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First-principles study of the electronic and optical properties of ZnO nanowires*

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The geometric, energetic, electronic structures and optical properties of ZnO nanowires (NWs) with hexagonal cross sections are investigated by using the first-principles calculation of plane wave ultra-soft pseudo-potential technology based on the density functional theory (DFT). The calculated results reveal that the initial Zn-O double layers merge into single layers after structural relaxations, the band gap and binding energies decrease with the increase of the ZnO nanowire size. Those properties show great dimension and size dependence. It is also found that the dielectric functions of ZnO NWs have different peaks with respect to light polarization, and the peaks of ZnO NWs exhibit a significant blueshift in comparison with those of bulk ZnO. Our results gives some reference to the thorough understanding of optical properties of ZnO, and also enables more precise monitoring and controlling during the growth of ZnO materials to be possible.

Keywords: density functional theory, ZnO nanowires, electronic structure, optical properties
PACC: 7230, 7115M, 7125, 7115A

1. Introduction

Hexagonal zinc oxide (ZnO), a typical wide bandgap (E_g = 3.37 eV) II–VI semiconductor with a large exciton binding energy (60 meV), has a stable wurtzite structure with lattice spacing a = 0.325 nm and c = 0.521 nm. It has recently attracted the most intensive research for many properties and potential applications in building optical and optoelectronic nanodevices.[1−6] ZnO nanostructures such as nanowires, nanotubes, nanobelts, nanosheets and nanorods are promising building blocks for optical and electronic devices because of the potential applications in the fields of blue-light emitting, short wavelength laser diodes with low thresholds in the UV light-emitting diodes, solar cells, transparent and conducting electrodes in solar cells, surface acoustic wave devices, and chemical and biological sensors.[7−12] Many experimental and theoretical investigations have been reported as regards ZnO NWs of various electronic and optical devices. Wang *et al* showed an approach to gaining the piezoelectric nanogenerators.[13] Huang *et al* measured the photoluminescence spectra of ZnO NWs and advanced the ZnO NWs nanolasers,[14] Luo *et al* studied the characterization of ZnO NWs-based ultraviolet photodiodes. But the electronic and optical properties of ZnO NWs are debated in the literature.[15−18] To our knowledge, very few systematical studies on the dimension and size-dependent properties of ZnO NWs have been made theoretically until now. In particular, the effects of surface electronic states due to the appearance of the sidewall in ZnO NWs on their electronic and optical properties are unclear. It is necessary for us to use the first principle method to study these issues for developing future applications of ZnO NWs.

2. Theoretical approaches

Our NWs are generated from a ZnO wutzite crystal structure, cut along the (0001) axis with period c as shown in Fig.1. The NWs have a diameter from 3 Å to 20 Å (1 Å=0.1 nm), including 12, 20, 26, 32, 38,

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48 and 108 atoms per unit cell.

In our study, all the structural optimizations, band structures, optical properties and energy calculations are performed by using the first principles calculations with the CASTEP software package[19] based on density functional theory (DFT). To minimize the surface-surface interaction effect due to the finite supercell, we placed the ZnO NWs within a square supercell with a vacuum 10.0 Å thick. The Perdew and Wang 91-parametrization is taken as the exchange-correlation potential in the generalized gradient approximation (GGA). The cutoff energy of the plane-wave is set to be 420 eV. The maximum root-mean-square convergent tolerance is less than 2×10^{-5} eV/atom, that is, the force imposed on each atom is not greater than 0.1 eV and 0.1 GPa for stress. The Brillouin zone integration is approximated by using a special K-points sampling scheme of Monkhorst–Pack and $1 \times 1 \times 24$ K-point grids are used. All calculations are performed in the reciprocal space.

3. Results and discussion

Firstly, we optimize the bulk ZnO structure. Our calculated ground state structural properties are shown in Table 1, which is in good agreement with the experimental and other GGA and LDA results.[20,21] Table 1 gives a list of the calculated lattice constants, binding energies and bulk modulus B_0 with different approximations. Our calculated lattice parameters are close to the experimental values, the value of the band gap is about 0.91 eV, which is small in comparison with the experimental value of about 3.37 eV.[25] The reason for such a disagreement is the well-known shortcoming of the theory frame of DFT-LDA. The underestimate of the band gap is 2.46 eV. When the scissor approximation (SA) makes the conduction band structure rigid shift towards higher energy by 2.46 eV, the band gap becomes 3.37 eV, in excellent agreement with the experimental results.

Table 1. Comparison between our present work and other calculations and experiments.

	our work	GGA[20,21]	LDA[21]	experiment[22−25]
a/Å	3.276	3.283	3.264	3.250
c/Å	5.258	5.289	5.273	5.207
u	0.381	0.380	0.379	0.3817
E_b/eV	7.35	7.69	9.769	7.56
B_0/Gpa	136	149	162.3	142.6
gap/eV	0.91	0.75	0.79	3.4

All the optimizated results of ZnO NWs are shown in Fig.1, the bottom views are the relaxed structures. We can see that oxygen atoms of outer layers move outwards, zinc atoms of the outer layer move inwards. The obvious difference is that the Zn–O double layers merge into single layers with both Zn and O atoms after relaxed nanowires, we also find that the deformation ratio of small nanowires is greater than large ones. The relaxation of surface atoms in ZnO NWs has the same varied mechanism as that in the ZnO[$10\bar{1}0$] surface,[26] the properties of large nanowires approach those of the bulk ZnO.

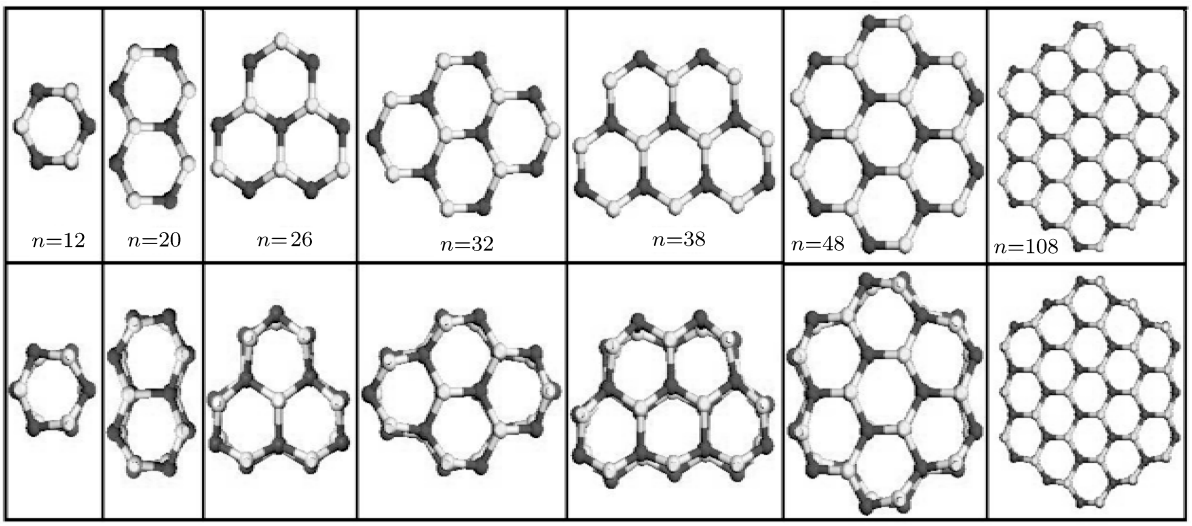


Fig.1. The top view of the initial (up) and relaxed (bottom) ZnO NWs. The dark and gray spheres represent O and Zn atoms, respectively.

Figure 2 shows the change of the binding energies and the (HOMO-LUMO) energy gaps of the optimized NWs. Obviously the binding energies and the (HOMO-LUMO) energy gaps decrease with the increase of ZnO NWs size, the smallest one (n = 12) has the widest energy gap (E_g = 2.0 eV) and the highest binding energy (E_b = −38.42 eV), the largest one (n = 108) has the lowest binding energy (E_b = −46.46 eV) and the smallest energy gap (E_g = 1.02 eV), which indicate the stability of the size-effect of ZnO NWs because more surface relaxations of these ZnO NWs are size-dependent, the smallest one is the most unstable structure and the largest one approaches the ZnO bulk values.

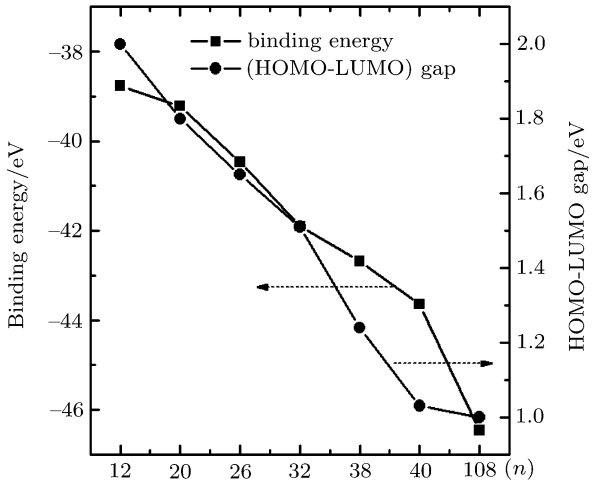


Fig.2. HOMO-LUMO gaps and binding energies of the relaxed ZnO NWs.

In order to reach a better understanding of the character of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), from Fig.3(a) we can see that the LUMO is quite delocalized and has been distributed to the whole nanowires. This indicates that it has the character of ZnO bulk state and large dispersion of LUMO of $\Gamma(0,0,0) \rightarrow Z(0,0,0.5)$ direction, which induces the LUMO energy to greatly increase with the decrease of the nanowires size due to the nanowire radial confinement and the quantum size effects in these low-dimensional nanostructures.[27] In Fig.3(b), it is found that the HOMO of ZnO NWs has some of the characteristics of π orbitals, the charge density of HOMO at the Γ point was mainly contributed by the oxygen $2p$ orbitals of surface atoms, and the zinc $3d$ orbitals have little contribution. These calculated results are in good agreement with those of the ZnO $(10\bar{1}0)$ surface.[28] The obvious gap-widening effect in the ZnO nanowires is quite important for building nanoscale optoelectronic devices.

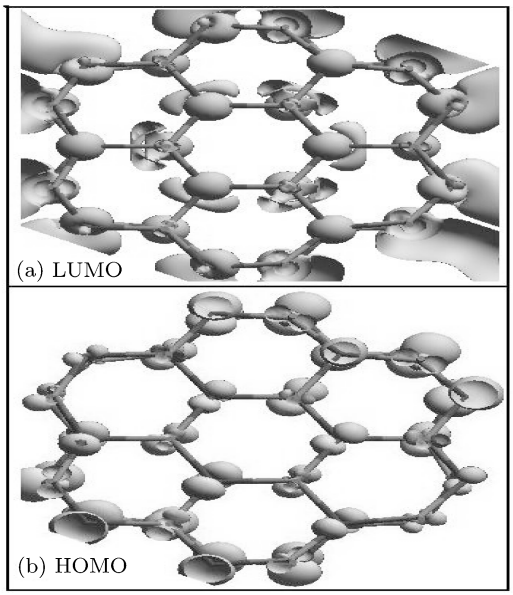


Fig.3. HOMO and LUMO states of ZnO NWs (n = 48). (a) The charge density of the LUMO state at Γ; (b) the charge density of the HOMO state at Γ.

The origin of the band gap change for these ZnO NWs can be seen from the band structures near the highest occupied (HO) states and the lowest occupied (LO) states. As clearly shown in Fig.4, it is found that these ZnO NWs have a direct gap at the relatively high dispersion along the $\Gamma(0,0,0) \rightarrow Z(0,0,0.5)$ direction. The conduction band moves towards the low energy and the optical band gap is narrowed with increasing ZnO NWs size in Figs.4(a)–4(g). But the calculated gaps of ZnO NWs are larger than the bulk band gap ($E_g = 0.91$ eV). The reasons are explained as follows: on the one hand, the lowest occupied (LO) state of ZnO NWs corresponds to the surface atoms, and is mainly contributed by oxygen $2p$ like dangling bonds. On the other hand, interactions among electric charges result in the delocalized character, and the electrons have greater mobility along these surfaces.

In Fig.5, we illustrate the total density of ZnO NWs (n = 48, n = 108), which shows the distribution of the electron cloud. As can be seen from Fig.5, ZnO NWs look like strong ionic characters rather than a covalent character. The pd hybridization is present in ZnO NWs, which indicates that the ZnO NWs are the mixed bonding semiconductor material with ionic bond much stronger than the covalent bond. We can also see that there is only a very weak overlap electron

density between outer layer and inner layer atoms, but the overlap of the same layer atoms is very strong. At the same time, the outer electron cloud produces a significant change in the electron redistribution due to the effect of surface states on electron transport in individual ZnO nanowires.

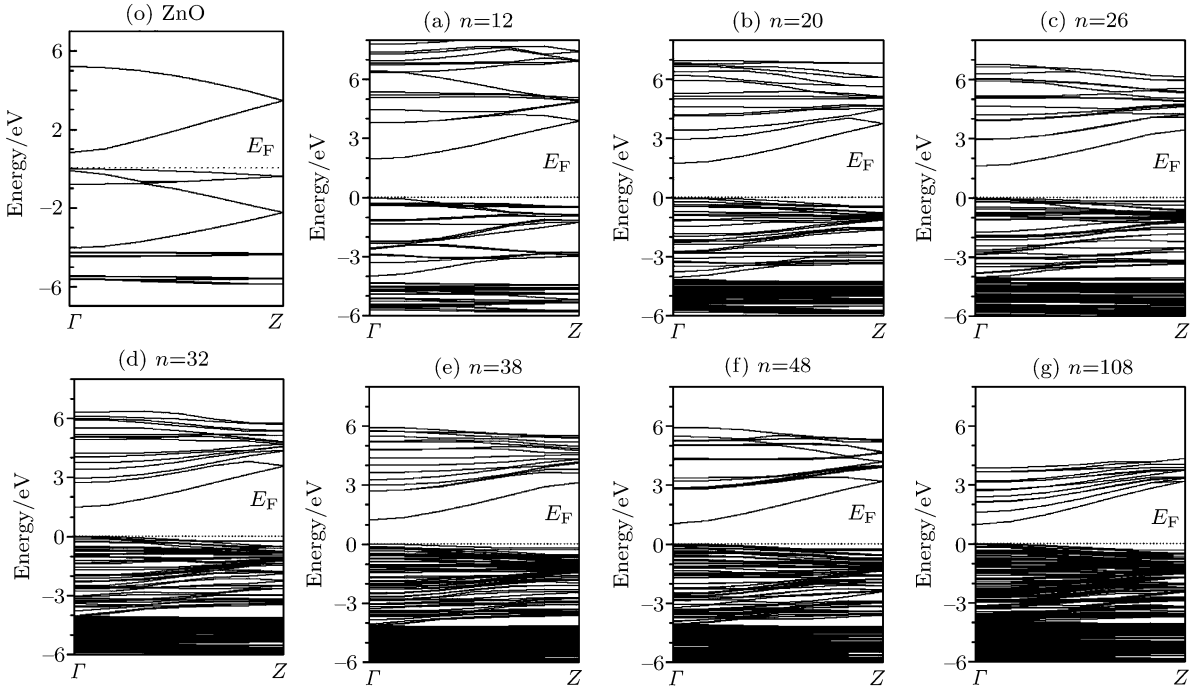


Fig.4. Electronic band structures at different ZnO NWs. Negative energies correspond to valence band states, and positive energies correspond to conduction band states.

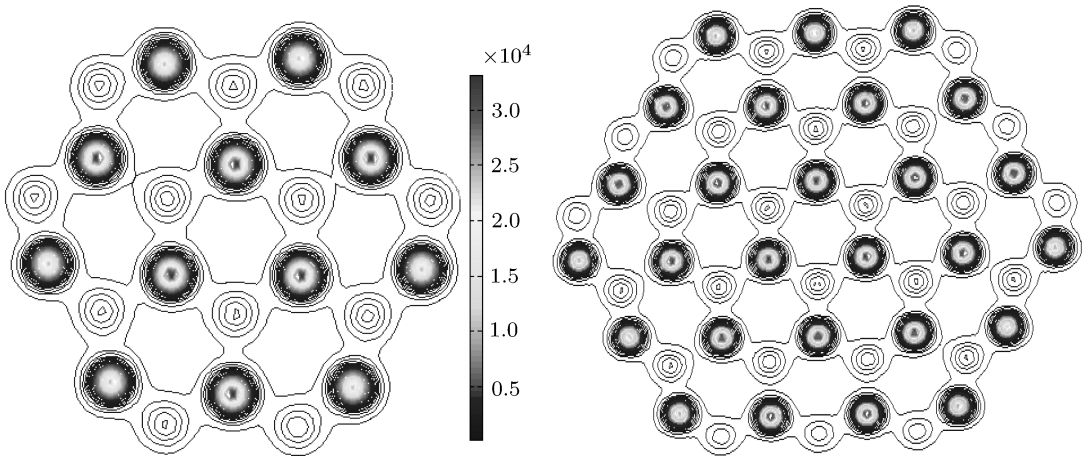


Fig.5. Plot of electron density of ZnO NWs along the (001) direction.

In order to gain further insight into the size-effect of ZnO NWs, the optical properties are calculated by using the first principles. The linear response of a system due to an external electromagnetic field with a small wave vector can be described with the complex dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + \mathrm{i}\varepsilon_2(\omega)$. The imaginary part of the dielectric function $\varepsilon_2(\omega)$ is calculated from the momentum matrix elements between the occupied and unoccupied wave function.[29]

$$\varepsilon_2(\omega) = \frac{Ve^2}{2\pi\hbar m^2\omega^2}\int \mathrm{d}^3k \sum_{n,n'} \langle kn|p|kn'\rangle|^2 f(kn)(1-f(kn'))\delta(E_{kn} - E_{kn'} - \hbar\omega), \quad (1)$$

where $\hbar\omega$ is the energy of the incident photon, V is the unit cell volume, p is the momentum operator, $|kn\rangle$ is a crystal wavefunction and $f(kn)$ is the Fermi distribution function. The other optical parameters like refractive index $n(\omega)$, extinction coefficient $k(\omega)$, reflectivity $R(\omega)$ and absorption coefficient $I(\omega)$ are calculated in terms of the components of the complex dielectric function

$$n(\omega) = \left(\frac{1}{\sqrt{2}}\left[\sqrt{\varepsilon_1(\omega)^2 + \varepsilon_2(\omega)^2} + \varepsilon_1(\omega)\right]\right)^{1/2}, \quad (2)$$

$$k(\omega) = \left(\frac{1}{\sqrt{2}}\left[\sqrt{\varepsilon_1(\omega)^2 + \varepsilon_2(\omega)^2} - \varepsilon_1(\omega)\right]\right)^{1/2}, \quad (3)$$

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}, \quad (4)$$

$$I = \frac{2K\omega}{c}. \quad (5)$$

The calculated absorption spectrum and the imaginary part of the dielectric function are shown in Figs.6 and 7. The scissor approximation (SA) makes the conduction bands rigid-shift towards the higher energy by 2.46 eV, the direct band gap of the ZnO bulk becomes 3.37 eV, in excellent agreement with the experimental results, and the absorption edge is located at 377 nm.[30]

The absorption spectrum of ZnO NWs is amended by the scissor approximation whose value is also equal to 2.46 eV. From Fig.6 we can see that these absorption edges are located at 336, 342, 356, 361, 369, and 373 nm, respectively. The calculated results indicate that the cut-off wavelength of absorption spectra is a significant blue shift with the decrease of the NWs size. These characters will attract much interest due to their significant potential applications in optoelectronic nano-devices.

The calculated dielectric functions $\varepsilon_2(\omega)$ of ZnO NWs are shown in Fig.7, our polarized radiation incident is in [0001] direction. The $\varepsilon_2(\omega)$ spectrum can be divided into two main groups: the low energy one from 2.5 eV to 5 eV and the high energy one from 5 eV to 10 eV. The interband transition absorption of NWs starts from 2.9 eV to 3.8 eV, which mainly originates from the transition from the valence band maximum to the conduction band bottom, and there is an obvious peak in the low energy region and moves greatly towards the high energy region with the decrease of the NWs size. In the high energy region, three prominent peaks come from the transition between the second or third unoccupied states and valence band states. Moreover, the shapes of the dielectric function spectra are very similar, which indicates that the dielectric function of ZnO NWs is relatively insensitive to the diameter. The values of the imaginary part of the dielectric function decrease in the high energy region in comparison with those of the bulk ZnO. The calculated results indicate that the resonance absorption is weakened.

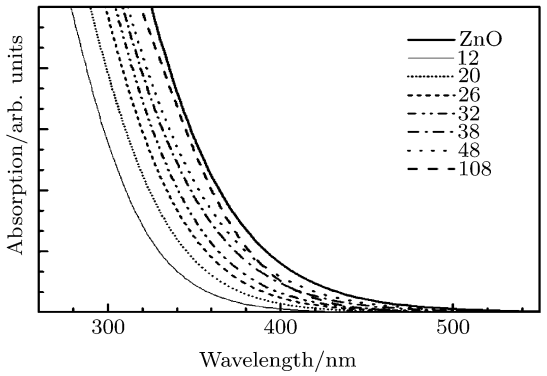


Fig.6. The absorption spectrum of ZnO NWs.

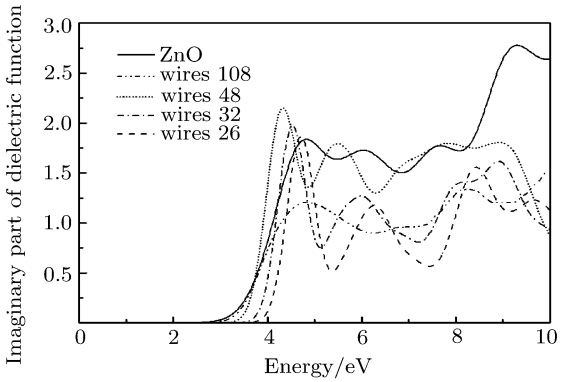


Fig.7. The imaginary part of the dielectric function of ZnO NWs.

4. Conclusions

In summary, we have studied the electronic and optical properties of ZnO NWs by using the first-principles calculation of the plane wave ultra-soft pseudo-potential technology based on the density functional theory (DFT). We find that the band gaps of ZnO NWs have a direct band gap, which is larger than that of ZnO bulk due to the quantum confinement effects, and the surface states of ZnO

NWs greatly affect the electronic structure and optical properties. The calculated results also indicate that the absorption edges shift towards the blue-light region with the decrease of the ZnO NWs size, and the imaginary part of the dielectric function moves towards the higher energy, the optical band gap is broadened. These results promote the application of ZnO NWs as nanodevices, nanoactuators and ultraviolet optoelectronic devices.

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