First-principles calculation of the band structure, electronic states, and optical properties of Cr-doped ZnS double-wall nanotubes

Yuhong Huang a, Zongquan Zhang a, Fei Ma b,c,*, Paul K. Chu c,*, Cuiping Dong a, Xiumei Wei a

a School of Physics & Information Technology, Shaanxi Normal University, Xi’an 710119, Shaanxi, China
b State Key Laboratory for Mechanical Behavior of Materials, X’ian Jiaotong University, X’ian 710049, Shaanxi, China
c Department of Physics and Materials Science, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong, China

A R T I C L E   I N F O

Article history:
Received 12 August 2014
Received in revised form 7 January 2015
Accepted 10 January 2015

Keywords:
ZnS
Double-wall nanotubes
Doping
Optical properties
First-principles calculation

A B S T R A C T

The density functional theory (DFT) and generalized gradient approximation plus U (GGA+U) are adopted to investigate the effects of chromium (Cr) doping on the band structure, density of states (DOS), dielectric functions, and optical absorption of (4,4)@(m,m) (m = 6, 7, 8) double-wall zinc sulfide nanotubes (DW-ZnSNTs). Cr doping is found to produce half-metallic features in the DW-ZnSNTs and the band gaps of the minority spin are expanded for (4,4)@(6,6) DW-ZnSNTs, while they are reduced for (4,4)@(7,7) and (4,4)@(8,8) DW-ZnSNTs. When Cr is doped in the double-wall nanotubes, both the static dielectric constants and static refractive index are increased, but the maximum values of the real and imaginary parts of the dielectric functions, the maximum extinction coefficients, the maximum refractive index and extinction coefficient are decreased slightly. Compared to the pristine ones, the absorption peaks of Cr doped (4,4)@(m,m) DW-ZnSNTs are reduced a little and new peaks appear in the ultraviolet region. If the separation between adjacent walls is increased, light absorption is enhanced but the effects of Cr doping decrease due to the reduced interactions between the inner and outer nanotubes. The results illustrate that the electronic and optical properties of ZnS nanotubes can be improved by metal doping, which is expected to expedite the use of the materials in applications, such as, ultraviolet light-emitting diodes, flat panel displays, and photocatalysis.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Zinc sulfide (ZnS), a II–VI compound semiconductor, with a wide band gap of 3.68 eV at room temperature, exhibits low dispersion in the visible and infrared range and good transmittance and has potential applications in ultraviolet light-emitting diodes, injection lasers, flat panel displays, catalysts, solar energy conversion, and so on. Since the band structure and optical properties of ZnS can be modified by introducing special nanostructures, many research works have been conducted to synthesize ZnS nanoparticles [1,2], nanospheres [3,4], nanosheets [5,6], nanorods [6,7], nanowires [8–11] and nanotubes [12–15] and to study the properties. In particular, ZnS nanotubes are attractive and the techniques, such as, solvothermal processing, hydrothermal method, solid–vacuum deposition and pulsed laser vaporization are exploited in the synthesis of ZnS nanotubes. Shao et al. [16] developed a simple method to prepare ZnS nanotubes by continuous ultrasonic irradiation and they ascribed the formation mechanism of ZnS nanotubes to the Kirkendall effect. Yi et al. [17] prepared ZnS nanotubes by a facile conversion process from ZnO nanorod precursors. In this process, the ZnO nanorods were synthesized and then converted into tubular ZnO/ZnS core/shell structures by a hydrothermal sulfide treatment and finally into ZnS nanotubes after removing the ZnO cores by KOH treatment. Zhai et al. [18] synthesized ZnS nanotube arrays with diameter in the range of 140–250 nm and the length up to tens of micrometers in porous anodic alumina (PAA) membranes by metal organic chemical vapor deposition (MOCVD) and green–blue emission at 510 nm was observed from the photoluminescence spectrum.

A great deal of theoretical works have also been performed to understand the structural stability, band structure, physical properties, as well as their dependence on the chirality, diameter, and wall thickness of ZnS nanotubes. Li et al. [19] found that the formation energy of the multi-wall ZnS nanotubes decreased monotonically with increasing wall thickness irrespective of the tube radius. Pal et al. [20] investigated the structural and energetic properties of ZnS nanotubes by the density functional tight-binding method
and found that ZnS nanotubes had a direct band gap at the Γ point. The band gap depended on the helicity and was always smaller for zigzag nanotubes than that for armchair ones. Moreover, the band gap of zigzag nanotubes decreased with increasing radius, but increased initially and then decreased for armchair nanotubes. Zhang et al. [21] illustrated that DW-ZnSNTs with faceted morphologies were energetically more favorable than single-wall ZnS nanotubes (SW-ZnSNTs) with rounded cross sections and DW-ZnSNTs exhibited stronger quantum confinement effect than ZnS nanosheets with the same thickness did. Li et al. [22] also found that the faceted single-wall ZnS nanotubes are always energetically preferred. In brief, ZnS nanotubes usually exhibit chirality, diameter and wall thickness dependent properties. To the best of our knowledge, the doping effects on ZnS have rarely been studied theoretically but a better theoretical understanding is needed to supplement the experimental results [23,24]. Chromium (Cr) doping can affect the magnetic properties of ZnS nanostructures considerably [25]. In this work, taking (4,4)@(m,m) (m = 6, 7, 8) DW-ZnSNTs (4 and m are the chirality index and the characteristic sizes of the inner and outer nanotubes) as examples, the effects of Cr doping on the band structures, electronic states, and optical properties are studied by first principles calculation.

2. Computational model and method

Nanotube models, such as, carbon nanotubes and boron nitride (BN) nanotubes can usually be constructed by one-atom-thick layer with hexagonal lattices along a given direction represented by a pair of indices (n, m). The integers, n and m, denote the number of unit vectors along the two directions in the honeycomb crystal lattice. The nanotubes are called zigzag if m = 0, while they are

Fig. 1. Cross-sectional view of pristine (4,4)@(7,7) DW-ZnSNT (a) before and (b) after geometric optimization, cross-sectional view of Cr doped (4,4)@(7,7) DW-ZnSNT (c) before and (d) after geometric optimization. Blue, red and green balls represent Zn, S and Cr atoms, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 2. (a) Band structure and (b) density of states of (4,4)@(6,6) DW-ZnSNTs.

Fig. 3. Spin-polarized band structures of Cr doped (4,4)@(6,6) DW-ZnSNTs using GGA+U: (a) majority spin and (b) minority spin.
armchair if $m = n$ [20]. $(4,4) @(m, m)$ DW-ZnSNTs with $m$ values of 6, 7 and 8 are investigated and both the inner and outer nanotubes are armchair orientated. The bond length between adjacent Zn and S atoms is set to be 2.3 Å. The lattice constant along the axial direction is 3.98 Å, the same as the experimental value, and the periodic condition is adopted along this direction to simulate infinitely long nanotubes. The diameter of the inner (4,4) ZnS nanotube is 8.79 Å and, the diameters of the outer (6,6), (7,7) and (8,8) ZnS nanotubes are 13.18 Å, 15.37 Å and 17.57 Å, respectively. A vacuum slab 20 Å thick is created along the radial direction to avoid interactions among adjacent nanotubes. The models of Cr doped structures are constructed by replacing one Zn atom on the inner tube wall by one Cr atom, corresponding to a doping composition of 4–5%. For example, Fig. 1 shows the atomic models of a pristine $(4,4)@(7,7)$ DW-ZnSNTs and Cr-doped configuration before and after geometric optimization. Apparently, after structural optimization, the double-wall configurations become distorted and faceted as a result of energy minimization.

First-principles calculation is performed based on the density functional theory (DFT) [26] implemented in the Cambridge

**Table 1**

Critical values of electronic band structures and optical parameters of the pristine and Cr doped $(4,4) @(m, m)$ DW-ZnSNTs calculated by using the GGA+U correlation-exchange potential.

<table>
<thead>
<tr>
<th>ZnS$(4,4) @(m, m)$</th>
<th>ZnS:Cr$(4,4) @(m, m)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Band gap (eV)</td>
<td>$E_g$</td>
</tr>
<tr>
<td></td>
<td>2.403</td>
</tr>
<tr>
<td>Half-metallic band gap (eV)</td>
<td>$E_g$</td>
</tr>
<tr>
<td></td>
<td>2.345</td>
</tr>
<tr>
<td>Real part of $\varepsilon$</td>
<td>$\varepsilon_1(0)$</td>
</tr>
<tr>
<td></td>
<td>2.04</td>
</tr>
<tr>
<td></td>
<td>1.78</td>
</tr>
<tr>
<td></td>
<td>2.24</td>
</tr>
<tr>
<td></td>
<td>1.78</td>
</tr>
<tr>
<td></td>
<td>2.24</td>
</tr>
<tr>
<td>Imaginary part of $\varepsilon$</td>
<td>$\varepsilon_2$</td>
</tr>
<tr>
<td></td>
<td>1.79</td>
</tr>
<tr>
<td></td>
<td>1.41</td>
</tr>
<tr>
<td></td>
<td>1.34</td>
</tr>
<tr>
<td></td>
<td>1.34</td>
</tr>
<tr>
<td>Refractive index</td>
<td>$n(0)$</td>
</tr>
<tr>
<td></td>
<td>1.43</td>
</tr>
<tr>
<td></td>
<td>1.34</td>
</tr>
<tr>
<td></td>
<td>1.34</td>
</tr>
<tr>
<td>Extinction coefficient</td>
<td>$k_{1}$</td>
</tr>
<tr>
<td></td>
<td>0.64</td>
</tr>
<tr>
<td></td>
<td>0.54</td>
</tr>
<tr>
<td></td>
<td>0.54</td>
</tr>
<tr>
<td>Absorption</td>
<td>$\alpha_{\infty}$</td>
</tr>
<tr>
<td></td>
<td>83189.29</td>
</tr>
<tr>
<td></td>
<td>62787.08</td>
</tr>
<tr>
<td></td>
<td>80195.68</td>
</tr>
<tr>
<td></td>
<td>60284.38</td>
</tr>
</tbody>
</table>

**Fig. 4.** (a) Spin-polarized total density of states and partial density of states (PDOS) of (b) Cr, (c) Zn, and (d) S in Cr doped $(4,4) @(6,6)$ DW-ZnSNTs using GGA+U.
Sequential Total Energy Package (CASTEP) [27]. The band gap, density of states, complex refractive index, complex dielectric functions, and optical absorption spectra of the Cr doped DW-ZnSNTs are analyzed and compared to those of the pristine DW-ZnSNTs. The generalized gradient approximation plus U (GGA+U) in the Perdew–Burke–Ernzerhof (PBE) form is selected as the exchange–correlation potential with the optimized U value of 10. The cutoff energy of the plane wave function is 350 eV. The structures of the pristine and Cr doped (4,4)@(m,m) DW-ZnSNTs are fully relaxed with an energy convergence of \( 5 \times 10^{-6} \) eV and a force convergence of 0.01 eV/Å. The maximum atom displacement is less than \( 5 \times 10^{-4} \) Å and self-consistent field (SCF) tolerance is \( 5 \times 10^{-7} \) eV. The Brillouin-zone integration is carried out by using a \( 1 \times 1 \times 6 \) k-mesh according to the Monkhorst–Pack scheme and the electronic configurations considered are Zn 3d\(^{10}\)4s\(^2\), Cr 3d\(^{5}\)4s\(^1\), and S 3s\(^2\)3p\(^4\).

3. Results and discussion

3.1. Band structure and density of states

All the pristine (4,4)@(m,m) DW-ZnSNTs have similar electronic band structures and density of states. For example, Fig. 2(a) and (b) present the results of the pristine (4,4)@(6,6) DW-ZnSNTs. As shown in Fig. 2(a), both the valence band top and the conduction band bottom are located at the same k point, G, characteristic of a direct band gap semiconductor. It means that the DW-ZnSNTs may exhibit strong electroluminescence and photoluminescence.

Fig. 2(b) shows that the valence band of the (4,4)@(6,6) DW-ZnSNTs is divided into three regions. The lower valence band in the energy range of \(-13.28 \text{ to } -10.07 \text{ eV} \) is mainly composed of the S-3p orbital, the middle valence band in the energy range of \(-7.37 \text{ to } -4.68 \text{ eV} \) is mainly contributed by the S-3p state. The upper valence band in the energy range of \(-4.68 \text{ to } 0 \text{ eV} \) is mainly contributed by the S-3p state. The calculated band gaps are 2.403 eV, 1.936 eV, and 2.345 eV for the pristine (4,4)@(6,6) DW-ZnSNTs with m values of 6, 7, and 8, respectively. They are much smaller than that of bulk wurtzite ZnS (3.77 eV) [28,29] due to the quantum confinement effect and the well-known limitation of the DFT method [30]. Moreover, the band gaps of the DW-ZnSNTs with even m values are nearly the same but larger than those of DW-ZnSNTs with odd m values, which is consistent with published works. This corroborates the selected calculation parameters for the DW-ZnSNTs.

Since Cr has highly localized 3d electrons, it is necessary to choose GGA+U as the exchange–correlation potential. For example, Fig. 3 shows the electronic band structure of Cr doped (4,4)@(6,6) DW-ZnSNTs using GGA+U as the exchange–correlation potential. The spin-polarized characteristics are identified, that is, the band structure is different for the majority and minority spins. As shown in Fig. 3(a), several discrete impurity levels appear in the band structure of the majority, i.e. spin-up state, and the Fermi level crosses the impurity bands. However, there is still a wide band gap for the minority, i.e. spin-down state, as shown in Fig. 3(b). It is characteristic of the half-metallic features. The half-metallic band gap is defined to indicate the energy difference between

![Fig. 5](image-url)  
Fig. 5. (a) Real part and (b) imaginary part of the complex dielectric function of pristine (4,4)@(m,m) DW-ZnSNTs, and (c) real part and (d) imaginary part of the dielectric function of Cr doped (4,4)@(m,m) DW-ZnSNTs.
the minimum of the conduction band and the maximum of the valence band of the minority state. The band gaps and half-metallic band gaps of the pristine and Cr doped (4,4)@((m, m)) DW-ZnSNTs are listed in Table 1. The half-metallic band gaps are 2.441 eV, 1.817 eV and 2.234 eV for Cr doped (4,4)@((m, m)) DW-ZnSNTs with m values of 6, 7 and 8, respectively by using GGA+U. The results change only a little when GGA+U rather than GGA correlation-exchange potential is adopted. The half metallic features suggest that the Cr doped DW-ZnSNTs may be adopted as diluted magnetic semiconductors.

Fig. 4 presents the total and partial density of states of the Cr doped (4,4)@((6,6)) DW-ZnSNTs. The lowest valence band in the energy range of −8.62 to −6.04 eV is mainly composed of the Zn-3d orbital and some hybridized Zn-3s, Zn-3p, S-3s and S-3p orbitals. The middle valence band in the energy range of −6.04 to −1.37 eV is contributed by all the atoms. The highest valence band in the energy range from −1.37 eV to the Fermi level is mainly contributed by the Cr-3d orbital and some hybridized S-3p orbital. As shown in Fig. 4(a), the total density of states is almost symmetrical below −1.37 eV for the majority and minority spin, but the total density of states for the majority exceeds that for the minority spin in the energy range from −1.37 eV to the Fermi level. The partial density of states of Cr is completely asymmetrical near the Fermi level for the majority and minority spins (Fig. 4(b)), but those of Zn and S atoms are almost symmetrical (Fig. 4(c) and (d)). Moreover, there is non-zero density of states across the Fermi energy only for the spin-up state of Cr-3d. So the exchange interaction between the spin-up and spin-down states of the Cr-3d orbital results in energy splitting and half-metallic characteristics.

3.2. Optical properties

The optical properties of semiconductors can usually be described by complex dielectric functions assuming that the optical response is in the linear range [31]. The complex dielectric function is defined as \( \varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) \) and closely related to the interactions of electrons and photons. The optical spectrum as well as inter-band transition of electrons can be obtained accordingly. The imaginary part of the dielectric function, \( \varepsilon_2(\omega) \), can be calculated by the correlation density of states in the occupied and unoccupied orbitals, whereas the real part of the dielectric function, \( \varepsilon_1(\omega) \), is obtained from \( \varepsilon_2(\omega) \) by the Kramers–Kronig relationship [32]. The refractive index, \( n(\omega) \), and the extinction coefficient, \( k(\omega) \), are also used to describe the optical properties and equivalent to \( \varepsilon_1(\omega) \) and \( \varepsilon_2(\omega) \) in most cases. The conversion relationships among \( \varepsilon_1(\omega) \), \( \varepsilon_2(\omega) \), \( n(\omega) \) and \( k(\omega) \) are:

\[
\varepsilon_1(\omega) = 1 + \frac{2}{\pi} \int_0^\infty \frac{\omega' \varepsilon_2(\omega') d\omega'}{\omega'^2 - \omega^2},
\]

\[
\varepsilon_2(\omega) = \frac{2\omega}{\pi} \int_0^\infty \frac{\varepsilon_1(\omega') - 1}{\omega'^2 - \omega^2} d\omega',
\]

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

\[
k(\omega) = \frac{1}{\sqrt{2}} \left[ (\varepsilon_1^2 + \varepsilon_2^2)^{1/2} - \varepsilon_1 \right]^{1/2}.
\]
Fig. 5 shows the dispersion relationships of dielectric functions of the pristine DW-ZnSNTs and Cr doped ones. As shown in Fig. 5(a), the static dielectric constants (at 0 eV) are 2.04, 1.92 and 1.78 for the pristine (4,4)@(6,6), (4,4)@(7,7) and (4,4)@(8,8) DW-ZnSNTs, respectively. Apparently, they decrease with increasing separations between adjacent tube walls or with increasing diameter of the outer nanotube. This can be ascribed to the weakened interaction between the inner and outer nanotubes. In the low energy region, the real parts of the dielectric functions increase with photon energy initially, reach at the maximum values of 2.65, 2.42 and 2.24 at 3.80 eV, 3.89 eV and 3.97 eV, and then decrease to the minimum values of 0.39, 0.52 and 0.58 at 9.12 eV, 8.90 eV, and 8.95 eV for the DW-ZnSNTs with m values of 6, 7 and 8, respectively. With regard to the imaginary part of each dielectric function (Fig. 5[b]), the peak values of 1.79, 1.58 and 1.41 are at 5.50 eV, 5.46 eV and 5.43 eV, respectively, and the peak slightly red-shifts with increasing diameter of the outer nanotube. All the critical optical parameters of pristine and Cr doped (4,4)@(m,m) DW-ZnSNTs are listed in Table 1.

The complex dielectric functions of the Cr doped DW-ZnSNTs resemble those of the pristine ones, but the static dielectric constant and the maximum values of the real and imaginary parts of the dielectric functions are increased due to Cr doping (Fig. 5[c] and [d]). The static dielectric constant is increased by 7.4%, 6.8%, and 10.7% for the Cr doped DW-ZnSNTs with m values of 6, 7 and 8, respectively. The maximum value of the real part of the dielectric function is increased by 2.6%, 2.1%, and 1.8% and the maximum value of imaginary part of the dielectric function is increased by 2.2%, 3.8%, and 0.7%. Hence, Cr doping should influence light absorption of the DW-ZnSNTs, depending on the separation between adjacent inner and outer nanotubes or the diameter of the outer nanotube.

As shown in Fig. 6(a) and (c), the static refractive indexes are 1.43, 1.39 and 1.34 for the (4,4)@(m,m) DW-ZnSNTs with m values of 6, 7 and 8, respectively and are increased to 1.48, 1.43 and 1.40 due to Cr doping. Moreover, red-shifts are observed from the peaks of refractive index n for the (4,4)@(6,6) and (4,4)@(7,7) DW-ZnSNTs. For example, the refractive index peak of (4,4)@(6,6) DW-ZnSNTs red-shifts from 3.89 eV to 3.97 eV. As shown in Fig. 6(b) and (d), two peaks appear in the extinction coefficients, which may be caused by the double-wall configuration, and it seems that the peaks are slightly decreased due to Cr doping.

As shown in Fig. 7, no absorption is observed in the infrared region before doping and the maximum absorption peaks appear at 8.07 eV, 8.03 eV and 8.03 eV for the (4,4)@(m,m) DW-ZnSNTs with m values of 6, 7, and 8, respectively. The adsorption peaks of Cr doped (4,4)@(m,m) DW-ZnSNTs are reduced a little at the energies of 8.14 eV, 8.01 eV and 8.03 eV, respectively due to Cr doping. Moreover, new peaks emerge at around 42 eV in the ultraviolet region. As a result, the optical properties of ZnS nanotubes can be improved or modified by metal doping thus boding well for application to ultraviolet light-emitting diodes, flat panel displays, photocatalysis, and solar energy conversion.

4. Conclusions

The electronic and optical properties of pristine and Cr doped (4,4)@(m,m) DW-ZnSNTs are investigated by first-principles calculation within the density functional frame and, GGA+U exchange correlation potential is adopted. The DW-ZnSNTs exhibit half-metallic features due to Cr doping, indicating the potential applications as diluted magnetic semiconductors. The half-metallic band gaps change only a little due to Cr doping. As for the pristine DW-ZnSNTs with m values of 6, 7 and 8, the static dielectric constants are 2.04, 1.92 and 1.78. The real parts of the dielectric functions have the maximum values of 2.65, 2.42 and 2.24 at 3.80 eV, 3.89 eV and 3.97 eV, respectively, while the imaginary parts have the maximum values at 5.50 eV, 5.46 eV and 5.43 eV. The complex dielectric functions of the Cr doped nanotubes resemble those of the pristine ones. The static dielectric constants are increased due to Cr doping, while the maximum values of the real and imaginary parts of the dielectric functions are decreased. Correspondingly, the static refractive index is increased, but the maximum refractive index and the maximum extinction coefficient are decreased slightly. The adsorption peaks are reduced a little and new peaks emerge in the ultraviolet region as a result of Cr doping. Hence, the electronic and optical properties of ZnS nanotubes can be modified by metal doping, which will have potential applications in ultraviolet light-emitting diodes, flat panel displays, photocatalysis, and solar energy conversion.

Acknowledgments

This work was supported by the National Science Foundation of China (Nos. 51302162, 51471130 and 51271139), the Fundamental Research Funds for the Central Universities Program (No. GK201302012), the Natural Science Foundation of Shaanxi Province in China (Nos. 2014Q1016 and 2013JM6002) and Guangdong-Hong Kong Technology Cooperation Funding Scheme (TCFS) GHP/015/12SZ.
References