

Photoluminescence polarization in individual CdSe nanowires

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The polarization of the photoluminescence (PL) spectra of individual CdSe nanowires grown parallel and perpendicular to the c axes of the wurtzite structure was studied. Both the excitation and emission of the nanowires show strong polarization dependence. Maximum PL intensity is obtained when the excitation field polarizes parallel to the long axes of the nanowires, regardless of their growth directions. The emission polarization of the nanowires also does not depend on the growth direction, but is mainly determined by the elongated shape of the nanowires. The origin of the polarization is considered mainly a result of the large contrast in dielectric constants between the CdSe nanowires and their surroundings, while the contribution from the symmetry of the crystal structure is negligible.

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One-dimensional (1D) nanoscale semiconductors, i.e., nanowires and nanorods, have been subjects of intensive research since Ijima discovered carbon nanotubes.¹ What motivates the research is the unique properties proposed or demonstrated in these kinds of materials, such as high emission efficiency,² supermechanical toughness,³ low lasing threshold,⁴ etc. CdSe nanowires have been prepared in a variety of approaches, such as template-assisted routes,^{5,6} thermal evaporation,⁷ metalorganic chemical vapor deposition (MOCVD),⁸ and solvothermal technique.⁹

While photoluminescence (PL) measurements are often employed to study the electronic transitions of semiconductors, polarized spectra, which are capable of providing additional information, are less used. Polarized light emission or absorption is closely related to the symmetry of the wave functions.¹⁰ Wurtzite CdSe is optically uniaxial, and a number of papers have demonstrated obtaining strong polarized spectra from spherical nanocrystals and prolonged quantum rods (generally several tens of nanometers or less in dimension) of CdSe.^{11–16} As for the polarization study on 1D nanowires of larger size (usually tens of nanometers in width and several micrometers in length), some reports can be found.^{17–23} However, most of them focused on cubic structured materials.^{18–21} Studies on the PL polarization in wurtzite-structured nanowires are very few, to the best of our knowledge.^{17,22,23} The polarization in cubic nanowires is usually attributed to the result from the difference in dielectric constants between the nanowires and the surrounding media.^{19,20} According to the classical electromagnetic theory, for electric fields perpendicular to the axis of an isotropic cylindrical nanowire, whose diameter is much smaller than the wavelength of light, the internal field is attenuated by a factor $2/(\epsilon+1)$ from the external electric field, where ϵ is the dielectric constant of the cylinder relative to its surrounding medium, while for electric fields parallel to the cylinder, the internal field remains the same as the external field.²⁴ As a result, the polarized PL along the long axes direction is stronger than that along the short axes of the nanowires. For the PL polarization in wurtzite-structured nanowires, Venugopal *et al.* found that the PL intensity reaches its maximum when the exciting field is perpendicular to the long axis (also the c axis) of CdSe nanobelts. They thought that the selection rules in the wurtzite structure are the cause of the polarization.²² Qi *et al.* also found in rod-shaped CdS quantum dot (QD)

ensembles that maximum PL intensity was obtained when the exciting light polarizes perpendicular to the long axis (also the c axis of the ensemble).²⁵ According to the selection rules, when the exciting light is polarized perpendicular to the c axis of wurtzite structures, both A and B excitons contribute to the PL; when it is parallel, only the B excitons contribute.²⁶ Efros has studied theoretically that the selective recombination can lead to polarization in wurtzite CdSe microcrystals.²⁷ However, Hsu *et al.* stated that the intensity of the band-edge emission of ZnO nanorods reaches its minimum when the exciting light is polarized perpendicular to the long axis (also the c axis), and reaches its maximum when parallel.²³ Their observations are totally different from what was observed in the above-mentioned CdS QD ensembles and CdSe nanobelts, although they are all wurtzite in structure. They thought the polarization in their case may come from the dipole transition as observed in quantum rods.²³ However, the dipole transition usually plays a significant role in very small-sized system, while their ZnO nanorods are 80–120 nm and 10–20 μm in length, which is well beyond the quantum confinement region. Since the wurtzite structures are intrinsically uniaxial, the polarization mechanism of PL in this structure is more complicated than that in zinc-blende systems. To explore the real origin of the polarization in wurtzite-structured nanowires and resolve the controversial observations mentioned above, polarization study on wurtzite-structured nanowires growing along a direction other than c axis is necessary.

In this paper, we present our studies on the PL polarization of individual wurtzite CdSe nanowires. We found that the CdSe nanowires, whether grown along or perpendicular to the c axes of wurtzite structure, show strong PL polarization, and that the excitation/emission of the nanowires exhibits maximum intensity when the exciting/emission E field polarizes parallel to the long axis of the nanowire, regardless of the direction of its c axis. We conclude the dielectric contrast and the elongated shape of the nanowires play the dominating role in determining the polarization of our CdSe nanowires, while their crystallographic growth direction plays a negligible role.

The preparation of the CdSe nanowires was carried out on GaAs(100) and (111) B substrates in an MOCVD system employing sputtered Au as a catalyst.²⁸ The growth temperature was maintained at 500 °C, and pressure at 500 Torr. The

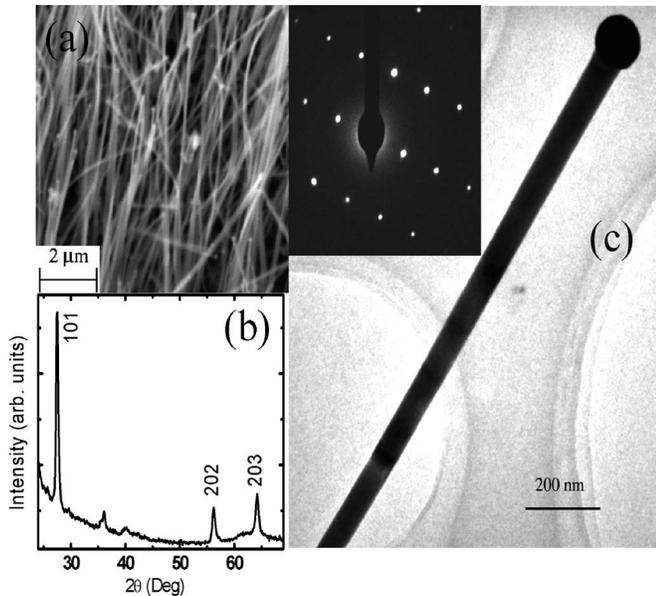


FIG. 1. (a) SEM image of the as-synthesized CdSe nanowires, (b) XRD pattern of the nanowires, revealing their wurtzite structure; (c) TEM image of an individual nanowires; the inset shows the electron-diffraction pattern of the nanowires.

morphology of the nanowires was characterized by a scanning electron microscope (SEM, LEO 1450VP). The structure and growth direction of the nanowires were determined by transmission electron microscopy (TEM Philips C120 and Tecnai 20, FEG). For PL analysis, a Renishaw 1000B micro-PL spectrometer was employed to collect the signals, and the 514.5 nm line of an Ar⁺ laser was used as the excitation source. To obtain the PL signals from individual nanowires, some of the as-grown nanowires were transferred to a Si wafer. The low density of the transferred nanowires and the high magnification microscope (50×) attached to the spectrometer ensure single-wire emissions were measured. A half-wave plate was used to rotate the polarization direction of the exciting laser, and the emitted light passes through a polarization analyzer before entering the spectrometer.

Figure 1(a) shows the SEM image of the as-prepared CdSe nanowires. Many wirelike structures can be seen on the substrate surface, revealing the formation of nanowires. The width of the nanowires is about 70 nm, while their length can reach several tens of micrometers. The XRD pattern of the nanowires was shown in Fig. 1(b), in which the peak at 36.1° is an artifact of the equipment. It is noted that the sample was tilted during the measurement to avoid interference from the diffraction peaks of the GaAs substrate. All the other peaks can be indexed to wurtzite CdSe (JCPDS 77-2307). The TEM image of an individual nanowire shown in Fig. 1(c) indicates that the nanowires have a smooth surface, and are of uniform size along the entire length. The inset in Fig. 1(c) is the electron-diffraction pattern of the nanowire, and this pattern can be indexed to the $[2\bar{1}\bar{1}0]$ zone of wurtzite structure. The clear spotty pattern indicates the single-crystalline nature of the CdSe nanowires.

Figure 2(a) shows a plan-view SEM image of the CdSe nanowires transferred to a bare Si wafer. As is evidenced, the nanowires are well separated on the Si wafer, which ensures

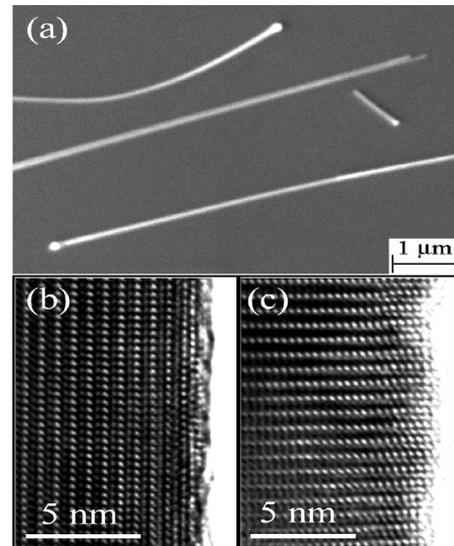


FIG. 2. (a) SEM image of some nanowires transferred to a bare Si wafer. The low density of the transferred nanowires ensures the collection of single-nanowire emission. (b) and (c) show typical high-resolution images of CdSe nanowires grown on GaAs(100) and GaAs(111)B, revealing their growth directions are along $\langle 10\bar{1}0 \rangle$ and $\langle 0001 \rangle$, respectively.

the single-wire emissions were detected during the PL measurements. Figures 2(b) and 2(c) show the lattice images of CdSe nanowires grown on GaAs(100) and GaAs(111)B, and they are both obtained with the electron beam parallel to the $[2\bar{1}\bar{1}0]$ direction of wurtzite structure. We examined about 10 nanowires on each substrate, and found that the nanowires grew exclusively along the $\langle 10\bar{1}0 \rangle$ direction on GaAs(100), and most grew along the $\langle 0001 \rangle$ direction on GaAs(111)B. Xiong *et al.* have also grown wurtzite ZnS nanowires with two orthogonal growth directions by the pulsed laser vaporization method.²⁹ The mechanism for how the substrate affects the growth direction of the nanowires is not clear, but Kuykendall *et al.* found that the growth direction of nanowires can indeed be affected by the substrate orientations, and they thought that the lattice matching between the substrate surface and the growth direction of the nanowires may be the cause.³⁰

Figure 3 shows the excitation polarization dependence of the nanowires, which was obtained by rotating the polarization direction of the exciting field by the half-wave plate. Figures 3(b) and 3(d) show the polarized PL spectra of the nanowires grown along the $\langle 0001 \rangle$ and $\langle 10\bar{1}0 \rangle$ directions, respectively. The spectra are composed of two emission bands, one at about 690 nm and another broad peak at 800–1000 nm. The peak at 690 nm comes from the near-band-edge (NBE) emissions, while the latter comes from deep levels in the nanowires. In this paper, only the polarization dependence of the NBE emissions is studied, while that of the deep-level emission is omitted. It is noted that regardless of their growth directions, the PL of the nanowires reaches maximum intensity when the exciting light field E_{ex} is parallel to the long axes of the nanowires l ($E_{\text{ex}} \parallel l$), and reaches minimum intensity when $E_{\text{ex}} \perp l$. Figures 3(a) and

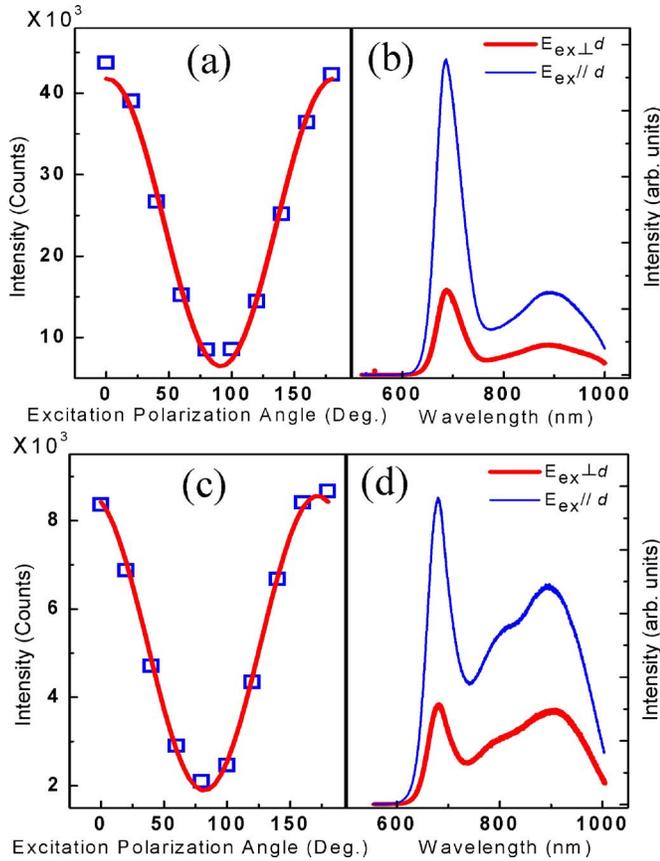


FIG. 3. (Color online) Emission spectroscopy of individual CdSe nanowires as a function of excitation polarization angle; (a) and (c) show room-temperature PL peak intensity dependent on excitation polarization angle of a single nanowire grown along $\langle 0001 \rangle$ and $\langle 10\bar{1}0 \rangle$, respectively. (b) and (d) show the PL spectra obtained with $E_{ex \parallel d}$ and $E_{ex \perp d}$ for nanowires grown along $\langle 0001 \rangle$ and $\langle 10\bar{1}0 \rangle$.

3(c) present the dependence of the peak intensity on the excitation polarization angle for the nanowires grown along the $\langle 0001 \rangle$ and $\langle 10\bar{1}0 \rangle$ directions. Note that $\theta=0$ means the polarization of the excitation light is parallel to the length of the nanowires. The experimental data denoted by the rectangles can be well fitted by a $\cos^2 \theta$ function, shown as the solid line in the figure. The two types of nanowires have the same excitation polarization dependence, despite their different growth directions.

The emission polarization dependence of the CdSe nanowires was shown in Fig. 4, which was obtained by rotating the analyzer in the emission pathway, while maintaining the polarization of the excitation light parallel to the long axis of the nanowire. In Figs. 4(b) and 4(d), we show the PL spectra of individual CdSe nanowires with the emission light field parallel ($E_{em \parallel d}$) and perpendicular ($E_{em \perp d}$) to the long axes of the nanowires. The maximum emission intensity is obtained when $E_{em \parallel d}$ for both types of nanowires. The dependence of the emission intensity on emission polarization angle θ also follows a $\cos^2 \theta$ law, as expected. It is noted that the polarizing effect of the optical elements involved on the polarization measurements of the nanowires can be neglected, since we found it only led to an intensity modulation

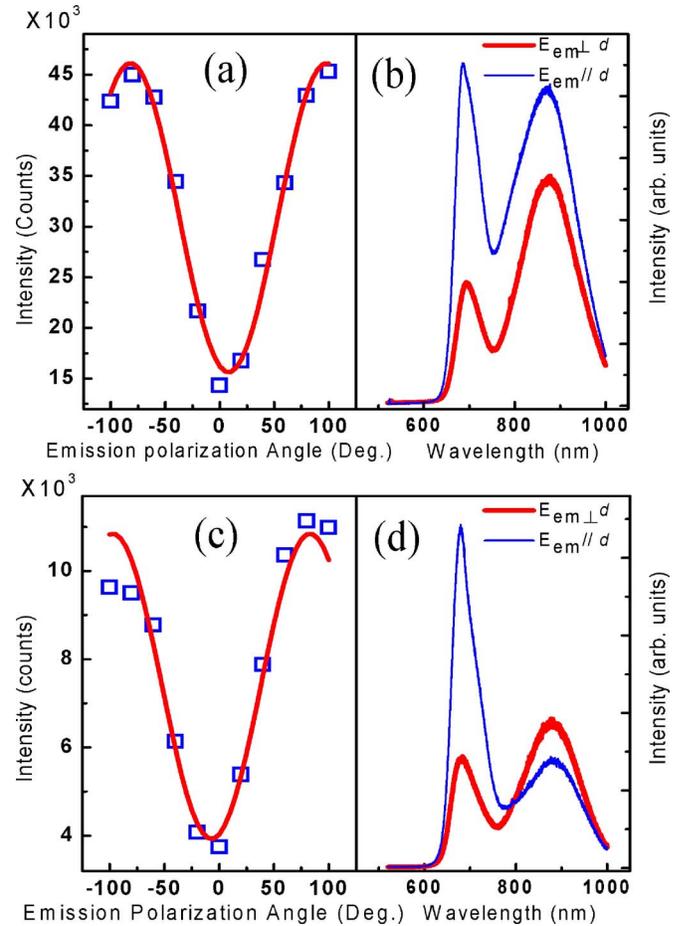


FIG. 4. (Color online) Emission spectroscopy of individual CdSe nanowires as a function of emission polarization angle; (a) and (c) show room-temperature PL peak intensity dependent on emission polarization angle of a single nanowire grown along $\langle 0001 \rangle$ and $\langle 10\bar{1}0 \rangle$, respectively. (b) and (d) show the PL spectra obtained with $E_{em \parallel d}$ and $E_{em \perp d}$ for nanowires grown along $\langle 0001 \rangle$ and $\langle 10\bar{1}0 \rangle$.

of less than about 25% (very small compared to the several-fold changes shown in the spectra) when an unpolarized light source was tested under the same experimental conditions.

As shown in Figs. 3 and 4, both the excitation and emission polarizations affect the PL intensity of the CdSe nanowires. For the excitation polarization-dependent PL spectra, whether the CdSe nanowires were grown along or perpendicular to the c axis, they both have the maximum emission intensity when the polarization of the excitation light is parallel to the length of the nanowire. Similarly, for the emission polarization-dependent PL spectra, they both have maximum emission intensity when the polarization of the emission light is parallel to the length of the nanowire. We have performed the polarization measurements on more than 10 nanowires for each type, and the same conclusion can be drawn. The above phenomena suggest that it is the shape, other than the intrinsic asymmetry of wurtzite lattice structure of CdSe nanowires, that dominates the polarization. This conclusion is corroborated by the results of polarized photoconductivity and PL in many zinc-blende quantum dots or nanowires,^{10,18–21,31,32} which have no intrinsic optical aniso-

tropy. Therefore, just like those observed in InP and Si nanowires,^{19,20} the polarization observed in our experiments mainly comes from the dielectric difference between the nanowires and their surroundings. The reason why our results differ from what was observed in wurtzite CdSe nanobelts in Ref. 22 may lie in the following facts: The length of the nanobelts is ten to hundreds of micrometers, width 0.1–3 μm , and the exciting light is 647 nm. Because both their length and width are comparable to or larger than the exciting wavelength, the light will not be attenuated either parallel or perpendicular to the length of the nanobelts. As a result, just as in bulk materials, only selection rules contribute to the polarization. Therefore, they found the maximum PL intensity when exciting light polarizes perpendicular to the c axes, and minimum when parallel. For the QD ensembles in Ref. 25, their length is 150–200 nm and their width 50 nm. Both dimensions are smaller than the exciting wavelength 354 nm, so the exciting light will be attenuated whether it polarizes parallel or perpendicular to the long axis of the ensembles. As a result, the contribution from the dielectric contrast becomes negligible. For our nanowires, the situations are different. Their width (about 70 nm) is much smaller than the wavelength of the exciting light (514.5 nm) but their length (several micrometers) is larger than the wavelength. Consequently, the light field is attenuated internally when the exciting field is perpendicular to the length of

the nanowires, while it is not when parallel. Consequently, just as those in cubic nanowires, the dielectric contrast dominates the polarization in our case.

In summary, the polarized optical properties of individual CdSe nanowires are studied in a micro-PL system. We performed the measurements on CdSe nanowires grown both along and perpendicular to the c axis of the wurtzite structure. Regardless of the growth direction, the dependence of PL intensity on the polarizations of the excitation and emission field is the same. For unanalyzed emission, maximum PL intensity is obtained when the excitation field polarizes parallel to its length. The emission intensity also reaches its maximum when it is polarized along the length. That is, the polarization of the nanowires is mainly determined by their shape and not any intrinsic asymmetry. We speculate that when the width of the nanowires is increased to a certain value comparable to or larger than the exciting wavelength, the selection rules will dominate the polarization just as in bulk wurtzite materials.

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