Photoluminescence study of the annihilation process of donor-bound excitons in ZnO: observation of quantum mechanical interference

Shenlei Shi (施申蕾)[1] and Tengchao Huang (黄腾超)[2*]

[1] *Department of Physics, China Jiliang University, Hangzhou 310018, China*

[2] *Department of Information Science and Electronic Engineering, Zhejiang University, Hangzhou 310027, China*

[*] *E-mail: superchao@zju.edu.cn*

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We report a photoluminescence observation of the coupling of donor-bound excitons and longitudinal optical phonons in high-quality ZnO crystals at 5 K. The first-order phonon Stokes line of donor-bound excitons exhibits a distinct asymmetric line shape with a clear dip at its higher energy side, suggesting that quantum mechanical interference occurs during the annihilation of donor-bound excitons. The donor binding energy is determined to be 49.3 meV from spectral featural.

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Research on ZnO has continued to progress from the time it began in the 1950s[1,2]. The current revival of interest in ZnO research began in the mid-1990s due to the advent of optically pumped lasing from ZnO polycrystalline thin films at room temperature[3−5]. Despite a long history of industrial application, however, some fundamental properties of ZnO remain unclear and even controversial. For example, information on multi-photon-absorption-induced luminescence in ZnO is quite limited; the same can be said of exciton-phonon interactions in ZnO. In this letter, we report on a photoluminescence (PL) observation of the coupling of donor-bound excitons and longitudinal optical (LO) phonons in high-quality ZnO crystals.

The ZnO samples used in the present study were commercial bulk crystals (Commercial Crystal Laboratories, USA). The 325-nm line of a He-Cd laser was employed to illuminate the Zn-terminated ZnO (0001) surface at a tilted angle of about 45°. The signal was collected using an SPEX 750M monochromator and amplified through standard lock-in techniques.

Figure 1 shows a representative low-temperature emission spectrum of the ZnO sample with Zn-terminated surface. The strongest peak is at ∼3.361 eV (369 nm), which is marked as 0. This peak is the zero phonon line (ZPL) of the neutral-donor-bound excitons (usually called I_2 line)[6,7]. The full-width at half-maximum (FWHM) of the ZPL is only about 3 meV, indicating the high quality of this ZnO sample. From the emission spectrum in Fig. 1, the first- and second-phonon Stokes lines (SLs) of donor-bound excitons, which are denoted as −1 and −2, respectively, are clearly observed. These lines represent the optical processes in which one and two LO phonons are created, respectively, and accompany the corresponding photon generations. The energy separation between any two adjacent SLs including the ZPL line remains at a constant value of ∼71 meV. This value is almost identical to the characteristic energy (574.1 cm^{-1} or 71.2 meV) of the A_1-LO mode of ZnO indicated by the Raman scattering spectrum shown in Fig. 2.

Figure 1 also shows that there is an additional group of emission lines appearing at the lower energy side of the ZPL; these are marked as two-electron satellite (TES) transition (3.324 eV or 373 nm), TES-1LO (3.253 eV or 381 nm), and TES-2LO (3.184 eV or 389 nm), respectively. From their energetic positions and relative intensities with respect to the ZPL line, this additional group of lines can be attributed to the TES of neutral-donor-bound excitons and their phonon replicas[8,9]. Under effective mass approximation, the donor binding energies can be determined by $\Delta E = \frac{3}{4}E_D$ from the energy difference ΔE between the ground state (1s) and the first excited state (2s). From the energy difference between the ZPL and TES, the donor binding energy E_D can be determined as 49.3 meV.

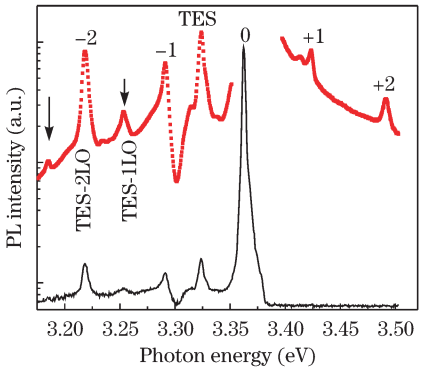

Fig. 1. Representative low-temperature PL spectrum of the exciton-phonon-electron coupling system in logarithmic scale measured in ZnO at 5 K. Enlarged spectra are shown by dashed lines. A series of LO phonon sidebands including ASLs and TES, as well as their phonon replicas, is clearly observed. Note the characteristic asymmetric lineshape of the first-order phonon sideband.

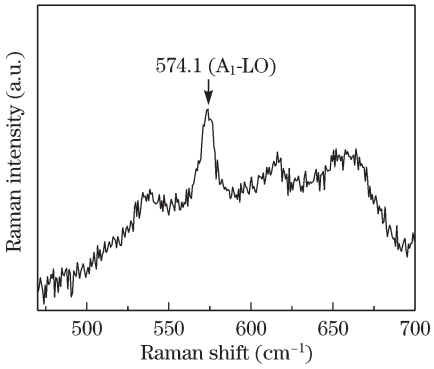

Fig. 2. Measured Raman scattering spectrum of ZnO at room temperature. The A_1-LO peak at 574.1 cm^{-1} is well resolved.

In addition to the SLs, the anti-Stokes lines (ASLs) at 3.413, 3.423, and 3.491 eV are also observed at the higher energy side of the ZPL. The first- and second-order ASLs are marked as +1 and +2, respectively. The first-order ASL is a double structure with energy splitting of about 10 meV. The peak at 3.413 eV may originate from the coupling of excitons with the donor electrons. The energy separations between the ASL and ZPL are noticeably smaller than those between the corresponding SL and ZPL. Hence, the ASL and corresponding SL are not mirror symmetric with respect to the ZPL.

The first-order phonon SL exhibits a distinct asymmetric lineshape as shown in Fig. 1; a clear dip is visible at the higher energy side. In addition to its distinct asymmetric lineshape, the intensity of the first-order phonon SL (marked −1) is weaker than that of the second-order phonon SL (marked −2), which is an unusual phenomenon in semiconductors, such as ZnO whose Huang-Rhys factor is much less than unity. These inconsistencies strongly suggest that a quantum mechanical interference occurs in the LO phonon-assisted transitions of neutral-donor-bound excitons.

In conclusion, we report on a PL observation of robust excitonic polarons due to the resonant coupling of donor-bound excitons and LO phonons in high-quality ZnO crystals. At low temperatures, the resonant coupling of excitons with LO phonons leads to not only a set of SLs but also up to second-order ASLs. Moreover, the energetic positions of ASLs and corresponding SLs are not mirror symmetric with respect to the ZPL. In addition, characteristic TES and their phonon replicas are observed in the spectra. From the energy difference between the ZPL and TES, the donor binding energy E_D can be determined as 49.3 meV. The first-order SL also exhibits a distinct asymmetric lineshape, suggesting quantum mechanical interference during the annihilation of donor-bound excitons. These findings lead to new insights into the fundamental effects of exciton-phonon-electron interactions in semiconductors.

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