Invariant wide bandgaps in honeycomb monolayer and single-walled nanotubes of IIB–VI semiconductors

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Abstract
The search for low-dimensional materials with unique electronic properties is important for the development of electronic devices in the nanoscale. Through systematic first-principles calculations, we found that the band gaps of the two-dimensional honeycomb monolayers (HMs) and one-dimensional single-walled nanotubes (SWNTs) of IIB–VI semiconductors (ZnO, CdO, ZnS and CdS) are nearly chirality-independent and weakly diameter-dependent. Based on analysis of the electronic structures, it was found that the conduction band minimum is contributed to by the spherically symmetric s orbitals of cations and the valence band maximum is dominated by the in-plane (dxy − px) and (dyz − p2) hybridizations. These electronic states are robust against radius curvature, resulting in the invariant feature of the band gaps for the structures changing from HM to SWNTs. The band gaps of these materials range from 2.3 to 4.7 eV, which is of potential application in electronic devices and optoelectronic devices. Our studies show that searching for and designing specific electronic structures can facilitate the process of exploring novel nanomaterials for future applications.

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((Some figures may appear in colour only in the online journal)

1. Introduction
Advances in modern technologies accelerate miniaturization of electronic devices, which drives the endeavors for exploring exotic materials in the nanoscale. In the last two decades, a lot of low-dimensional materials such as clusters [1], nanotubes [2], and atomically thin films [3, 4] have been discovered. These low-dimensional materials exhibit intriguing and abundant physical properties, ranging from metallic conductor to semiconductor, which guarantee them promising wide applications in electronic and optoelectronic devices in the nanoscale [5–9].

As the first discovered one-dimensional material [2], carbon single-walled nanotubes (SWNTs) were investigated extensively for possible applications in a new generation of electronic devices. However, the electronic properties of the carbon SWNTs depend on their chirality and diameter. For example, the (n, m) carbon SWNTs are metallic when n − m = 3l (l is an integer), while the others are semiconducting [10–12]. This largely hinders the application of carbon SWNTs, because it is difficult to repeatedly fabricate carbon SWNTs with exactly the same chirality and diameter, so that all the products (i.e. carbon SWNTs) have the same electronic property. Therefore, invariably semiconducting SWNTs such as boron nitride (BN) SWNTs are more favorable for applications in electronic devices [13–16]. Interestingly, the band gaps of armchair (n, n) BN SWNTs are almost constant and independent of the diameters, while
those of zigzag \((n, 0)\) BN SWNTs decrease as the diameters decrease [13, 15]. These electronic features are mainly attributed to the \(sp^2\sigma + pp\pi\) hybridizations of the valence orbitals [12, 16]. The \(sp^2\sigma\) hybridization mainly contributes strong in-plane chemical bonds, while the \(pp\pi\) hybridization contributes electronic states near the Fermi energy. Therefore, the electronic properties of the carbon and BN SWNTs are mainly dominated by \(pp\pi\) hybridization. It is known that \(pp\pi\) hybridization occurs between the \(p\) orbitals. Since the spatial distribution of the \(p\) orbital is perpendicular to the cylinder surface of carbon and BN SWNTs, \(pp\pi\) hybridization is sensitively affected by the chirality and diameter of the carbon and BN SWNTs. Consequently, the electronic properties of carbon and BN SWNTs are chirality- and diameter-dependent.

Recently, the SWNTs of wide-bandgap semiconductor ZnO were studied extensively [17–22]. It was found that the band gaps of ZnO SWNTs are almost insensitive to the chirality and diameter, being significantly different from carbon and BN SWNTs. However, the microscopic origin of this feature in ZnO SWNTs is still unclear. Furthermore, no SWNTs of wide-bandgap semiconductor have been synthesized in experiments so far. Nevertheless, recent first-principles calculations predicted that the ultrathin (0001) surface of wurtzite (WZ) IIB–VI and III–V semiconductors prefers to adopt a honeycomb lattice due to the electrostatic interaction between cation and anion layers [23]. This prediction was confirmed by experiments for the cases of ZnO [24] and GaN [25]. These achievements are the precursors for fabricating SWNTs of WZ IIB–VI and III–V semiconductors, because the SWNTs are the transformation of a honeycomb monolayer (HM) by rolling up the latter [26]. Therefore, the HMs and SWNTs of WZ IIB–VI and III–V semiconductors may be produced in experiment under proper conditions and applied in electronic devices in the future. Clearly, revealing the electronic features of the HMs and SWNTs of these semiconductors is useful and important for the design of these materials in electronic devices.

In this paper, taking ZnO, CdO, ZnS and CdS as the prototypes of IIB–VI semiconductors, we studied the stabilities and electronic properties of the HMs and SWNTs, by using first-principles calculations. We found that both the HMs and SWNTs are structurally stable, and their band gaps are insensitive of their chirality and diameter. The analysis of the electronic structures revealed that the \(d\) orbital of Zn and Cd play crucial roles in the electronic characteristics.

2. Computational details

All calculations were performed by using the first-principles pseudopotential method based on density functional theory (DFT) within local density approximation (LDA) as implemented in the SIESTA package [27]. The pseudopotentials were constructed by the Troullier–Martins scheme [28]. The Ceperley–Alder exchange-correlation functional [29] as parameterized by Perdew and Zunger [30] was employed. In our calculations, the double-\(\zeta\) plus polarization basis sets were chosen for all atoms. For the HMs and SWNTs, the \(20 \times 20 \times 1\) and \(1 \times 1 \times 20\) \(k\)-grid meshes within the Monkhorst–Pack scheme [31] in the Brillouin zone were considered, respectively. The atomic structures were fully relaxed using the conjugated gradient method until the Hellman–Feynman force on each atom is smaller than 0.01 eV Å\(^{-1}\). The generalized gradient approximation (GGA) with PBE functional [32] within the SIESTA package and B3LYP hybrid functional [33] within the CRYSTAL03 package were also employed to explore the effect of different functionals on the electronic properties. In the B3LYP calculations, the Stuttgart–Dresden effective core pseudopotentials (ECP) [34] were used.

3. Results and discussions

3.1. WZ bulk versus HM

Most IIB–VI and III–V compounds crystallize WZ structure as shown in figure 1(a). The cations and anions stack layer by layer alternatively along the (0001) direction. If we cut a two-layer slab composed of one cation layer and one anion layer as indicated by the dashed rectangle in figure 1(a), the Coulomb interaction between them transforms the slab into a planar honeycomb structure [23], as shown in figure 1(b). Therefore, we chose ZnO, CdO, ZnS and CdS as the prototypes of WZ IIB–VI semiconductors to investigate the structural and electronic properties of their HMs. We firstly optimized the atomic structures of ZnO, CdO, ZnS and CdS in WZ and HM phases. As listed in table 1, the bond length between cation and anion in the HM phase is shorter by 3%–5% than that in the corresponding WZ phase, due to the reduction of dimensions of the materials. In addition, the binding energies of all considered cases are negative, indicating that the interaction between cations and anions are energetically exothermal. For each compound, the binding energy of the HM phase is higher than that of the WZ phase, which is reasonable because the WZ is the ground state phase.
Table 1. Bond length (in Å) between cations and anions, and binding energy (\(E_b\), in eV per formula unit), and band gap (\(E_g\), in eV) of ZnO, CdO, ZnS and CdS in WZ and HM. Δ is the contraction of bond lengths in HM compared to that in WZ. The values in parentheses are experimental band gaps.

|       | Bond length | \(E_b\) | \(E_g\) |
|-------|-------------|---------|---------|
|       | WZ          | HM      | WZ      | HM      |
| ZnO   | 1.99        | 1.90    | 4.62    | −9.19   | −8.26   | 0.94 (3.44) | 2.03 |
| CdO   | 2.18        | 2.10    | 3.44    | −7.81   | −6.82   | 0.00 (0.84) | 0.77 |
| ZnS   | 2.34        | 2.23    | 4.95    | −7.69   | −6.81   | 2.19 (3.91) | 2.79 |
| CdS   | 2.53        | 2.42    | 4.46    | −6.82   | −5.93   | 0.96 (2.48) | 1.64 |

To further investigate the stability of the HM phase of these compounds, we calculated the phonon dispersions of ZnO HM by using the ‘frozen phonon’ approach [35]. As shown in figure 1(c), the optical and acoustical branches are well separated and all branches have a positive frequency. Therefore, the HM phase is a metastable phase of ZnO, in agreement with the experimental observation [24]. This conclusion can be extended to other compounds considered in this work.

Then we calculated the band gaps of all cases as listed in table 1. Clearly, the band gap (\(E_g\)) of the HM phase is significantly larger than that of the WZ phase for each compound. For example, the \(E_g\) of ZnO HM increases by about 1.1 eV, from 0.94 eV in WZ ZnO to 2.03 eV. Note that the \(E_g\) of WZ ZnO from our LDA calculation is much smaller than the experimental value (3.4 eV) [36, 37], because the DFT calculations usually underestimate the band gaps of semiconductors. It is even worse for WZ CdO, of which the calculated \(E_g\) is less than 1 meV, in agreement with previous theoretical reports [38, 39], but obviously wrong since CdO is a semiconductor with indirect \(E_g\) of 0.84 eV and direct \(E_g\) of 2.28 eV [40]. This problem may be relieved by using a hybrid functional such as B3LYP [41], which will be discussed in more details later. Nonetheless, the significant widening of the band gaps is still qualitatively reasonable, since it originates from the change of geometric symmetry and quantum confinement effect.

To reveal the electronic feature of these HMs, we chose ZnO as prototype and plotted the band structures and DOS in WZ and HM phases in figure 2. From the band structures in figures 2(a) and (b), it can be seen that both WZ and HM ZnO are direct-band gap semiconductors, with the valence band maximum (VBM) and conduction band minimum (CBM) at \(\Gamma\) point. However, the band dispersions are significantly different. Furthermore, a gap from \(-5\) to \(-4\) eV appear in the band structure of the HM phase. From the DOS in figures 2(c) and (d), the states from \(-6.5\) to 5 eV are mainly contributed from Zn–3d orbitals, the states ranging \(-4\) to 0 eV are from O–2p orbitals, and the states near the CBM are from Zn–4s orbital.

In the WZ structure, any atom locates at the center of the tetrahedron composed of four neighboring atoms of the other type of element. Therefore, the \(s\) and \(p\) orbitals of anions adopt the \(sp^3\) hybridization and then hybridize with all components of the \(d\) orbitals of cations. On the contrary, in the HM phase, the \(s\) and \(p\) orbitals of anions adopt the \(sp^2\) hybridization, and the \(d\) orbitals of cations split into three group: \(d_{xz/yz}\), \(d_{x^2−y^2}\) and \(d_{3z^2−r^2}\). Consequently, hybridizations in the HM phase should be significantly different from those in the WZ phase. To reveal the role of hybridizations in the electronic properties, we calculated the radial wavefunctions of the energy levels at \(\Gamma\) point. The VBM of ZnO HM is doubly degenerate and mainly originates from the anti-bonding states of the in-plane \((d_{xy}−p_x)\) and \((d_{z^2}−p_z)\) hybridizations, as shown in the insets in figure 2(b). The corresponding bonding states are 6.6 eV below, manifesting the strong interactions between O–2p and Zn–3d and Zn–4p orbitals. In addition, the energy level at \(-2.3\) eV (\(\Gamma\) point) is mainly contributed from O–2p orbital, mixed with a little part of Zn–4p orbital. This state represents weak pp\(\pi\) hybridization between O–2p and Zn–4p orbitals. The narrow bands near \(-5.0\) eV are from \(d_{z^2}\) and \(d_{x^2−y^2}\) of Zn atom, implying that the \(d_{z^2}\) and \(d_{x^2−y^2}\) orbitals maintain an atomic orbital feature and do not hybridize with O–2p orbitals. Therefore, the in-plane \((d_{xy}−p_x)\) and \((d_{z^2}−p_z−p_y)\) hybridizations dominate both the chemical bonds and electronic states around the Fermi energy, which is different from the electronic nature of C and BN monolayers. The electronic structures of other compounds considered in this work have similar features as ZnO, but the relative positions of the energy levels are different due to the different atomic sizes and bond lengths (see table 1).

3.2. Single-walled nanotubes

The atomic structures of the SWNTs of ZnO, ZnS, CdO and CdS are similar to the BN SWNTs, with cations (Zn and Cd) and anions (O and S) replacing the B and N atoms, respectively. For all compounds, we considered zigzag SWNTs from \((5, 0)\) to \((21, 0)\) and armchair SWNTs from \((3, 3)\) to \((12, 12)\), with the radius varying from 2.9 to 14.5 Å. Both the atomic positions and the axial lattice constants are optimized. In these SWNTs, the walls are buckled, with the outer and inner cylinders composed of anions and cations, respectively. From figure 3(a), it can be seen that the amplitudes of the buckling are dependent on the radii of the SWNTs but independent of the chirality. For each compound, the smaller the radius is, the larger the buckling is. Interestingly, the overall radius buckling of the oxide SWNTs is much smaller than that of the sulfide SWNTs. The buckling can be as large as 0.6 Å for small CdS SWNTs (e.g. \((5, 0)\) and \((3, 3)\)), and still be \(\sim 0.4\) Å for those with radii of \(\sim 14\) Å. On the other
hand, the buckling is only $\sim 0.2\,\text{Å}$ for $(5, 0)$ and $(3, 3)$ ZnO SWNTs whose radii are smaller than $3\,\text{Å}$, and decreases to $\sim 0.05\,\text{Å}$ when the radius reaches $11\,\text{Å}$. This phenomenon originates mainly from the different ionicity of oxide and sulfide compounds. In fact, the ionicity of oxide compounds (ZnO and CdO) is much stronger than that of sulfide compounds (ZnS and CdS). Therefore, the Coulomb interaction in oxide compounds is stronger than that in sulfide compounds, which results in smaller radius buckling between cation and anion cylinders.

Usually, rolling up a HM to form a SWNT requires extra energy which is defined as strain energy ($E_s$) [19],

$$E_s = E_{\text{SWNT}} - E_{\text{HM}},$$

where $E_{\text{SWNT}}$ and $E_{\text{HM}}$ are the total energies per formula unit of a SWNT and a HM, respectively. Usually, the probability of the formation of SWNTs depends on their strain energies: smaller strain energy corresponds to larger probability. As shown in figure 3(b), the amplitudes of the strain energies are almost independent of the chirality for all the SWNTs. Consequently, the probabilities of the formations of zigzag and armchair SWNTs of the same compound are nearly the same, if their diameters are the same. For the oxide SWNTs, the strain energies are positive, which implies that the oxide SWNTs are less stable than the corresponding HMs. In addition, the $E_s$ decreases as the radius increases, and approaches to zero for large SWNTs. On the contrary, the strain energies of sulfide SWNTs are negative, which indicates that the process of rolling up a sulfide HM is energetically exothermic. Therefore, a sulfide HM may not exist, it rolls up to form a SWNT spontaneously. As a consequence, it may be easier to fabricate sulfide SWNTs than oxide SWNTs.

Then we calculated the band structures of all SWNTs and plotted the band gaps in figure 4. Obviously, it can be seen that all SWNTs are semiconducting. The band gaps of CdO, ZnS and CdS SWNTs are larger than that of the corresponding HMs and decrease as the radii increase. The maximum deviations of the band gaps from those of the HMs are 0.23, 0.20 and 0.42 eV, respectively for CdO, ZnS and CdS SWNTs. Nonetheless, these deviations are much smaller than

![Figure 2. Band structures and density of states (DOS) of ZnO in the WZ phase ((a) and (c)) and the HM phase ((b) and (d)). The valence band maximum is set to zero point of energy. The insets in (b) are the spatial distribution of the radial wavefunctions of the energy levels indicated by the red arrows at $\Gamma$ point. These energy levels correspond to the bonding and anti-bonding states of $(d_{xy} - p_y)$ (left) and $(d_{z^2}-p_z)$ (right) hybridizations, respectively. The cutoff of the isosurfaces is 0.1 electrons Å$^{-3}$. The red and gray spheres stand for O and Zn atoms, respectively. The green and blue isosurfaces represent positive and negative wave functions. The gray areas in (c) and (d) are the total DOS. The black, red and blue curves are the projected density of states of $O-2p$, Zn-4s and Zn-3d orbitals, respectively.](image)
other kinds of SWNTs such as BN and SiC SWNTs in literature (about 1–3 eV) [15, 16, 42, 43]. Furthermore, the band gaps of these SWNTs are independent of the chirality. On the contrary, the band gaps of ZnO SWNTs with radii smaller than 6 Å depend on the chirality: the band gaps of the zigzag SWNTs are smaller than that of the HM ZnO, whereas the band gaps of the armchair SWNTs are larger than that of the HM ZnO. However, the deviations of the band gaps from that of the HM ZnO is quite small, with the maximum difference of only 0.08 eV and the band gaps of the ZnO SWNTs with radii larger than 6 Å are almost the same as that of HM ZnO. We should point out that the invariant character of the band gaps of these materials implies that it is not necessary to exactly control the chirality and diameter of the SWNTs to obtain one-dimensional semiconductors with the same band gap. Therefore, opposite to the carbon SWNTs whose chirality- and diameter-dependent electronic property hinders their applications in the electronic devices, the oxide and sulfide SWNTs considered in this work are very promising for future applications in electronic devices, because their particular electronic property affords large flexibility for the process of producing these SWNTs as building blocks of electronic devices.

It is known that DFT calculations with conventional functionals such as LDA and GGA usually underestimate the band gaps of semiconductors. Fortunately, hybrid functional B3LYP can significantly relieve the band-gap problem. For example, the $E_g$ of WZ ZnO from the B3LYP calculation was predicted as 3.41 eV [41] which reproduces the experimental measurement [36, 37]. Therefore, we carried out calculations with the B3LYP functional to obtain more accurate band gaps and further check whether the band gaps are still invariable. Interestingly, it can be seen from figure 4 that the band gaps of oxide SWNTs are almost the same as the $E_g$ of the corresponding HM, around 4.7 and 2.3 eV for ZnO SWNTs and CdO SWNTs, respectively. The band gaps of ZnS are also steady but smaller by 0.2–0.5 eV than the $E_g$ of HM ZnS (4.3 eV). For the CdS SWNTs, the band gaps vary within ±0.4 eV with respect to the $E_g$ of HM CdS (2.9 eV). The larger deviations of the band gaps of the sulfide SWNTs relative to the oxide SWNTs originate from the larger radius buckling in the sulfide SWNTs. Nevertheless, the band gaps of the sulfide SWNTs are still quite close to those of the corresponding HMs. Furthermore, we used the GGA functional to calculate the band gaps of the HM and SWNTs of ZnO and found that the band gaps are steady around 1.7 eV as shown in figure 4(a). Therefore, the invariant feature of the band gaps of the oxide and sulfur SWNTs is predicted by the LDA, GGA and B3LYP calculations.

We emphasize that our findings mentioned above are significantly different from conventional SWNTs such as C, BN and SiC SWNTs where $sp^2\sigma$ and $pp\pi$ hybridizations contribute chemical bonds and the electronic states near the Fermi energy, respectively. These special hybridizations lead to the strongly chirality- and diameter-dependent electronic properties. For the IIB–VI compound SWNTs, however, the electronic properties are almost independent of the chirality and weakly dependent on the diameter. To illustrate the underlying mechanism, we investigated the electronic properties of these SWNTs. Take ZnO SWNTs for example, we plotted the band structures of (6, 0) and (5, 5) ZnO SWNTs in figure 5. Clearly, these SWNTs are direct-band gap semiconductors, with their gaps of 1.96 eV and 2.07 eV, respectively, very close to that of ZnO HM (2.03 eV). In addition, the CBM and VBM of both ZnO SWNTs locate at $\Gamma$ point. We found that the CBM is contributed mainly from the Zn–4s orbital, and the VBM characterizes anti-bonding states of $(d_{x^2} - p_{y^*})$ and $(d_{y^*} - p_y)$ hybridizations (figure 5). Obviously, these states maintain the main electronic nature of HM ZnO (figure 2(b)), even though the ZnO HM is rolled up and the radius curvature is induced. Both the spherically symmetric Zn–4s orbital, the in-plane $(d_{x^2} - p_{y^*})$ and $(d_{y^*} - p_y)$ hybridizations are robust against the radius curvature, which results in the constant band gaps of ZnO SWNTs. This mechanism applies to all cases considered in this work.

4. Summary

In summary, we studied the stabilities and electronic properties of the HMs and SWNTs of IIB–VI semiconductors ZnO, CdO, ZnS and CdS, through systematic first-principles calculations. The sulfide SWNTs are easier to be fabricated.
Figure 4. Band gaps of zigzag (open symbols) and armchair (filled symbols) SWNTs. The circles, diamonds and triangles are from LDA, GGA and B3LYP calculations. The horizontal dashed lines represent the band gaps of the HMs with different functionals.

Figure 5. Band structures of (a) (6, 0) and (b) (5, 5) ZnO SWNTs. The VBM is set to zero point of energy. The insets show the spatial distribution of the radial wavefunctions of the VBM. The cutoff of the isosurfaces is 0.1 electrons Å⁻³. The red and gray balls stand for O and Zn atoms, respectively.
than the oxide SWNTs, because the strain energies of the former are lower. Interestingly, the band gaps of the HMs and SWNTs of all the compounds are nearly chirality-independent and weakly diameter-dependent. This feature is contributed from the special electronic character of these materials. The CBM characterizes the s orbitals of cations which are spherically symmetric, and the VBM originates from in-plane \((d_{xy} - p_x)\) and \((d_{xz} - p_y)\) hybridizations. The band gaps of these materials range from 2.3 to 4.7 eV, which make them suitable to be building-block semiconductors in electronic devices and optoelectronic devices in the nanoscale.

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