano lineshape with a unity asymmetric parameter $(q=1)$ in the sidebands, especially in the one phonon sideband.[23] Taking the phonon mixing into account, we obtain the PL spectrum

$$\rho(\varepsilon) = \sum_m \sum_{\{n_l\}} |c_{m,\{n_l\}}|^2 \left(\prod_l \alpha_l^{nl}\right) \theta(E_{\mathrm{laser}} - E_m) \times \delta(\varepsilon - E_m + \sum_l n_l\hbar\omega_l). \tag{12}$$

Using Eq. (12), we calculate the emission spectrum of ZnO shown in Fig. 2. All the modes l with small coupling strength V_l with the exciton result in the formation of the second set of the phonon sidebands including a ZPL near ε_0 marked as 0, SLs -1, -2,… and ASLs $+1$, $+2$,… . The energy distance between the both ZPLs of the two sets is close to Δ_0 which is determined by the coupling strength V_0. Note that the intensity and width of line 0 are much larger than those of $0'$, because of the huge number of modes with small V_l making the contributions. The theoretical spectrum catches the essential features observed in Fig. 1, but a quantitative agreement with the experimental curve is not achieved, particularly for the Fano resonance feature around

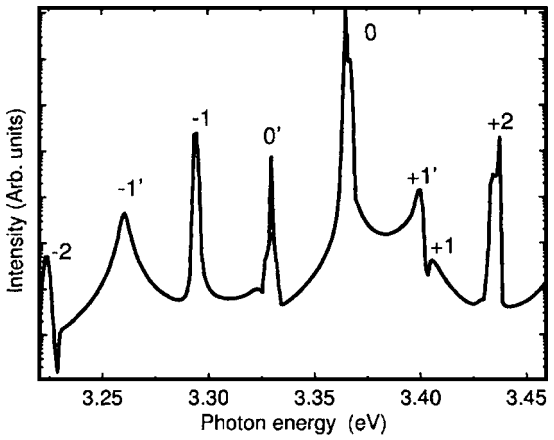

FIG. 2. Calculated emission spectrum of the exciton-phonon coupling system in ZnO.

the first LO sideband. As mentioned earlier, the exciton-phonon coupling in solids is a very complicated many-body problem and at the same time contains a wealth of physics. This makes it remain an active issue even after extensive studies in the past few decades. The Fano resonance in the present model is attributed to the quantum mechanical interference of the LO phonon components in the excitonic polaron states with the continuous phonon bath. Indeed, the Fano resonance features can be seen in some peaks of the theoretical spectrum despite the fact that they are partially smeared by the summation in Eq. (12). Here the coupling of the LO mode and the bath modes is treated as coherent for the whole phonon band. In real material systems, this coherence may be frequency dependent. Besides the coupling between sharp LO phonon mode and continuous bath modes, another resonant coupling mechanism which was discussed in CdS and CdSe by Henry and Hopfield[31] may exist in the ZnO samples studied in the present work. As pointed out by Henry and Hopfield, the resonant interactions between LO phonons and continuum states of donors may cause the Fano line shape of the first LO phonon sideband of the bound excitonic luminescence at low temperature. It is thus a possible way to improve the agreement between theory and experiment if such a resonance is taken into account.

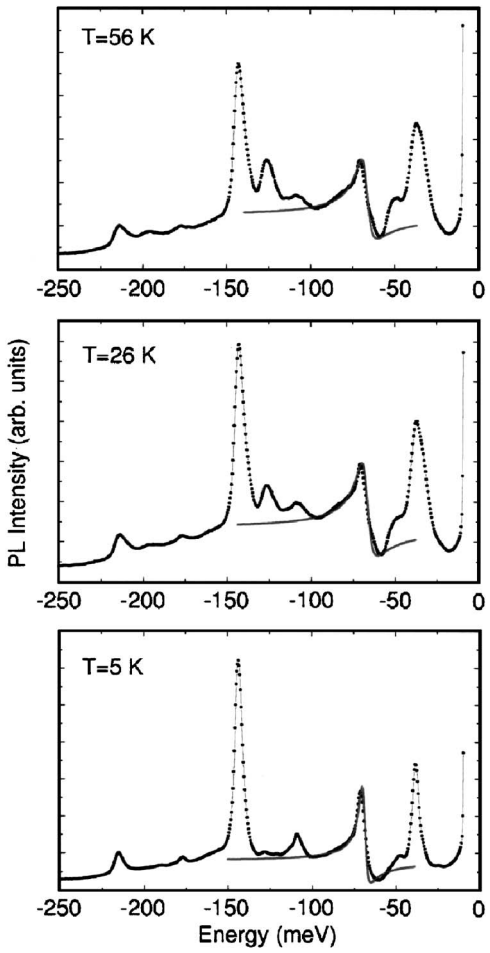

FIG. 3. Representative emission spectra of the exciton-phonon coupling system in ZnO at three different temperatures. The energy is measured from the strongest ZPL line. The solid thin lines are the fitting curves using the Fano lineshape function.

Since temperature effect is not considered in the newly developed model briefly described above, we use the well-known Fano lineshape function[23] to fit our experimental spectra at different temperatures to get more information of Fano interference. The fitting curves at three typical temperatures are plotted in Fig. 3 as the solid lines. The obtained values of the asymmetry parameter q range from 1.43 to 1.85. The theoretical unity value of the parameter is close to them. Another major parameter associated with Fano interference is the resonance width Γ. It is found that it increases monotonously with increasing temperature in the range of study. This means that the mean lifetime of the excitonic polarons becomes shorter as the temperature increases. From Fig. 1, the line width of the ZPL is $\sim$2.5 meV at 5 K. However, the first phonon SL line already broadens to about 4 meV at the same low temperature. The resonance energy E_r varies within a small range between 67 and 69 meV for the temperature range studied, which is several meV less than the standard LO phonon energy of ZnO.

In conclusion, the resonant coupling of bound exciton-LO phonon in high quality ZnO crystal has been investigated with low-temperature photoluminescence. The spectral evidence of the existence of robust excitonic polarons due to the resonant coupling of exciton-phonon was obtained. The phonon mediated Fano-type quantum mechanical interference effect was observed for the first time in the low-temperature luminescence spectra. Together with our theoretical model, the results provide a novel and consistent picture for the exciton-phonon strong coupling system. The work also shows that the Fano-type quantum mechanical interference is a rather general phenomenon in solid state physics.

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