



In-situ optical transmission electron microscope study of exciton phonon replicas in ZnO nanowires by cathodoluminescence

Shize Yang, Xuezheng Tian, Lifeng Wang, Jiakuo Wei, Kuo Qi, Xiaomin Li, Zhi Xu, Wenlong Wang, Jimin Zhao, Xuedong Bai, and Enge Wang

Citation: *Applied Physics Letters* **105**, 071901 (2014); doi: 10.1063/1.4893444

View online: <http://dx.doi.org/10.1063/1.4893444>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/apl/105/7?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Single-step in-situ synthesis and optical properties of ZnSe nanostructured dielectric nanocomposites](#)
J. Appl. Phys. **115**, 134309 (2014); 10.1063/1.4870292

[Structural recovery of ion implanted ZnO nanowires](#)
J. Appl. Phys. **111**, 083524 (2012); 10.1063/1.4704697

[In situ probing electrical response on bending of ZnO nanowires inside transmission electron microscope](#)
Appl. Phys. Lett. **92**, 213105 (2008); 10.1063/1.2936080

[Free exciton emission and dephasing in individual ZnO nanowires](#)
Appl. Phys. Lett. **91**, 161911 (2007); 10.1063/1.2793178

[Depth-resolved optical studies of excitonic and phonon-assisted transitions in ZnO epilayers](#)
Appl. Phys. Lett. **89**, 201903 (2006); 10.1063/1.2388252



AIP | Journal of
Applied Physics

Journal of Applied Physics is pleased to
announce **André Anders** as its new Editor-in-Chief

In-situ optical transmission electron microscope study of exciton phonon replicas in ZnO nanowires by cathodoluminescence

Shize Yang,^{1,2} Xuezheng Tian,² Lifan Wang,² Jiake Wei,² Kuo Qi,² Xiaomin Li,² Zhi Xu,^{2,a)} Wenlong Wang,² Jimin Zhao,² Xuedong Bai,^{2,a)} and Enge Wang^{1,a)}

¹International Center for Quantum Materials, School of Physics, Peking University and Collaborative Innovation Center of Quantum Matter, Beijing, China

²Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China

(Received 3 June 2014; accepted 5 August 2014; published online 18 August 2014)

The cathodoluminescence spectrum of single zinc oxide (ZnO) nanowires is measured by *in-situ* optical Transmission Electron Microscope. The coupling between exciton and longitudinal optical phonon is studied. The band edge emission varies for different excitation spots. This effect is attributed to the exciton propagation along the *c* axis of the nanowire. Contrary to free exciton emission, the phonon replicas are well confined in ZnO nanowire. They travel along the *c* axis and emit at the end surface. Bending strain increases the relative intensity of second order phonon replicas when excitons travel along the *c*-axis. © 2014 AIP Publishing LLC.

[<http://dx.doi.org/10.1063/1.4893444>]

ZnO is an important II-VI semiconductor material with a large direct band gap (3.37 eV) and large exciton binding energy of 60 meV, which is larger than the thermal activation energy 25 meV. Thus, the excitonic processes can be easily observed even at room temperature.¹ ZnO nanowires can function as fine waveguides,²⁻⁴ nanolasers,^{5,6} optical waveguides,⁷ photodetectors,⁸ and light emitting diodes.⁹ For those optical applications, the coupling between exciton and longitudinal optical phonon (LO) is an important issue.¹⁰⁻¹⁴ The coupling is related to the crystal structure and defect concentration, and is affected by strain.¹⁵⁻¹⁹ Here, we study the coupling effect by room temperature *in-situ* Transmission Electron Microscope (TEM) cathodoluminescence (CL). At different excitation spots, the respective spectra have different shapes. This can be attributed to the exciton phonon coupling when exciton propagates along the nanowire *c* axis. Further experiments show that the free exciton phonon replicas (FX-LO) are well confined in ZnO nanowire. They travel along the *c* axis of the ZnO nanowire and emit at the end surface. Bending strain was applied to the ZnO nanowire by tungsten tip. It was found that bending strain enhances the relative intensity of FX-2LO lines.

Our optical measurement system is based on a home-made *in-situ* optical TEM holder as shown in Figure 1(a). An optical fiber of 2 mm in diameter is mounted on the holder, from which optical signals from the sample can be collected and recorded. The holder is also equipped with a piezo-driven manipulator to control a tungsten tip. The sharp tungsten tip can be used to select and manipulate individual nanowires. A grating monochromator iHR 320 from Horiba Inc. and a liquid nitrogen cooled Charge Coupled Device (CCD) were used to record spectra data. The field emission TEM (JEOL 2010F) operates at 200 keV, and the electron beam was used to excite the materials. ZnO nanowires were grown by a simple chemical vapor deposition (CVD)

method. Carbon and zinc oxide powders were mixed to provide zinc source. Argon was mixed with oxygen as the oxygen source. Silicon dioxide coated with a few nanometers of gold was used as growth substrate and was placed in the center of a quartz tube. The temperature slew rate of the growth area was set at 20 °C/min, and the temperature was kept at 900 °C for 120 min. After the reaction process, white powder appeared on the substrate. The as-grown ZnO nanowires were characterized by field emission scanning electron microscope (FESEM), X-ray diffraction (XRD), and TEM. They have a hexagonal structure JCPDS 36-1451 or JCPDS 65-3411. TEM characterization confirmed that the nanowire grow along the [001] direction or *c*-axis.

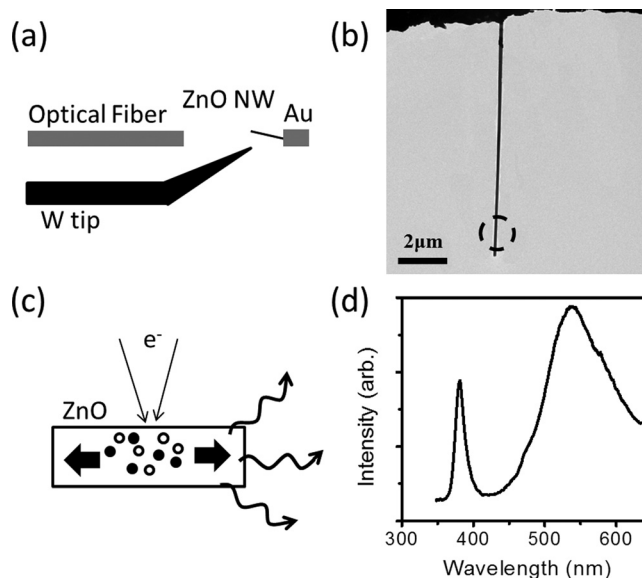


FIG. 1. The experimental setup and a typical CL spectrum. (a) Scheme of the optical TEM holder. (b) TEM image of a single ZnO nanowire, electron beam is focused on the nanowire end to collect the CL spectrum in (d). (c) illustration of the CL spectrum; electrons are irradiated on the ZnO nanowire and electrons and holes are excited, and they propagate along the nanowire and finally emit from the nanowire surface, electrons are represented by black dots and holes are represented by black circles.

^{a)}Authors to whom correspondence should be addressed. Electronic addresses: xuzhi@iphy.ac.cn; xdbai@iphy.ac.cn; and egwang@pku.edu.cn

A typical room temperature CL spectrum of ZnO nanowires is shown in Figure 1(c). The nanowire end surface is set towards the optical fiber. The spectrum has two luminescence regions: one is around 380 nm (3.26 eV), which corresponds to band edge emission; the other is around 530 nm (2.34 eV), which corresponds to intrinsic defects or oxygen vacancies and is referred to as green luminescence. The intensity ratio between band edge emission and green luminescence indicates the defect concentration. The green luminescence in Figure 1(f) has comparable intensity with the band edge emission. This result can be accounted to the side wall surface defects. As earlier experiments found that oxygen defect density is higher on the side walls.²⁰ The near band edge emission comes from the direct recombination of electrons and holes. At low temperatures, the excitonic emission peaks can be clearly distinguished. The spectrum consists of FX, BX, SX,²¹ and their phonon replicas.¹⁵ As temperature increases, the BX and SX gradually diminish. At room temperature, the free exciton emission and its phonon replicas dominate the band edge emission. The reported peak energies are: FX(3.300 eV), FX-1LO (3.249 eV), and FX-2LO (3.180 eV).¹³ The exciton energies can be determined by first principles calculation.¹⁸

We selected a single ZnO nanowire attached to a gold wire as shown in Figure 2(a). The diameter of the nanowire was 165 nm. Electron beam was focused onto three different spots marked as 1, 2, and 3. The measurement condition was kept the same for those spots. Corresponding CL spectrum is shown in Figures 2(b) and 2(d). The scattering of free excitons with LO phonons is determined by the Fröhlich interaction and first order process, such as FX-1LO recombination, are forbidden in perfect structures for parity conservation.¹³ Practical nanowires have defects which introduce alternative parity into the Fröhlich scattering. Thus, FX-1LO peak has a larger intensity for high defect density crystals. The band edge emission from the tip of the nanowire (spot 1) has a

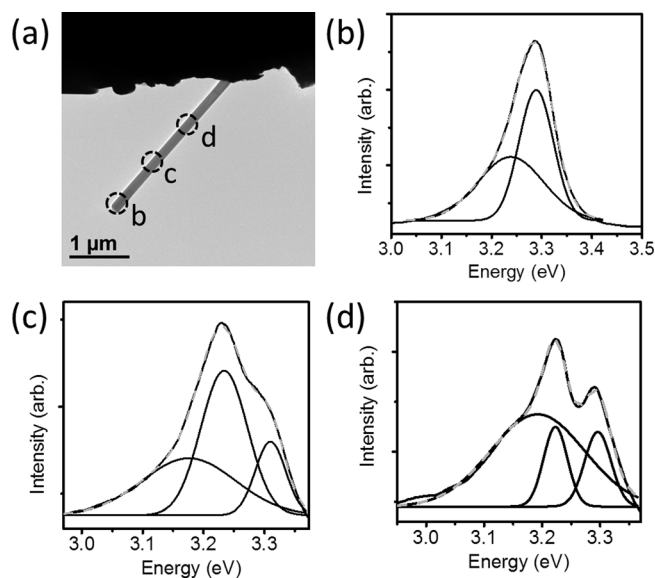


FIG. 2. Observation of exciton peaks of a single ZnO nanowire. (a) A single ZnO nanowire attached to a gold wire, the irradiated segments were denoted by 1, 2, 3; (b)–(d) shows the band edge emission spectra corresponding to 1, 2, and 3 in (a), respectively.

TABLE I. Fitted Gauss peaks for CL spectra in Figures 2(b)–2(d).

Peaks	Energy (eV)	FWHM (eV)	Area (Counts)	Relative intensity	Assignment
1-2	3.238	0.154	138.403	0.93	FX-1LO
1-1	3.289	0.081	149.005	1	FX
2-3	3.176	0.181	62.786	0.79	FX-2LO
2-2	3.234	0.090	79.867	1	FX-1LO
2-1	3.310	0.059	26.307	0.33	FX
3-3	3.192	0.191	187.500	1	FX-2LO
3-2	3.223	0.048	41.127	0.22	FX-1LO
3-1	3.296	0.054	42.922	0.23	FX

large FX-1LO intensity. The intensity ratio of FX-1LO to FX is nearly 1:1. Surface defects contributed to the strong FX-1LO line.

From the tip to the base of the ZnO nanowire, the edge emission spectra changed a lot, from one peak at the tip to two peaks at the base. The CL spectra measured are fitted with gauss peaks and the fitted parameters are listed in Table I. From the table we can see that, the relative intensity of FX is gradually reduced from the tip to base. The relative peak amplitudes (relative amplitudes normalized to the largest value) for spot 2 are: FX 0.33, FX-1LO 1, and FX-2LO 0.79. For spot 3, the relative peak amplitudes are: FX 0.23, FX-1LO 0.22, and FX-2LO 1. The FX-1LO peak from spot 3 has a very small FWHM of 48 meV and thus the CL spectrum from spot 3 has distinguished peak features. The increase in phonon replica intensities can be attributed to the propagation of excitons. At the spot of electron irradiation, free

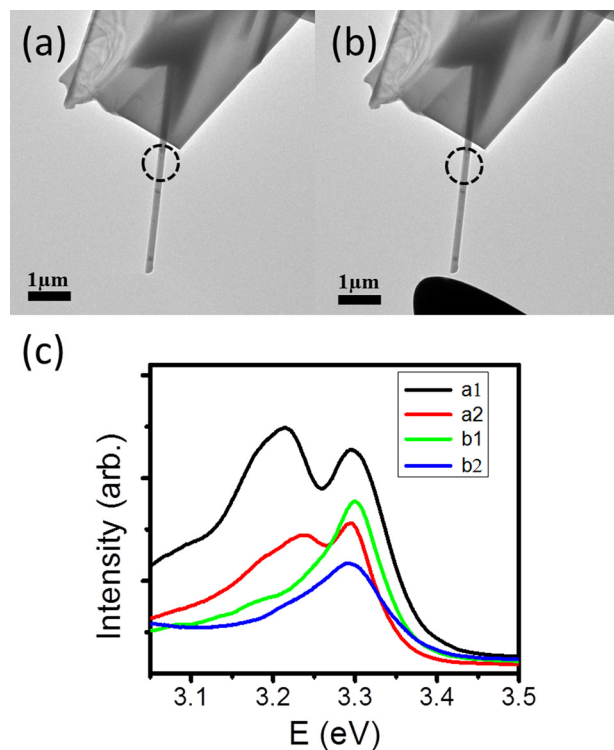


FIG. 3. Control experiments on the exciton peaks. (a) a single ZnO connected to ZnO sheets. (b) the ZnO was blocked by a tungsten tip. (c) CL spectrum measured with configurations in for two times denoted as 1 and 2, from the dashed circle area in (a) and (b).

excitons are generated. They can travel along the nanowire axis or radially towards the side surface. The excitons that travel along the *c* axis gradually couple with phonons. They eventually emit at the end surface with a loss of energy.

To confirm the directional coupling of exciton and phonon, we carried out experiments in which the tip of the nanowire was blocked by a large tungsten tip. The tungsten tip was set 100 nm apart from the end surface of the nanowire and the blocking segment had a diameter of 1.1 μm . Thus, light emitted from the nanowire end surface within a cone of semi-angle of 79° was blocked. The experimental configuration is shown in Figures 3(a) and 3(b). The corresponding CL spectra are shown in Figure 3(c). With tungsten tip blocking, the FX emission around 3.3 eV decreases a little, while the phonon replicas decrease a lot. This phenomenon indicates that the FX either emits from the end surface with a large angle or emits from the side surfaces. However, the FX phonon replicas are well confined and mainly emit from the end surface at small angles. Due to the one-dimensional confinement, the LO phonon has a very large wave vector along the *c* axis of the nanowire.^{22,23} Thus, FX phonon replicas are effectively confined to propagate along the *c* axis, resulting in the great diminish of phonon replicas with blocking.

The strain effects on the exciton phonon coupling were further studied. A tungsten tip was used to apply strain to the nanowire. No strain was applied as shown in Figure 4(a). Then, the tungsten tip was moved to contact the nanowire side wall to apply a small strain, Figure 4(b). Larger bending

strain was applied in Figure 4(c). Their corresponding CL spectra are shown in Figure 4(d). With increasing bending strain, the relative intensity of FX-2LO emission line gradually increases. The FX emission is suppressed probably due to the bending-induced defects or traps. The nanowire has compressive strain on the inner side of the bending part and tensile strain on the outer side. Excitons travel through the bending part to emit at the end surface. The bending strain enhanced the electron phonon coupling when exciton propagates along the *c* axis. Both the tensile and compressive strain might account for the enhancement of exciton phonon coupling. Further study is needed to clarify the detailed mechanism. In a previous study,¹⁸ theoretical methods were used to simulate the strain effect on the exciton dynamics along the axial direction. Theoretical calculation might be further developed to explain the coupling between propagating excitons and phonons.

In summary, we have investigated the CL spectra of single ZnO nanowires at room temperature in an *in-situ* optical TEM. The free exciton emission and its phonon replicas have been measured. The excitonic peak intensities change with different excitation spots. This is attributed to the exciton propagation along the *c* axis of the nanowire. The free exciton emission phonon replicas are effectively confined to propagate along the *c*-axis of ZnO nanowire and emit at the nanowire endpoint. Bending strain enhances exciton-phonon coupling when excitons move along the *c*-axis. New challenges are posed to computational chemistry as how to simulate the dynamics processes involving the coupling of propagating excitons and phonons. These results are helpful for design of optoelectronic devices with ZnO nanowires.

This work was supported by the National 973 Program (Grant Nos. 2012CB933003 and 2013CB93201), Collaborative Innovation Center of Quantum Matter, Natural Science Foundation (Grant No. 51172273), and Strategic Priority Research Program B of the Chinese Academy of Sciences (Grant No. XDB07030100) of China.

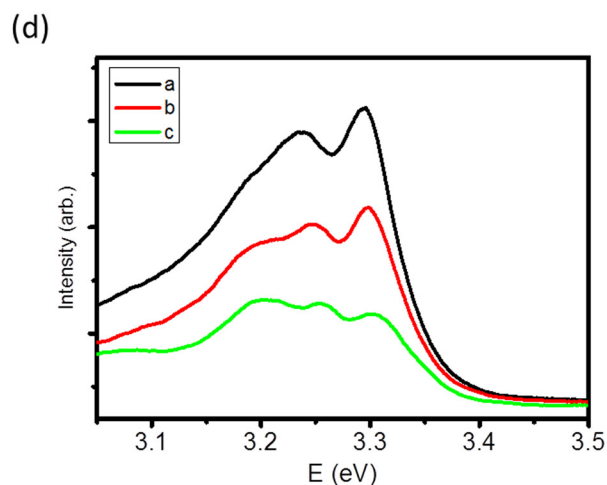
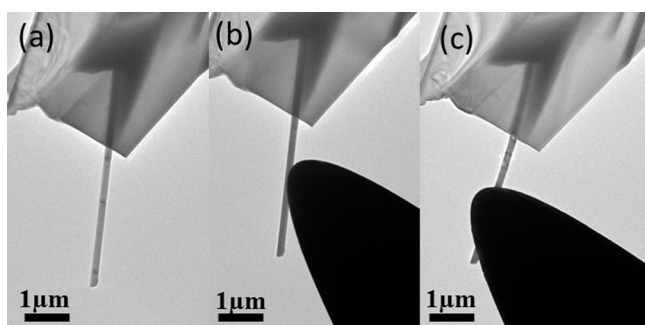


FIG. 4. Strain effects on the bandedge emission. (a) Original configuration without strain. (b) Strain applied by a tungsten tip. (c) Larger strain applied by moving the tungsten tip. (d) CL spectra measured for configurations of (a)–(c).

¹W. I. Park, Y. H. Jun, S. W. Jung, and G.-C. Yi, *Appl. Phys. Lett.* **82**(6), 964 (2003).

²M. Law, D. J. Sirbuly, J. C. Johnson, J. Goldberger, R. J. Saykally, and P. Yang, *Science* **305**(5688), 1269 (2004).

³W. Li, M. Gao, X. Zhang, D. Liu, L.-M. Peng, and S. Xie, *Appl. Phys. Lett.* **95**(17), 173109 (2009).

⁴W. L. Li, M. Gao, R. Cheng, X. X. Zhang, S. S. Xie, and L. M. Peng, *Appl. Phys. Lett.* **93**(2), 023117 (2008).

⁵D. Vanmaekelbergh and L. K. v. Vugt, *Nanoscale* **3**(7), 2783 (2011).

⁶M. H. Huang, S. Mao, H. Feick, H. Yan, Y. Wu, H. Kind, E. Weber, R. Russo, and P. Yang, *Science* **292**(5523), 1897 (2001).

⁷R. Yan, D. Gargas, and P. Yang, *Nat. Photonics* **3**(10), 569 (2009).

⁸H. Kind, H. Yan, B. Messer, M. Law, and P. Yang, *Adv. Mater.* **14**(2), 158 (2002).

⁹M. A. Zimmler, T. Voss, C. Ronning, and F. Capasso, *Appl. Phys. Lett.* **94**(24), 241120 (2009).

¹⁰Y. Bin, C. Rui, Z. Weiwei, Z. Jixuan, S. Handong, G. Hao, and Y. Ting, *Nanotechnology* **21**(44), 445706 (2010).

¹¹M. Gao, R. Cheng, W. Li, Y. Li, X. Zhang, and S. Xie, *J. Phys. Chem. C* **114**(25), 11081 (2010).

¹²C. H. Ahn, S. K. Mohanta, N. E. Lee, and H. K. Cho, *Appl. Phys. Lett.* **94**(26), 261904 (2009).

¹³T. Voss, C. Bekeny, L. Wischmeier, H. Gafsi, S. Börner, W. Schade, A. C. Mofor, A. Bakin, and A. Waag, *Appl. Phys. Lett.* **89**(18), 182107 (2006).

- ¹⁴H. C. Hsu and W. F. Hsieh, *Solid State Commun.* **131**(6), 371 (2004).
- ¹⁵Z.-M. Liao, H.-C. Wu, Q. Fu, X. Fu, X. Zhu, J. Xu, I. V. Shvets, Z. Zhang, W. Guo, and Y. L.-Wang, *Sci. Rep.* **2**, 452 (2012).
- ¹⁶L. Sun, D. H. Kim, K. H. Oh, and R. Agarwal, *Nano Lett.* **13**(8), 3836 (2013).
- ¹⁷X. Fu, G. Jacopin, M. Shahmohammadi, R. Liu, M. Benameur, J.-D. Ganière, J. Feng, W. Guo, Z.-M. Liao, and B. Deveaud, *ACS Nano* **8**(4), 3412 (2014).
- ¹⁸X. Fu, C. Su, Q. Fu, X. Zhu, R. Zhu, C. Liu, Z. Liao, J. Xu, W. Guo, J. Feng, J. Li, and D. Yu, *Adv. Mater.* **26**(16), 2572 (2014).
- ¹⁹X.-W. Fu, Q. Fu, L.-Z. Kou, X.-L. Zhu, R. Zhu, J. Xu, Z.-M. Liao, Q. Zhao, W.-L. Guo, and D.-P. Yu, *Front. Physiol.* **8**(5), 509 (2013).
- ²⁰M. Foley, C. T.-That, and M. R. Phillips, *Appl. Phys. Lett.* **93**(24), 243104 (2008).
- ²¹L. Wischmeier, T. Voss, I. Rückmann, J. Gutowski, A. C. Mofor, A. Bakin, and A. Waag, *Phys. Rev. B* **74**(19), 195333 (2006).
- ²²L. K. v. Vugt, S. Rühle, P. Ravindran, H. C. Gerritsen, L. Kuipers, and D. Vanmaekelbergh, *Phys. Rev. Lett.* **97**(14), 147401 (2006).
- ²³S. Rühle, L. K. van Vugt, H. Y. Li, N. A. Keizer, L. Kuipers, and D. Vanmaekelbergh, *Nano Lett.* **8**(1), 119 (2008).