Vol 17 No 9, September 2008
1674-1056/2008/17(09)/3433-05

Chinese Physics B

© 2008 Chin. Phys. Soc.
and IOP Publishing Ltd

Common electronic band gaps and similar optical properties of ZnO nanotubes*

Yang Yu-Rong(杨玉荣)[a)b)], Yan Xiao-Hong(颜晓红)[a)c)†], Guo Zhao-Hui(郭朝晖)[a)], and Deng Yu-Xiang(邓宇翔)[a)]

[a)] *College of Science, Nanjing University of Aeronautics and Astronautics, Nanjing* 210016, *China*
[b)] *Physics Laboratory Center, Nanjing University of Aeronautics and Astronautics, Nanjing* 210016, *China*
[c)] *Interdisciplinary Center of Theoretical Studies and Institute of Theoretical Physics, Chinese Academy of Sciences, Beijing* 100190, *China*

(Received 16 November 2007; revised manuscript received 25 March 2008)

Electronic and optical properties of single-walled zinc oxide (ZnO) nanotubes are investigated from the first-principles calculations. Electronic structure calculations show that ZnO nanotubes are all direct band gap semiconducting nanotubes and the band gaps are relatively insensitive to the diameter and chirality of tubes. The origin of the common electronic band gaps of ZnO nanotubes is explained in terms of band-folding from the two-dimensional band structure of graphite-like sheet. Moreover, the optical properties such as dielectric function and energy loss function spectra of different ZnO nanotubes are very similar, relatively independent of diameter and chirality of tubes. The calculated dielectric function and loss function spectra show a moderate optical anisotropy with respect to light polarization.

Keywords: nanotubes, first-principles calculations, optical constants
PACC: 7125, 7115A, 7820D

1. Introduction

ZnO has attracted extensive attention because of its electron mobility, wide band gap, and large exciton binding energy. ZnO nanostructures such as nanowires, nanotubes, and nanobelts are promising building blocks for optical, electronic, and chemical sensing devices.[1−4] Several synthetic routes have yielded multiwalled ZnO nanotubes.[5−9] These tubes are 20–450 nm in diameter and have a wall thickness range of 4–100 nm. Though single-walled ZnO nanotubes (SWZONTs) have not been reported experimentally, the ZnO graphitic-like monolayers which could be rolled into SWZONTs is revealed by using surface x-ray diffraction and scanning tunnelling microscopy.[10] The stability and the electronic structure of SWZONTs have been studied theoretically.[11−15] Tu and Hu[11] and Wang *et al*[13] predicted that the tubes could be fabricated under some experimental conditions. Wang *et al*[13] and Xu *et al*[14] showed that all SWZONTs were direct band gap semiconducting nanotubes with relatively uniform band gaps. But origin of the common electronic band gaps is still unknown. Here we explain the uniform electronic gaps of SWZONTs by using the method of Brillouin zone foldings and show a systematic investigation of the optical properties for SWZONTs.

2. Theoretical method

The plane wave pseudopotential method in the generalized gradient approximation[16] is used in our *ab initio* total energy calculations.[17] We choose ultrasoft pseudopotentials[18] for all the atoms and a cutoff energy of 400 eV. The Brillouin zone integration is performed within the Monkhorst–Pack scheme.[19] Periodical boundary condition along the tube axis is employed for ZnO nanotubes with a vacuum region (1 nm) between tubes. The ideal nanotubes were constructed by rolling up a ZnO graphitic sheet.[11] Their atomic positions and lattice constants were then fully relaxed by a conjugate gradient technique. Theoretical equilibrium nanotube structures were obtained when the forces acting on all the atoms and the uniaxial stress tensor were less than 0.5 eV/nm and 0.1 GPa,

*Project supported by the National Natural Science Foundation of China (Grant No 10674070) and the Program for New Century Excellent Talents in University, China (Grant No NCET-04-0779), and Changjiang Scholars and Innovative Research Team in University, China (Grant No IRT0534).
†E-mail: xhyan@nuaa.edu.cn

respectively.

3. Electronic band gaps of ZnO nanotubes

The energy bands of armchair, zigzag, and chiral ZnO nanotubes studied here are shown in Fig.1. Only representative ZnO nanotubes of each type of ZnO nanotubes, namely, (5,5) armchair, (9,0) zigzag, (2,8) chiral nanotubes are selected for display. All the calculated band structures of ZnO nanotubes are semiconducting with a direct band gap at Γ point in the Brillouin zone (Fig.1). The diameter and the chirality dependences of band gaps are investigated for ZnO nanotubes, and results are presented in Table 1. All of the ZnO nanotubes have a direct band gap of about 1.8 eV at Γ point, which is comparable with the band gap of ZnO graphite sheet. Note that the band gaps are significantly underestimated by the density functional theory (DFT). The band gaps of ZnO nanotubes are relatively insensitive to the diameter and the chirality of tubes. This behaviour is quite different from those of C,[20] BN,[21] GaN[22] and SiC[23] nanotubes. The uniform electronic gaps of ZnO nanotubes may be related to the two-dimensional band structure of ZnO graphite-like sheet.

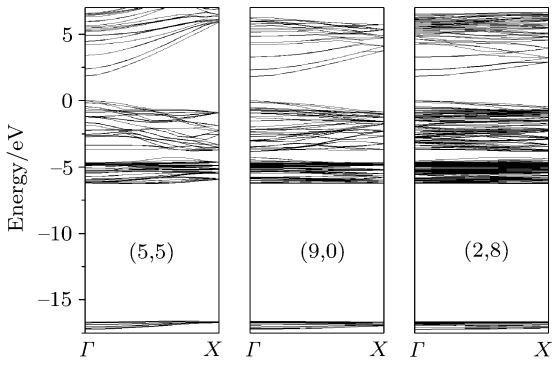


Fig.1. Band structures of (a) armchair (5,5), (b) zigzag (9,0), and chiral (2,8) ZnO nanotubes.

Table 1. Diameter D, relaxed lattice constant T and band gap Δ of ZnO nanotubes.

tubes	D/nm	T/nm	Δ/eV
(4, 4)	0.7256	0.326	1.81
(5, 5)	0.9023	0.326	1.84
(6, 6)	1.0859	0.324	1.81
(7, 7)	1.2560	0.326	1.86
(9, 9)	1.6197	0.325	1.85
(11,11)	1.9786	0.325	1.86
(5, 0)	0.5367	0.556	1.85
(6, 0)	0.6419	0.558	1.81
(9, 0)	0.9459	0.561	1.81
(10, 0)	1.0517	0.561	1.81
(12, 0)	1.2566	0.562	1.82
(14,0)	1.4676	0.561	1.82
(2,8)	0.9542	0.860	1.84

Figure 2(a) shows the band structures of ZnO graphitic sheet. One can see that the band of graphitic sheet has a direct band gap of about 1.86 eV at Γ point in the Brillouin zone. The energy of the second highest occupied state at K point is 0.8 eV lower than that of the highest occupied state at Γ point. The energy of the second lowest unoccupied state at Γ point is 2.8 eV higher than that of the lowest unoccupied state at Γ point. This is different from those of a graphitic carbon sheet and a graphitic BN sheet. For a graphitic carbon sheet, the bonding and the antibonding π bands are degenerate at the K point. The energy band gap of carbon sheet is 0 eV. For a graphitic BN sheet, it has an indirect gap of about 4 eV with the highest occupied state at K point and the lowest unoccupied state at M point.[21] The difference in band between graphitic sheets may result in different bands for nanotubes.

Figures 2(b) and 2(c) show the Brillouin zone (BZ) of graphitic sheet. For nanotubes, the periodic boundary condition along the tube axis is the same as that for graphitic sheet, while that perpendicular to the tube axis is imposed for a finite period. This results in Bloch wavefunctions with discretely selected wave vectors.[20,24] Figures 2(b) and 2(c) show the situations for the armchair (5,5) nanotube and the zigzag (9,0) nanotube, respectively. The vertical lines show the allowed wave vectors. For the (5,5) nanotube, the vertical lines are found to cross the points which divide the straight line of doubled $\Gamma - M$ into 10 parts. For (9,0) nanotube, the vertical lines are found to cross the points which divide the straight line of doubled $\Gamma - M$ into 9 parts. For carbon, as the bonding π band and the antibonding π band are degenerate at the K point in the BZ of a graphite sheet, the band structures of nanotubes would show metallic characteristic if a vertical line of BZ of nanotube crosses the K point (armchair tubes and $(3q, 0)$ zigzag tubes, q is an integer), namely, armchair tubes are metallic tubes and zigzag tubes are small-to-moderate gap semiconducting tubes.[20] As the BN graphitic sheet has an indirect gap $(K - M)$,[21] under the "band-folding" effect[20] and the curvature effect[25] the BN nanotubes have a

direct or indirect gap. For the ZnO graphitic sheet, it has a direct band gap at Γ point in the Brillouin zone. The set of wave vectors which are allowed by periodic boundary conditions for a nanotube always contains the Γ point for all (n, m) nanotubes. Therefore, all the (n, m) ZnO nanotubes would have a direct band gap at Γ point in a nanotube BZ and the gaps are comparable with the band gaps of ZnO graphite sheet, though the curvature effect may slightly change the size of band gap.

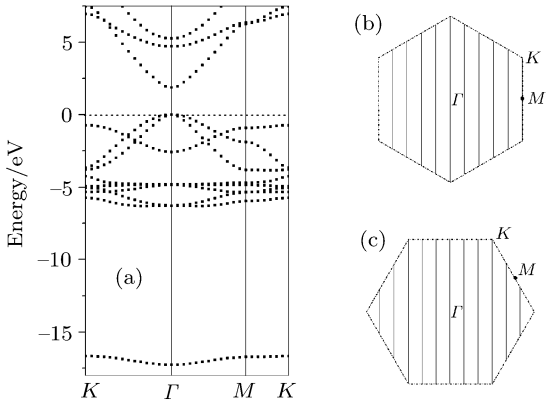


Fig.2. Band structure and first Brillouin zone of ZnO graphitic sheet. Panel is (a) is for band structure of ZnO graphitic sheet. The wave vectors are allowed by the periodic boundary condition along the circumference for (b) armchair (5,5) nanotube and (c) zigzag (9,0) nanotube. The regions surrounded by the dashed line refer to the first Brillouin zone of a graphitic sheet.

Figures 3(a), 3(b) and 3(c) show the density of states (DOS) of representative chiral, armchair and zigzag ZnO nanotubes, respectively. One can see that all ZnO nanotubes have very similar DOS spectra in the figures, despite small differences in shape and amplitude of DOS spectra. The valence bands of all ZnO nanotubes are derived from O 2s, Zn 3d and O 2p orbitals. The bands between 0 and –4.4 eV come mainly

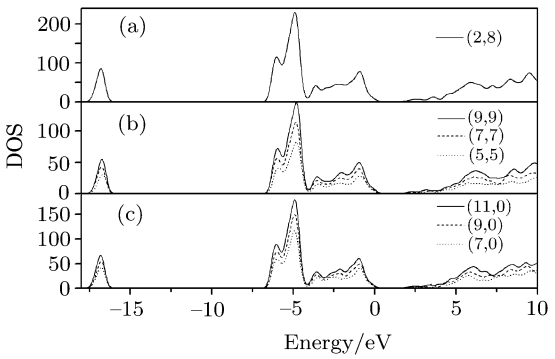


Fig.3. DOS of the representative (a) chiral, (b) armchair and (c) zigzag ZnO nanotubes.

from O 2p orbitals. The major contributions to valence bands between –4.4 and –0.68 eV are derived from Zn 3d orbitals. The valence bands between −16.8 and –17.7 eV are derived from O 2s orbitals. The states at the bottom of conduction band are primarily of Zn 4s orbitals. Form Fig.3, one can also see that all the nanotubes have similar band gaps which are relatively insensitive to the diameter and chirality.

4. Optical properties of ZnO nanotubes

It is well known that the interaction of a photon with the electrons in the system can be described in terms of time-dependent perturbations of the ground-state electronic states. Transitions between occupied and unoccupied states, including plasmons and single particle excitations, are caused by the electric field of photon. The spectra resulting from these excitations can be thought of as a joint DOS between the valence and conduction bands. The imaginary part $\varepsilon_2(\omega)$ of the dielectric function can be calculated from the momentum matrix elements between the occupied and unoccupied wavefunctions within the selection rules. The real part $\varepsilon_1(\omega)$ of dielectric function can be evaluated from imaginary part $\varepsilon_2(\omega)$ by Kramers–Kronig relationship. The other optical constants can be derived from $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$.[15,26] Figure 4 shows the relations between imaginary part $\varepsilon_2(\omega)$ and energy for (2,8) chiral, (11,0) zigzag, and (7,7) armchair ZnO nanotubes. Because of the similar electronic structures of ZnO nanotubes, the $\varepsilon_2(\omega)$ spectra of the different nanotubes are rather similar in shape and energy position of peaks, indicating that ZnO nanotubes have similar optical properties. For the parallel light polarization, the $\varepsilon_2(\omega)$ spectra of the three different ZnO nanotubes each have three main peaks around 2.1, 7.2 and 12.0 eV. The peak at around 2.1 eV mainly comes from the electron transition between the O 2p and Zn 4s orbitals. The transition between the Zn 3d and O 2p orbitals may lead to the peak at about 7.2 eV. And the peak at 12.0 eV is mainly derived from the transition between the Zn 3d and O 2s orbitals. There are some differences in energy position of weak peaks between the main peaks among different ZnO nanotubes, which may be due to the small difference in conduction band of DOS (Fig.3). For the perpendicular light polarization, the amplitude of $\varepsilon_2(\omega)$ spectrum is smaller than that for the parallel light polar-

ization. In the $\varepsilon_2(\omega)$ spectrum for the perpendicular light polarization there are three main peaks appearing at about 2.5, 7.2 and 10.4 eV, separately. One can see that the moderate optical anisotropy from the $\varepsilon_2(\omega)$ spectra for the parallel and perpendicular light polarizations.

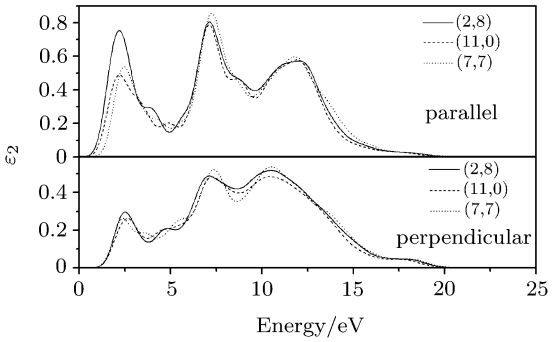


Fig.4. Calculated imaginary part $\varepsilon_2(\omega)$ of the dielectric function of representative ZnO nanotubes. "Parallel" and "perpendicular" denote light polarizations parallel and perpendicular to the nanotube axis, respectively.

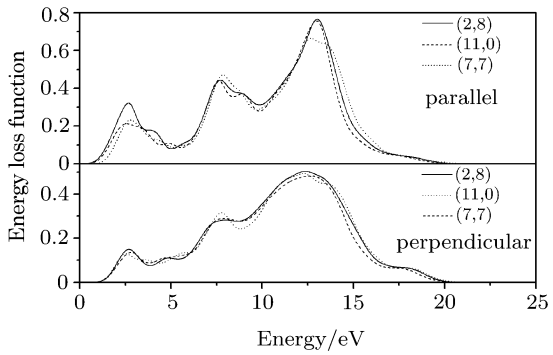


Fig.5. Calculated energy loss functions of the representative ZnO nanotubes. "Parallel" and "perpendicular" denote light polarizations parallel and perpendicular to the nanotube axis, respectively.

The energy loss functions of (2,8) chiral, (11,0) zigzag, and (7,7) armchair ZnO nanotubes are shown in Fig.5. Like $\varepsilon_2(\omega)$ spectrum, the energy loss functions of different nanotubes look rather similar. For the parallel and the perpendicular light polarizations, the energy loss functions of ZnO nanotubes each have three main peaks at about 2.6, 6.8 and 13.0 eV. But the shapes and the amplitudes of energy loss functions for the parallel and the perpendicular light polarizations are different, showing a moderate optical anisotropy in ZnO nanotubes. Note that the optical properties of much more armchair and zigzag ZnO nanotubes are calculated, the similar results are found as shown in Figs.4 and 5. The similar $\varepsilon_2(\omega)$ and energy loss function spectra show that the optical properties of ZnO nanotubes are relatively independent of diameter and chirality of tubes.

5. Summary

The structures, electronic and optical properties of SWZONTs are studied by using the *ab initio* pseudopotential density functional method. All (n, m) ZnO nanotubes are found to be direct band gap semiconducting nanotubes with band gaps relatively independent of diameters and chirality. The origin of common features of the electronic structures for ZnO nanotubes is explained in terms of band-folding effects. The imaginary part $\varepsilon_2(\omega)$ of dielectric function and energy loss functions show that the optical properties of ZnO nanotubes are relatively independent of diameters and chirality of nanotubes. The $\varepsilon_2(\omega)$ spectrum has three main peaks at about 2.1, 7.2 and 12.0 eV for the parallel light polarization and three main peaks at about 2.5, 7.2 and 10.4 eV for the perpendicular light polarization. The energy loss functions have three main peaks at about 2.6, 6.8 and 13.0 eV for both the parallel and the perpendicular light polarizations. Both dielectric function and loss function spectra of ZnO nanotubes show the moderate optical anisotropy with respect to the light polarization. The common feature of electronic and optical properties of different ZnO nanotubes could avoid the roadblock of selective synthesis of prespecified chirality nanotubes, which is a key issue for carbon nanotubes in nanoelectronic applications. The unique electronic and optical properties of ZnO nanotubes make it possible to apply the ZnO nanotubes to nanoscale optical and optoelectronic devices.

References

[1] Fan Z and Lu J G 2005 *J. Nanosci. Nanotechnol.* **5** 1561
[2] Wu Y Y and Yang P D 2001 *J. Am. Chem. Soc.* **123** 3165
[3] Xuan K, Yan X H, Ding S L, Yang Y R, Xiao Y and Guo Z H 2006 *Chin. Phys.* **15** 0460
[4] Chen L, Zhang G M, Wang M S and Zhang Q F 2005 *Chin. Phys.* **14** 0181
[5] Wu J J S, Liu C, Wu C T, Chen K H and Chen L C 2002 *Appl. Phys. Lett.* **81** 1312
[6] Zhang X H, Xie S Y, Jiang Z Y, Zhang X Z, Tian Q, Xie Z X, Huang R B and Zheng L S 2003 *J. Phys. Chem.* B

107 10114

[7] 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** 1689

[8] Kong X H, Sun X M, Li X L and Li Y D 2003 *Mater. Chem. Phys.* **82** 997

[9] Sun Y, Fuge G M, Fox N A, Riley D J and Ashfold M N R 2005 *Adv. Mater.* **17** 2477

[10] Tusche C, Meyerheim H L and Kirschner J 2007 *Phys. Rev. Lett.* **99** 026102

[11] Tu Z C and Hu X 2006 *Phys. Rev.* B **74** 035434

[12] Shen X P, Allen B, Muckerman J T, Davenport J W and Zheng J C 2007 *Nano. Lett.* **7** 2267

[13] Wang B L, Nagase S, Zhao J J and Wang G H 2007 *Nanotechnology* **18** 345706

[14] Xu H, Zhang R Q, Zhang X, Rosa A L and Frauenheim Th 2007 *Nanotechnology* **18** 485713

[15] Yang Y R, Yan X H, Xiao Y and Guo Z H 2007 *Chem. Phys. Lett.* **446** 98

[16] Perdew J P and Wang Y 1992 *Phys. Rev.* B **45** 13244

[17] Segall M D, Lindan P L D, Probert M J, Pickard C J, Hasnip P J, Clark S J and Payne M C 2002 *J. Phys.: Condens. Matter* **14** 2717

[18] Vanderbilt D 1990 *Phys. Rev.* B **41** 7892

[19] Monkhorst H J and Pack J D 1976 *Phys. Rev.* B **13** 5188

[20] Hamada N, Sawada S I and Oshiyama A 1992 *Phys. Rev. Lett.* **68** 1579

[21] Rubio A, Corkill J L and Cohen M L 1994 *Phys. Rev.* B **49** 5081

[22] Lee S M, Lee Y H, Hwang Y G, Elsner J, Porezag D and Frauenheim T 1999 *Phys. Rev.* B **60** 7788

[23] Zhao M W, Xia Y, Li F, Zhang R Q and Lee S T 2005 *Phys. Rev.* B **71** 085312

[24] Saito R, Dresselhaus G and Dresselhaus M S 1998 *Physical Properties of Carbon Nanotubes* (London: Imperial College Press)

[25] Blase X, Benedict L X, Shirley E L and Louie S G 1994 *Phys. Rev. Lett.* **72** 1878

[26] Cai M Q, Yin Z and Zhang M S 2004 *Chem. Phys. Lett.* **388** 223

[27] Guo G Y and Lin J C 2005 *Phys. Rev.* B **71** 165402