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## Observation of numerous $E_2$ mode phonon replicas in the room temperature photoluminescence spectra of ZnO nanowires: Evidence of strong deformation potential electron-phonon coupling

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The authors report the observation of numerous ( $>20$ ) phonon replica peaks in the room temperature photoluminescence spectrum of ZnO nanowires embedded in 50 nm diameter pores of an anodic alumina film. The peaks are spaced in energy by  $\sim 54$  meV, which is the energy of a nonpolar phonon with symmetry  $E_2$  in ZnO. These peaks are possibly caused by resonant phonon-assisted decay of photoexcited electrons to an impurity band, followed by radiative recombination. These results suggest that even though ZnO is strongly polar, deformation potential coupling to a nonpolar phonon mode may be stronger than Fröhlich coupling to polar phonon modes. © 2006 American Institute of Physics. [DOI: [10.1063/1.2360255](https://doi.org/10.1063/1.2360255)]

Zinc oxide (ZnO) nanostructures have attracted significant attention because of their possible applications in short wavelength electro-optical devices, lasers, field emitters, piezoelectric devices, solar cells, and gas sensors. The optical properties of ZnO have been studied widely, but mostly in bulk material<sup>1–8</sup> with few studies focused on nanostructures.<sup>9–15</sup> While the photoluminescence (PL) spectra of bulk materials often show a few ( $\sim 4$ ) phonon replicas,<sup>8</sup> the PL spectra of nanostructures typically do not reveal phonon replicas because of poor material quality, surface states, and/or structural defects. The PL spectra of ZnO nanostructures usually consist of two dominant bands:<sup>10,13,14</sup> a low frequency (green) band associated with emissions from deep levels caused by structural defects and a high frequency (ultraviolet) band associated with exciton recombination.

In this letter, we report the observation of numerous phonon replicas in the PL spectra of ZnO nanowires at room temperature. We have observed at least 20 phonon replicas and there are possibly many more which could not be captured because of the finite bandwidth of our charge coupled device (CCD) detector.

The ZnO nanowires were prepared as follows. A 99.997% pure Al foil was degreased and electropolished in a solution of perchloric acid, butyl cellulosolve, ethanol, and distilled water to produce a mirrorlike surface.<sup>16</sup> This film was then washed in distilled water, air dried, and anodized in 3% oxalic acid at room temperature using a constant anodizing voltage of 40 V. The anodization was carried out for several hours to form a thick porous alumina film on the surface. This film was stripped off in hot chromic/phosphoric acid and the anodization repeated again for 5 min to form another porous alumina film of thickness less than 1  $\mu\text{m}$ . The two-step anodization process<sup>17</sup> yielded an anodic alumina film with a well ordered array of 50 nm diameter pores.

The pores were then selectively filled up with Zn using ac electrodeposition in a nonaqueous solution. The solution consisted of  $\text{ZnClO}_4$  (10.5 g),  $\text{LiClO}_4$  (2.5 g), and dimethyl sulfoxide (250 ml). The porous film was immersed in the solution and an ac potential of 25 V rms and frequency of 250 Hz was imposed between the aluminum substrate and a graphite counter electrode. The temperature was maintained at 75 °C. During the negative cycle of the ac voltage, the  $\text{Zn}^{++}$  ions in solution were reduced to zero-valent Zn atoms which were selectively electrodeposited within the pores since they offered the least impedance path for the ac (displacement) current to flow. During the positive ac cycle, the Zn atoms were not oxidized back to  $\text{Zn}^{++}$  ions since alumina is a valve metal oxide. Metallic Zn within the pores was then oxidized to ZnO by immersion in  $\text{H}_2\text{O}_2$  at room temperature for 5 h. This method is slightly different from the technique employed in Ref. 14. A transmission electron microscope image of an isolated ZnO nanowire synthesized by our technique can be viewed in Ref. 18. The lengths of the nanowires vary because of the electrodeposition process; however, the typical length is between 0.5 and 0.8  $\mu\text{m}$ , while the diameter is 50 nm.

For PL measurement, the samples were excited by coupling a 50 mW HeCd laser emitting at 325 nm to a UV-LabRamHR micro-PL/Raman system from Jobin-Yvon and the luminescence detected with a  $\text{LN}_2$  cooled CCD detector. The spot size of the exciting beam was 10  $\mu\text{m}$  in diameter and the excitation beam was normally incident on the sample surface. The small spot size revealed that there is significant inhomogeneity in the samples on the size scale of 10  $\mu\text{m}$ . Some regions of the sample do not luminesce well and do not show any phonon replicas, while some other regions luminesce brightly and show numerous phonon replicas. We believe that this inhomogeneity accrues from the randomness of interface states and defects. Some regions have more interface states and defects that provide a route for nonradiative recombination of photoexcited carriers, which quench the PL, while other regions are relatively defect-free and

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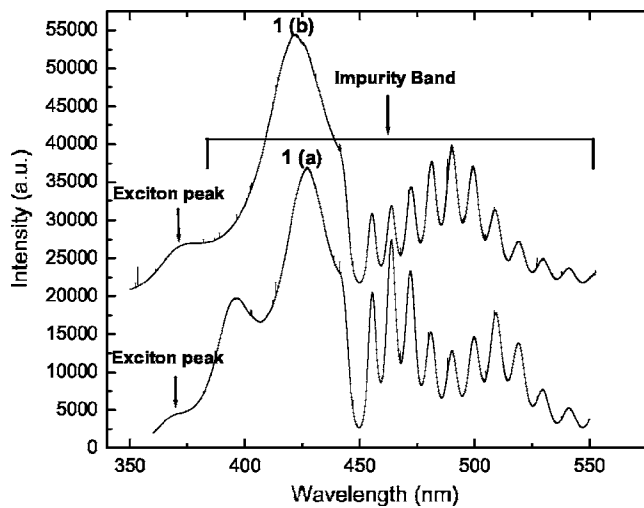


FIG. 1. PL spectra of ZnO nanowires showing numerous phonon replica peaks. The energy separation between neighboring peaks is 54 meV which corresponds to the nonpolar high frequency  $E_2$  phonon in ZnO. Different peaks are labeled to elucidate their origin. The spectra from two different samples are shown. The broad dominant peak is due to  $F^+$  centers in alumina. The excitation spot size is 10  $\mu\text{m}$ .

show bright PL. If we use a large spot size (2 mm) to illuminate the sample, then we do not observe the phonon replicas because of ensemble averaging over many regions that are highly defective. In Figs. 1(a) and 1(b), we show the PL spectra of two samples collected from  $\sim 10 \mu\text{m}$  regions that show bright luminescence and phonon replicas.

The PL spectra in Fig. 1 show a high frequency peak centered at 370 nm wavelength (energy=3.31 eV) which is about 60 meV below the room temperature band gap of bulk ZnO (3.37 eV).<sup>19</sup> Our samples are too large for any significant blueshift of the band edge due to quantum confinement. Since the free exciton binding energy in ZnO is  $\sim 60 \text{ meV}$ ,<sup>20</sup> we can assign this peak to free exciton recombination. Thus, the dominant PL mechanism at this wavelength is *free* exciton recombination. This result is in contrast to Ref. <sup>21</sup> which found that in ZnO quantum dots (as opposed to nanowires), the dominant PL peak is due to acceptor-bound exciton recombination at all temperatures from 8.5 to 300 K. That fact that we see free exciton recombination attests to the relatively high quality of these nanowires.

There is a broader peak centered at a wavelength of 430 nm. This peak, which has the highest intensity, is not related to ZnO, but is due to optical transitions in singly ionized oxygen vacancies ( $F^+$  centers) in the alumina host,<sup>22,23</sup> and its origin has been confirmed by electron paramagnetic resonance measurements in the past.<sup>23</sup> Unfortunately, this peak masks some of the phonon replicas.

The phonon replicas, however, are easily discernible. The associated peaks are equally spaced in energy with an interval of 54 meV. ZnO has a number of phonon modes. Because bulk ZnO typically has a wurtzite crystal structure, the frequencies of both longitudinal optical (LO) and transverse optical phonon modes are split into two frequencies with symmetries  $A_1$  and  $E_1$ .<sup>24</sup> In addition, there are two nonpolar phonons with symmetry  $E_2$ . The low frequency  $E_2$  mode is associated with vibrations of the Zn sublattice and the high frequency  $E_2$  mode is caused by vibration of oxygen atoms.

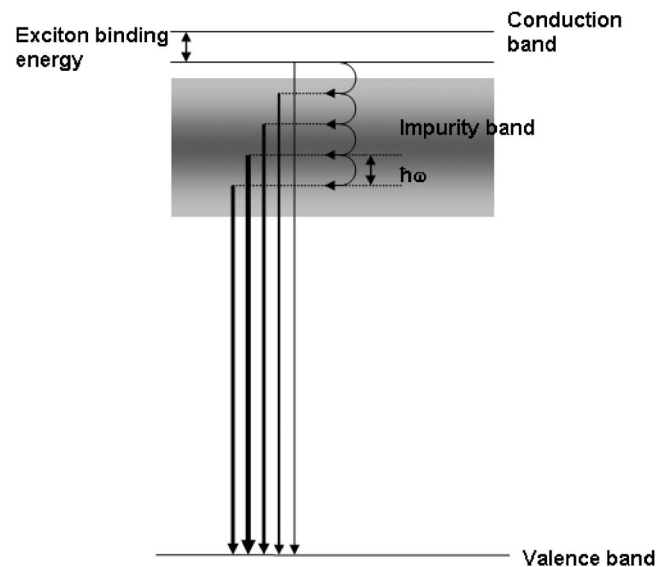


FIG. 2. Energy diagram explaining why the  $n$ -phonon peak can be more intense than the zero-phonon peak. The quantity  $\hbar\omega$  is the energy of the  $E_2$  phonon. The vertical straight arrows indicate radiative recombination processes and the curved arrows indicate nonradiative phonon-assisted decay. The thicknesses of the straight arrows correlate with the efficiencies of the corresponding radiative recombination process.

The high frequency  $E_2$  phonon has an energy of 54 meV (Ref. <sup>24</sup>) which matches the energy spacing between the peaks we observe. Therefore, we ascribe the phonon replicas to transitions involving this phonon. Normally, one observes phonon replicas associated with polar LO phonons in ZnO.<sup>7-9</sup> Phonon replicas associated with the nonpolar  $E_2$  phonon have never been observed before, and no observation of phonon replicas seems to have been reported in ZnO nanostructures.

Phonon replicas appear in PL spectra when photogenerated electrons and holes (or excitons) recombine by simultaneous emission of phonons and photons. The excited electron first emits one or more phonons to decay to a lower energy level, and from there it emits a photon to decay to the valence band and recombine with a hole. The initial phonon emissions require that the electrons couple strongly with phonons. Since ZnO is a polar material, we expect the Fröhlich coupling with polar LO phonons to be particularly strong. However, we find that at least in the nanowires, the photogenerated carriers interact more strongly with the nonpolar  $E_2$  phonon via deformation potential coupling. This is a surprising result that needs further theoretical exposition.

The data in Fig. 1 also show that the  $n$ -phonon peak ( $n \neq 0$ ) is more intense than the zero-phonon peak. One possible explanation for this odd behavior is a resonance effect. Resonant enhancement of phonon replicas has been observed before in quantum dots.<sup>25-29</sup> It is possible that the deep levels in the ZnO nanowires, which are responsible for the green emission band,<sup>10,13,14</sup> merge to form an impurity band in the band gap. The electron first decays nonradiatively to this band by emitting one or more  $E_2$  phonons and then decays to the valence band radiatively to recombine with a hole. If the efficiency of radiative recombination from certain states in the impurity band exceeds that of the direct exciton recombination, then we will expect the  $n$ -phonon peak ( $n \neq 0$ ) associated with these "high efficiency states" to be more in-

tense than the zero-phonon peak. This situation is illustrated in Fig. 2.

In conclusion, we have observed numerous phonon replicas in the PL spectrum of ZnO nanowires, which are associated with the high frequency nonpolar  $E_2$  phonon mode caused by vibration of oxygen atoms. Our results show that there is strong deformation potential coupling between photoexcited electrons and nonpolar  $E_2$  phonon modes in ZnO nanowires, even though ZnO is a strongly polar material. This is an unusual result that can shed light on the nature of electron-phonon coupling in nanostructures.

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