

Lack of dependence of the Raman frequency of optical vibrational modes on excitation wavelength in polar nanosemiconductors

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(Received 14 January 2006; accepted 2 July 2006; published online 8 August 2006)

A lack of dependence of the Raman frequency of optical vibrational modes on excitation wavelength in polar nanosemiconductors was observed. This is in contrast to the earlier observed dependence in nonpolar nanomaterials: carbon nanotubes and Si nanowires. This difference has been ascribed to the different crystallographic natures of their Raman spectra: crystalline for nonpolar and amorphous for polar nanosemiconductors. The result has been explored theoretically to the Raman spectra being insensitive to sample sizes and thus indicates that the size confinement effect, a basic effect in nanomaterials, does not exhibit in the optical vibrational modes of polar nanosemiconductors. © 2006 American Institute of Physics. [DOI: 10.1063/1.2335622]

Nanomaterials have promised huge potentials in science and technology. Raman spectroscopy has become one of the preferred choices to characterize and investigate nanomaterials.^{1,2} In conventional Raman spectroscopy, Raman frequency does not shift with excitation wavelength.³ However, this characteristic was found invalid in the optical vibrational modes of nonpolar nanomaterials, which was ascribed to the resonant size selection effect.^{4,5} Thus one expected that the similar phenomenon should be present in other nanomaterials.⁵ We report in this letter a study on the above expectation⁵ in polar nanosemiconductors.

The polar nanosemiconductor samples used were ZnO nanoparticles (NPs),⁶ GaN NPs,⁷ SiC nanorods (NRs),⁸ and CdSe NRs.⁹ Spectral measurements were performed using a Renishaw 1000 Raman microprobe and a Fourier Raman spectrophotometer (RFS) (100/s Bruker NIR-FT spectrophotometer) excited by 325, 488, 515, 633, 785, and 1064 nm lasers at room temperature in the backscattering geometry. The high resolution transmission electron microscope (HRTEM) images were obtained from a Hitachi H-9000NAR transmission electron microscope, with an accelerating voltage of 300 kV.

The HRTEM images in Fig. 1 show that the samples are consisted of a collection of grains with different sizes. The average sizes of the inner crystalline grains are 8, 7, 10, and 4 nm for ZnO NPs, GaN NPs, SiC NRs, and CdSe NRs, respectively. This exhibits that all samples are size-distributed nanomaterials.

The photoluminescence (PL) spectra of the samples were measured (not shown). Figure 2 summarizes the energy regions of optical transition of bulk and nanoscale ZnO, GaN, SiC, and CdSe determined by PL from this work and Refs. 10–17.

The Raman spectra with different excitation wavelengths of the samples are shown in Fig. 3(a). Based on the results

shown in Figs. 1 and 2, the spectra in Fig. 3(a) were confirmed to satisfy the requirement to show the resonant size selection effect. To see the dependence of Raman frequency on excitation wavelength clearly in Fig. 3(a), the fitted Raman frequencies are plotted versus excitation wavelength in Fig. 3(b), in which the lines are drawn to guide the eyes. The largest variation of the fitted frequencies of all bands is less than 2–3 cm⁻¹. Considering that the Raman measurements were performed with two different Raman instruments and with several different excitation wavelengths, these deviations are within measurement accuracy. Moreover, we note that the frequency shift of Si nanowires (NWs) in an excitation energy (wavelength) region of 0.96 eV (488–785 nm) is 17 cm⁻¹.⁵ The frequency shift in Fig. 3, if any, is negligible. Thus, we conclude that the Raman frequencies of optical vibrational modes in polar nano-semiconductors do not shift with excitation wavelength, which is different from the predication.⁵

It is well known that the crystalline or amorphous nature of nanomaterials' Raman spectra can be identified by fitting the spectra calculated by the microcrystal model or the amorphous model, respectively. In the microcrystal model,¹⁸ the Raman intensity, $I(\omega)$, is expressed as

$$I(\omega) = \int \frac{d^3q \cdot |C(0, \mathbf{q})|^2}{[\omega - \omega(\mathbf{q})]^2 + (\Gamma_0/2)^2}, \quad (1)$$

where ω is the Raman frequency, $\omega(\mathbf{q})$ is the phonon dispersion relation, $C(0, \mathbf{q})$ is the weighting function reflecting the contribution of the mode of the \mathbf{q} branch to the total spectrum, and Γ_0 is the Raman linewidth.

In the amorphous model,¹⁹ considering that the crystallite orientations of the samples are random, there is no need to distinguish different polarization. $I(\omega)$ is expressed as

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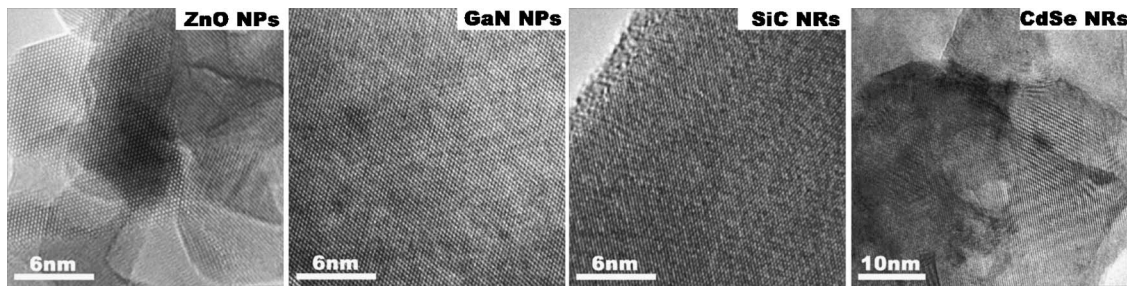


FIG. 1. High-resolution TEM images of ZnO NPs, GaN NPs, SiC NRs, and CdSe NRs.

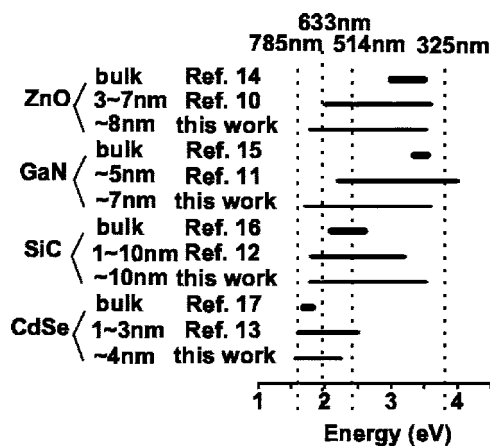


FIG. 2. Energy regions of optical transition of ZnO, GaN, SiC, and CdSe determined by PL from this work (light lines) and Refs. 10–17 for bulk (heavy lines) and nanoscale (thick lines) materials.

$$I(\omega) = \sum_b C_b (1/\omega) [1 + n(\omega)] D_b(\omega), \quad (2)$$

where $D_b(\omega)$ is the vibrational density of states (VDOS) of Raman band b , $n(\omega) = [\exp(h\omega/kT) - 1]^{-1}$ is the population of the vibrational mode at frequency ω and C_b is the weighting factor of the b band. Equation (2) can be rewritten to ease the comparison between calculated and observed spectra as

$$I(\omega)_R = D_w(\omega), \quad (3)$$

where $I(\omega)_R = \omega \times I(\omega) / [1 + n(\omega)]$ is the reduced Raman intensity derived from the observation of $I(\omega)$ and $D_w(\omega) = \sum_b C_b D_b(\omega)$ is the weighted VDOS derived from the calculation of VDOS.

To identify the crystallographic nature of the observed spectra, we took Si NWs and SiC NRs as representatives of nonpolar and polar nanosemiconductors, respectively. In the calculation of the microcrystal model, we adopted the same procedure as Ref. 20 by using dispersion curves in Refs. 21 and 22, respectively.

The VDOS calculations of SiC NRs and Si NWs were carried out by using first-principles method within the framework of density functional theory. In the calculation, Becke's 1988 exchange function and the correlation function²³ of Lee *et al.* were used.²⁴ All of these calculations were completed

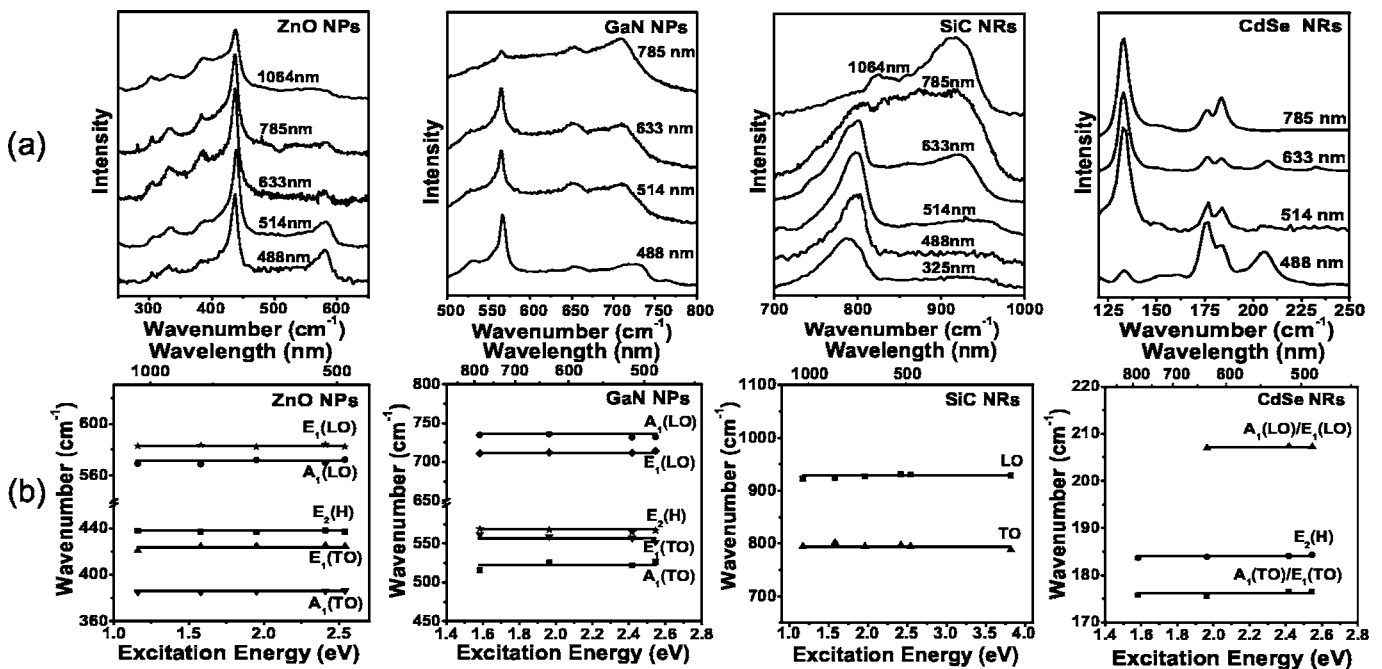


FIG. 3. (a) Raman spectra excited at various wavelengths; (b) dependence of Raman frequency on excitation wavelength/energy for ZnO NPs, GaN NPs, SiC NRs, and CdSe NRs.

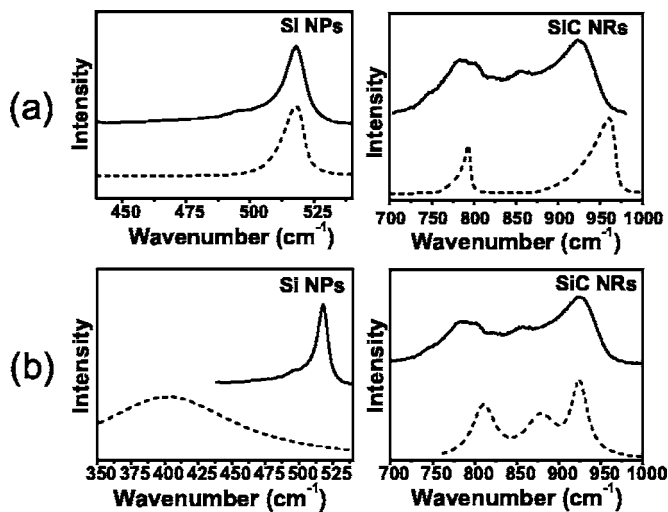


FIG. 4. (a) Observed Raman spectra (solid lines) and calculated Raman spectra by the microcrystal model (dashed lines); (b) reduced Raman spectra (solid lines) and the weighted VDOSs by the amorphous model (dashed lines) for Si nanowires and SiC NRs.

by using the GAUSSIAN 03 program package.²⁵ The VDOSs were decomposed into several bands to match the vibrational bands of corresponding bulk spectra.²⁶ Finally, $D_w(\omega)$ was produced by multiplying coefficient C_b obtained by fitting the reduced spectra.

Figure 4 shows the observed (reduced) and calculated Raman spectra in solid and dashed lines, respectively. Fitting was only good for Si NWs using the microcrystal model and for SiC NRs using the amorphous model. This indicates that the Raman spectra of Si NWs and SiC NRs possess crystalline and amorphous natures, respectively.

We have found that the weighted VDOS of optical modes in SiC NRs is insensitive to sample size.²⁷ To confirm this in other polar semiconductors, the VDOSs were calculated for InSb NPs with 2.10, 3.07, and 4.04 nm. The calculation was done by the molecular-dynamics method modeled by cubic molecular clusters and with universal force field.²⁸ The calculated peak frequencies of optical modes O1 and O2 in VDOS of InSb clusters with various sizes are 150 and 182 cm^{-1} , respectively, as shown in Fig. 5. From Fig. 5, we can see clearly that the VDOS, i.e., the Raman frequency of optical modes, does not change with the size of the cluster.¹⁹

In conclusion, the independence of the Raman frequency of optical vibrational modes on excitation wavelength was observed in polar nanosemiconductors, indicating that, un-

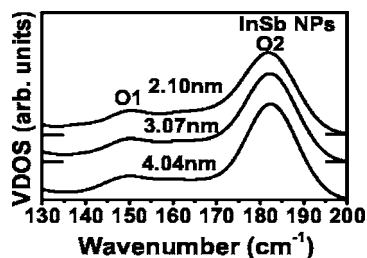


FIG. 5. VDOSs of InSb nanosemiconductors of different sizes calculated by molecular-dynamics method.

like nonpolar nanomaterials, polar nanosemiconductors do not show the resonant size selection effect in the Raman spectra of optical vibrational modes. This difference has been interpreted theoretically to be originated from the different crystallographic natures of their Raman spectra: crystalline for nonpolar and amorphous for polar nanosemiconductors.

The authors acknowledge the support from the NSFC under Grant Nos. 60290083, 50334040, and 50272017, and RGC of Hong Kong under Grant No. 401003, as well as from the State Key Laboratory for Inferred Physics and the Beijing Key Laboratory for Nano-Photonics and Nano-Structure. The author thank the Nano-Chemical Group of Peking University for technical assistance, Shou Shan Fan for providing samples, and K. T. Yue and S. K. Hark for their help in writing.

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