Rapid Communication

Finite size effect on Raman frequency of phonons in nano-semiconductors*

Xia Lei(夏 磊)[a], Zhong Kai(钟 凯)[a], Song Yang(宋 阳)[a], Lu Xin(陆 欣)[a], Xu Lü-Shun(许旅顺)[a], Yan Yan(阎 研)[a], Li Hong-Dong(李红东)[a], Yuan Fang-Li(袁方利)[b], Jiang Jian-Zhong(蒋建中)[c], Yu Da-Peng(俞大鹏)[a], and Zhang Shu-Lin(张树霖)[a]†

[a] *School of Physics, Peking University, Beijing* 100871, *China*

[b] *Institute of Process Engineering, Chinese Academy of Sciences, Beijing* 100080, *China*

[c] *International Center for New-Structured Materials (ICNSM), Laboratory of New-Structured Materials, and State Key Laboratory of Silicon Materials & Department of Materials Science and Engineering, Zhejiang University, Hangzhou* 310027, *China*

(Received 31 March 2012; revised manuscript received 15 May 2012)

A comprehensive study on Raman spectroscopy with different excitation wavelengths, sample sizes, and sample shapes for optic phonons (OPs) and acoustic phonons (APs) in polar and non-polar nano-semiconductors has been performed. The study affirms that the finite size effect does not appear in the OPs of polar nano-semiconductors, while it exists in all other types of phonons. The absence of the FSE is confirmed to be originated from the long-range Fröhlich interaction and the breaking of translation symmetry. The result indicates that the Raman spectra of OPs cannot be used as a method to characterize the scale and crystalline property of polar nano-semiconductors.

Keywords: Raman spectral, finite size effect, nano-semiconductor

PACS: 78.30.Am **DOI:** 10.1088/1674-1056/21/9/097801

1. Introduction

Due to the finite size effect (FSE), the Raman spectral feature of phonons will change with sample sizes and shapes.[1] The FSE on the Raman frequency has been observed in Ge,[2] Si,[3] diamond,[4] and single-wall carbon nanotubes (NTs).[5] Besides, we observed in nano-semiconductors that the Raman frequency also shifted with the excited light wavelength, which was named as diameter-selective Raman scattering (DSRS)[6] or resonant size selection effect (RSSE),[7] and had been confirmed to be a manifestation of the FSE.[6,7] Although the FSE on Raman spectral features has been accepted widely, the RSSE and the FSE were not observed in some nano-semiconductors.[8−10] Up to date, the absence of RSSE and FSE was reported only in optic phonons (OPs) of polar nano-semiconductors, and it is not clear whether they exist in OPs of non-polar nano-semiconductors and acoustic phonons (APs), as well as, whether they relate with the sample shapes. Moreover, the origin and the nature of the absence of the FSE have not been exposited yet. Obviously, it is very important not only in science but also in technologic application. In this paper, we present a comprehensive Raman spectral study on the FSE of the Raman frequency for not only OPs but also APs in both polar and non-polar nano-semiconductors with different sample shapes. The origin and the nature of the absence of the FSE will be discussed. We have found some new phenomena in this comprehensive study based on a series of previous experiments.

2. Experiment

In the experiments, the size-distributed samples with different shapes were used, which were the polar ZnO nano-particles (NPs, 8 nm)[11] and NTs (30–100 nm),[12] polar GaN nano-wires (NWs, 6–13 nm)[13] and NPs (20–80 nm),[14] and non-polar diamond NPs (20 nm).[15] Besides, the nearly uniform

*Project supported by the National Basic Research Program of China (Grants Nos. 2009CB929403 and 2012CB825700) and the National Natural Science Foundation of China (Grants Nos. 10774006 and 60876002).

†Corresponding author. E-mail: slzhang@pku.edu.cn

© 2012 Chinese Physical Society and IOP Publishing Ltd

sized ZnO NPs ($d_1 \sim 5.7$ nm, $d_2 \sim 17.5$ nm, and $d_3 \sim 18.2$ nm)[16] and diamond NPs ($D_1 \sim 10$ nm, $D_2 \sim 20$ nm, and $D_3 \sim 30$ nm)[15] were also used.

Spectral measurements were performed by using Renishaw 1000 Raman microprobes at room temperature with the back-scattering geometry. The lasers of 488 nm, 515 nm, 633 nm, and 785 nm were used on different samples in the experiments respectively. The Raman spectral measurements were done with a spectral resolution of about 1–2 cm^{-1}, which was dependent on the excitation wavelength. The laser power was kept low, and thus no heating effect was observed.

3. Results and discussion

Firstly, the results of study on the RSSE, i.e., the dependence of Raman frequency on the excitation wavelength λ_{ex}, for polar ZnO NPs and NTs, GaN NWs and NPs, and non-polar diamond NPs are shown in Figs. 1 and 2. In Fig. 1, the Raman spectra of the first-order APs do not appear as we could not measure them, which is because the first-order scattering of APs is forbidden in bulks[1] and the first-order scattering permitted in nano-semiconductors is usually pretty weak. Instead, the observed Raman spectra of second-order APs $2\mathrm{TA}^H$ and $2\mathrm{LA}^M$ are shown together with the second-order OP $2\mathrm{E}_2(\mathrm{L})^M$.

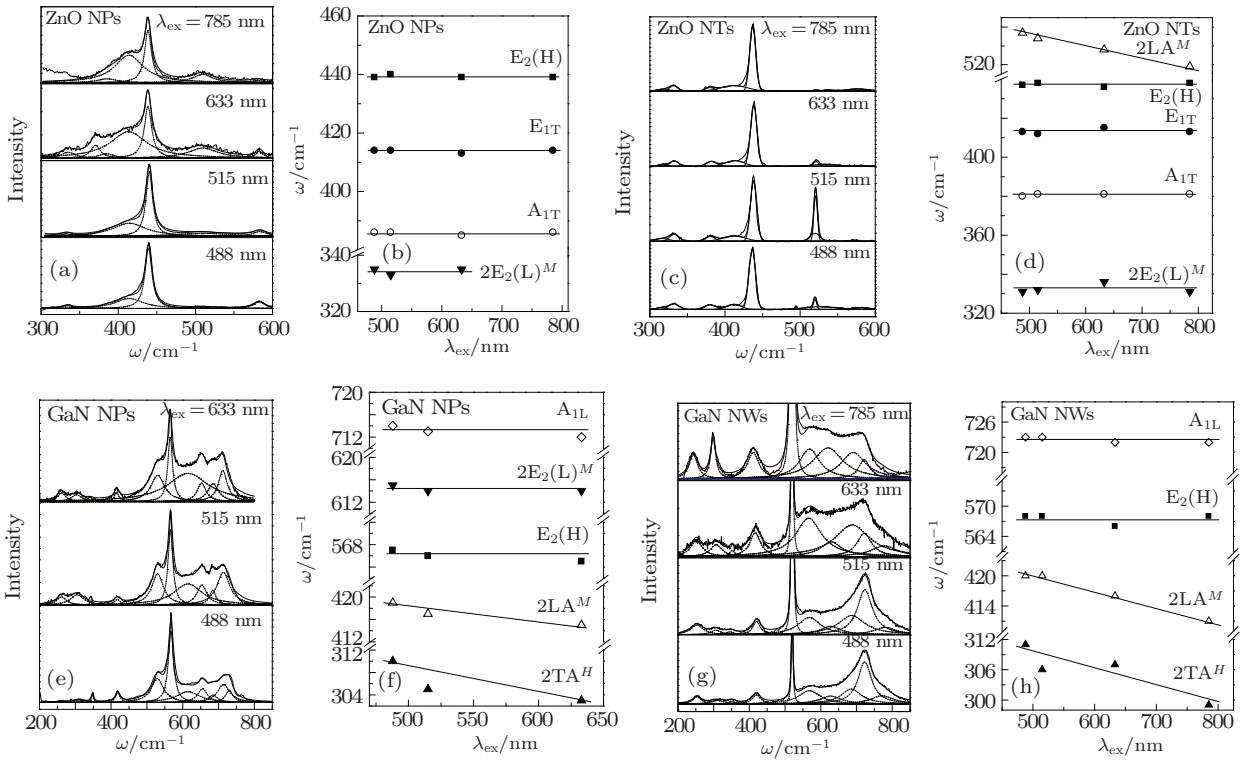


Fig. 1. Observed Raman spectra and Raman frequency shifts versus excitation wavelength λ_{ex} for polar ZnO NPs ((a) and (b)) and NTs ((c) and (d)), as well as polar GaN NPs ((e) and (f)) and NWs ((g) and (h)). Labels $\mathrm{E}_2(\mathrm{L})$, $\mathrm{E}_2(\mathrm{H})$, $\mathrm{E}_{1\mathrm{T}}$, $\mathrm{A}_{1\mathrm{T}}$, and $\mathrm{A}_{1\mathrm{L}}$ mark low-frequency E_2, high-frequency E_2, transverse E_1, transverse A_1, and longitudinal A_1 OP modes, respectively; LA and TA mark longitudinal and transverse A symmetry APs, respectively. Superscripts M and H mean the frequency values taken at M and H boundary points of the Brillouin zone, respectively. Number 2 represents the second-order scattering.

From Fig. 1, it can be found that the frequencies ω of all observed first-order OPs $\mathrm{E}_2(\mathrm{H})$, $\mathrm{E}_{1\mathrm{T}}$, $\mathrm{A}_{1\mathrm{T}}$, $\mathrm{A}_{1\mathrm{L}}$ and second-order OP $2\mathrm{E}_2(\mathrm{L})^M$ do not shift with the excitation wavelength, while the frequencies of double longitudinal and transverse APs $2\mathrm{LA}^M$ and $2\mathrm{TA}^H$ at M and H boundary points of the Brillouin zone both change with the excitation wavelength, and the later matches the observed Raman spectral results of first order APs in ZnO NPs with various sizes reported in Ref. [17]. These results affirm that the RSSE does not exist in OPs but exists in APs of ZnO and GaN nano-semiconductors, which is also independent of the sample shapes. Figure 2 shows that the RSSE exists in OPs of diamond NPs.

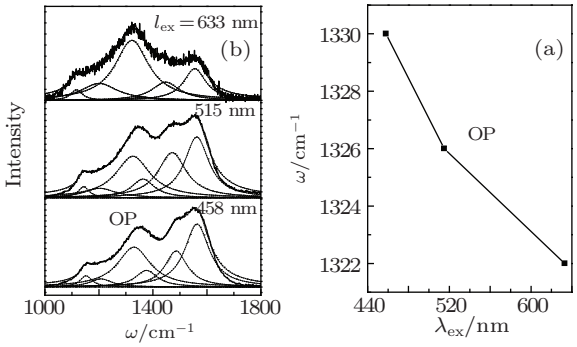


Fig. 2. (a) Observed Raman spectra and (b) Raman frequency shift versus excitation wavelength λ_{ex} for non-polar diamond NPs. Label OP marks the optical phonon mode.

The direct exhibition of FSE on Raman frequency is shown by using the observed results of Raman frequency shifts with sample sizes for polar ZnO and non-polar diamond NPs. The results are shown in Fig. 3, which indicate that the FSE does not exist in OPs of ZnO NPs, but exists in APs of ZnO NPs and OPs of diamond NPs. These results corroborate the results shown in Figs. 1 and 2.

The results shown in Figs. 1–3 exhibit a regular pattern that the FSE only absents in the OPs of polar nano-semiconductors regardless the shapes of the samples, while the other kinds of phonons including all of APs and the OPs in non-polar nano-semiconductors exhibit the FSE.

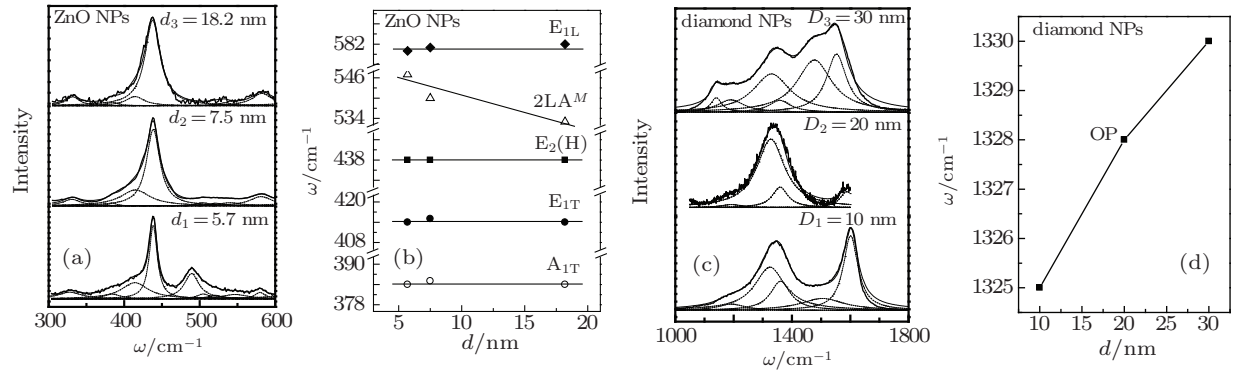


Fig. 3. Observed OP Raman spectra and Raman frequency shifts versus sample sizes for polar ZnO NPs ((a) and (b)) and non-polar diamond NPs ((c) and (d)).

For the absence of the FSE, Demangeot *et al.*[10] suggested that it could be explained by using a very flat optical phonon dispersion curve near the center of the Brillouin zone, resulting in that the FSE could not cause a notable effect on the change of phonon energies. Note that in general, the phonon dispersion relation of nano-semiconductors is not the same as that of the bulk materials, therefore, the validity of the suggestion based on the traditional bulk dispersion curve is questionable. Nevertheless, we test this explanation based on bulk dispersion curves. According to the theoretical dispersion curves of ZnO[18] and GaN[19] bulks, we estimate the deviated values away from the zone center at 1/3 position along high-symmetry directions $\Gamma \to K$, $\Gamma \to M$, and $\Gamma \to A$ of the Brillouin zone, as listed in Table 1.

Table 1. Estimated wavenumber values (cm^{-1}) deviated away from the zone center at 1/3 along high-symmetry directions $\Gamma \to K$, $\Gamma \to M$, and $\Gamma \to A$ of the Brillouin zone for ZnO[18] and GaN.[19]

Phonon mode	GaN			ZnO		
	$\Gamma \to K$	$\Gamma \to M$	$\Gamma \to A$	$\Gamma \to K$	$\Gamma \to M$	$\Gamma \to A$
E_{1L}	–5	0	–[a)]	30	14	–2
A_{1T}	10	10	–[a)]	13	13	–[a)]
A_{1L}	–[a)]	–[a)]	–5	19	10	2
$E_2(H)$	15	15	0	19	11	–5
E_{1T}	10	2	0	–16	–16	–8
$E_2(L)$	45	20	–5	0	0	–16

[a)] In these high-symmetry directions, the dispersion curves were not presented in Refs. [18] and [19].

We consider that if the deviated value is larger than the largest measured error of 2 cm^{-1}, the corresponding dispersion curve cannot be considered as a flat one near the center of the Brillouin zone. From Table 1, we can see that for all the OP modes, there is no phonon with its deviated wavenumber smaller than 2 cm^{-1} away from the zone center at 1/3 along the three high symmetry directions of the Brillouin zone. However, the experiments shown that no FSE appears in these modes, meaning that the above interpretation is not reasonable. To seek a reasonable interpretation, we should get rid of the traditional idea and start from the analyzing of all experimental facts carefully.

We pay attention to the fact that the absence of the FSE summarized above appears only in the OPs of polar nano-semiconductors. It is well known that the key difference between polar and non-polar semiconductors is whether the individual atoms carry electrical charge or not. This implies that the polar semiconductors must possess a long-range Coulomb potential induced by the electrical charge, in addition to the short-range van der Waals deformation potential that exists in all non-polar and polar semiconductors. Moreover, note that the OPs are the collective excitation of out-phase vibration of atoms/ions in lattices, while the APs are the in-phase vibration.[20] Thus, the OPs in polar semiconductors produce a unique long-range Fröhlich electron–phonon interaction. Therefore, it is reasonable to expect that the Fröhlich interaction is the origin of the absence of the FSE.

The relation of Fröhlich interaction $H_{\rm Fr}$ with phonon wavevector q and sample volume V can be approximately expressed as[21]

$$H_{\rm Fr} \sim q^{-1}V^{-1/2}. \quad (1)$$

Formula (1) demonstrates that the small volume V makes the Fröhlich interaction be critical in the nano-semiconductors comparing with its role in the bulks. In fact, the Fröhlich interaction induced scattering in nano-semiconductors and superlattices has been emphasized.[22] Besides, formula (1) indicates that the Fröhlich interaction plays a key role at $q \approx 0$ of the Brillouin zone. Based on the above two factors, the Raman scattering of OPs in polar nano-semiconductors is possible to occur at $q \approx 0$ only, and thus the frequency must be independent of the sizes of nano-semiconductor samples. Therefore, the absence of the FSE observed above is possible to be well interpreted by means of the Fröhlich interaction. Moreover, for multi-phonon (MP) Raman scattering, the occurring of Raman scattering only at $q \approx 0$ also implies that Raman frequencies of higher order k phonons, ω_k, should be integral times of the frequency of the first order phonon ω_1, i.e., $\omega_k = k\omega_1$. This is against to the traditional viewpoint that the MP Raman spectrum is related to the phonon density of states (PDOS) and thus the Raman frequencies of MP should not be integral multiples of SP, i.e., $\omega_k = k\omega_1$ should not occur.[23] This implies that if $\omega_k = k\omega_1$ is observed, the above proposition on the origin of the absence of the FSE is confirmed independently. The relation of $\omega_k = k\omega_1$ has been observed in the experiments reported by our group,[24] and thus a solid confirmation for the above explanation has been given.

The active region of Fröhlich interaction $H_{\rm Fr}$ is estimated at the scale of a unit cell, i.e., 1–10 nm, while that of the deformation potential interaction is the space between atoms at the lattice sites, i.e., around 0.1 nm. This implies that the characteristic lengths of the phonons possessing the Fröhlich interaction and the deformation potential interaction are 1-10 nm and 0.1 nm, respectively. It is well known that an infinite system possesses the translation symmetry. However, no physical system is ever infinite in a spatial space, so an infinite system is described as such a system that the boundary influences can be ignored.[25] Obviously, the boundary influences for the phonons with the deformation potential interaction and with the Fröhlich interaction cannot show any difference in the case of bulk samples with the scale of larger than 100 nm; however, it must be different for the nano-semiconductor samples with the size of around 10 nm. Thus, it should be expected that the translation symmetry is broken for the OPs in polar nano-semiconductors and is maintained for all the other kinds of phonons with only the deformation potential interaction. Moreover, it is well known that if a solid has no translation symmetry, it must not have the long-range order and be amorphous; correspondingly, its Raman spectrum should possess an amorphous feature.[26] Therefore, the feature of Raman spectra can be used to test whether the maintenance or breaking of the translation symmetry. Reference [27] reported that although the Raman spectra of non-polar crystalline semiconductors, such as porous silicon and Si NWs, exhibited the crystalline Raman feature, the Raman spectra of OPs in polar nano-crystalline semiconductors GaN and ZnO pos-

sessed amorphous features. Thus it can be conclude that the proposition on the loss of long-range order and the breaking of translation symmetry is true.

4. Conclusion

In summary, we perform a comprehensive Raman spectral study and affirm that the FSE occurs in all APs and OPs except for the OPs of polar nanocrystalline semiconductors. Based on the fact that the long-range Fröhlich interaction occurs only in the OPs of polar semiconductors, we propose that the absence of the FSE is originated from the Fröhlich interaction. This proposition is confirmed by the observed relation of MP Raman frequency $\omega_k = k\omega_1$. We also suggest that the Fröhlich interaction in polar nanosemiconductors results in the loss of long-range order and the breaking of translation symmetry in OPs. This suggestion is confirmed by the amorphous feature of the Raman spectra of OPs in polar nano-crystalline semiconductors. The above results are very important in Raman spectral applications, for example, Raman spectra of OPs in polar nano-semiconductors cannot be used as a characteristic method to test the FSE and to obtain the information on scale and crystalline property of polar nano-semiconductors, although it has been successfully and widely used as a characteristic method in bulk and nano-materials.

References

[1] Zhang S L 2012 *Raman Spectroscopy and its Application in Nanostructures* (Chichester: John Wiley)

[2] Bottani C E, Mantini C, Milani P, Manfredini M, Stella A, Tognini P, Cheyssac P and Kofman R 1996 *Appl. Phys. Lett.* **69** 2409

[3] Ehbrecht M, Kohn B, Huisken F, Laguna M A and Paillard V 1997 *Phys. Rev.* B **56** 6958

[4] Sun Z, Shi J R, Tay B K and Lau S P 2000 *Diam. Relat. Mater.* **9** 1979

[5] Duesberg G S, Loa I, Burghard M, Syassen K and Roth S 2000 *Phys. Rev. Lett.* **85** 5436

[6] Rao A M, Richter E, Bandow S, Chase B, Eklund P C, Williams K A, Fang S, Subbaswamy K R, Menon M, Thess A, Smalley R E, Dresselhaus G and Dresselhaus M S 1997 *Science* **275** 187

[7] Zhang S L, Ding W, Yan Y, Qu J, Li B, Li L Y, Yue K T and Yu D 2002 *Appl. Phys. Lett.* **81** 4446

[8] Zhang S L, Zhang Y, Liu W, Fu Z, Yan Y, Chen J, Ma R, Song Y, Zhao J, Xu L S, Wu S, Gao M and Li H 2006 *Appl. Phys. Lett.* **89** 063112

[9] Zhang S L, Zhang Y, Fu Z, Wu S N, Gao M, Liu M, Chen J, Niu L, Jiang J Z, Ling Y, Wang Q and Chen H 2006 *Appl. Phys. Lett.* **89** 243108

[10] Demangeot F, Paillard V, Chassaing P M, Pages C, Kahn M L, Maisonnat A and Chaudret B 2006 *Appl. Phys. Lett.* **88** 071921

[11] Yuan F, Hu P, Yin C, Huang S and Li J 2003 *J. Mater. Chem.* **13** 634

[12] Xing Y J, Xi Z H, Xue Z Q, Zhang X D, Song J H, Wang R M, Xu J, Song Y, Zhang S L and Yu D P 2003 *Appl. Phys. Lett.* **83** 1690

[13] Chen X, Xu J, Wang R M and Yu D 2003 *Adv. Mater.* **15** 419

[14] Li H D, Yang H B, Yu S, Zou G T, Li Y D, Liu S Y and Yang S R 1996 *Appl. Phys. Lett.* **69** 1285

[15] Yan Y, Zhang S L, Hark S K, Liu E K, Han Y S, Xuan Z W, Gu C Z, Liu W and Ding M Q 2004 *Chinese Journal of Light Scattering* **16** 131

[16] Qian D, Jiang J Z and Hansen P L 2003 *Chem. Commun.* 1078

[17] Chassaing P M, Demangeot F, Combe N, Saint-Macary L, Kahn M L and Chaudret B 2009 *Phys. Rev.* B **79** 155314

[18] Serrano J, Manjón F J, Romero A H, Ivanov A, Cardona M, Lauck R, Bosak A and Krisch M 2010 *Phys. Rev.* B **81** 174304

[19] Ruf T, Serrano J, Cardona M, Pavone P, Pabst M, Krisch M, D'Astuto M, Suski T, Grzegory I and Leszczynski M 2001 *Phys. Rev. Lett.* **86** 906

[20] Born M and Huang K 1985 *Dynamical Theory of Crystal Lattice* (London: Oxford Univ. Press)

[21] Yu P Y and Cardona M 2010 *Fundamentals of Semiconductors* (4th edn.) (New York: Springer-Verlag)

[22] Huang K, Zhu B F and Tang H 1990 *Phys. Rev.* B **41** 5825

[23] Martain R M and Falicov L M 1983 *Light Scattering in Solids* (2th edn.) (Berlin: Springer)

[24] Liu M X, Liu W, Fu Z D and Zhang S L 2007 *J. Light Scattering* **19** 321

[25] Born M and Karman T V 1912 *Phys. Zeit.* **13** 271

[26] Shuker R and Gammom R W 1970 *Phys. Rev. Lett.* **25** 222

[27] Zhang S L, Zhang Y, Liu W, Fu Z D, Yan Y, Chen J, Ma R, Song Y, Zhao J, Xu L S, Wu S N, Gao M, Li H, Li Y and Yuan F 2006 *Appl. Phys. Lett.* **89** 063112