First-principles study on structural, electronic and elastic property of ZnS nanotubes

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Abstract. The structural, stability and elastic property of single-walled ZnS nanotubes (SW-ZnS NTs) with armchair and zigzag forms were investigated using first-principles approaches. We have investigated a size dependence of stability and elastic modulus in SW-ZnS NTs. It is found that both the stability and the Young's modulus are decrease dramatically with increasing diameter and proportional to the Zn-S bond length.

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Key words: density functional theory, nanotube, stability, elastic modulus

1 Introduction

Zinc sulfide (ZnS) is an important II-VI compound semiconductor with potential applications in electronics and optoelectronics because of its wide direct band gap 3.77 eV [1]. One-dimensional (1D) ZnS nanostructures have been attracting growing attention, because they possess unique properties compared to the bulk crystal due to the quantum confinement effect and the surface effect [2]. Over the past few years, considerable efforts have been placed on the synthesis of ZnS tubular structures [3-13]. The synthesized nanotubes mainly have hexagonal cross section (HCS) with widths of hundreds nanometers and lengths of up to a few millimeters. On the theoretical side, Pal *et al.* first studied armchair and zigzag SW-ZnS NTs using density functional tight-binding method [14]. They found that the energy gaps of the SW-ZnS NTs depend on their helicity and are always smaller for zigzag $(n, 0)$ nanotubes than armchair (n, n) ones. Then, Zhao *et al.* studied SW-ZnS NTs with HCS using interatomic potential calculations [15-17]. They found

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that the formation energies of the multiwalled nanotubes decrease with increasing wall thickness, irrespective of tube diameter.

Recently, ZnS nanostructures have shown a great promise as functional and structural nanobulilding blocks in nanoelectronics, nanooptoelectronics, and nanolasers [18-25]. Since the mechanical properties are crucial for designing such device, there is an increasing interest in the elasticity of 1D nanostructure. The elastic properties of ZnS nanowires have been investigated that the Young's modulus were decreased with increasing diameters [26,27]. Previous theoretical researches on single-walled ZnO nanotubes showed that the Young's modulus was increased dramatically with the increased diameters and inversely proportional to the Zn-O bond length [28].

Despite the increasing volume of researches on ZnS NTs, to the best of our knowledge, only very limited experimental information is currently available on their mechanical properties. In the absence of definitive experimental results, the first-principles calculations can provide robust predictions of SW-ZnS NTs mechanical properties. However, to our knowledge, there was no the reported mechanical results on ab initio calculations of SW-ZnS NTs. To understand the stability and elastic property of SW-ZnS NTs, we carried out a systematical computational study on the SW-ZnS NTs. We investigated a size dependence of stability and elastic modulus in SW-ZnS NTs. Both the stability and the Young's modulus are decrease dramatically with the increased diameters and proportional to the Zn-S bond length.

2   Theoretical method and computational details

As is well known, Single-walled carbon NTs, which can be viewed as a graphene sheet rolled into tubes, are usually indexed by a pair of integers (n, m) to represent their helicities [29]. Here we have considered two types of SW-ZnS NTs, namely, armchair and zigzag. The original structures of armchair (m, m) and zigzag $(n, 0)$ SW-ZnS NTs are constructed by rolling up a ZnS graphitic sheet. Due to the limitation of computer facilities available, the index m varies from 5 to 10, and n varies from 7 to 12, respectively. All SW-ZnS NTs are modeled in a tetragonal supercell and are infinitely long along their axes by applying periodic boundary conditions. The axial direction is along z axis and a vacuum region of at least 10 Å is applied in x and y axis to avoid the interactions between SW-ZnS NTs.

Our calculations were performed in the framework of density functional theory (DFT) within the Perdew-Burke-Ernzerhof correction (PBE) generalized-gradient approximation (GGA) [30] as implemented in the DMol package [31]. Density functional semi-core pseudopotentials (DSPP) with double numerical plus d-functions basis set (DND) are used. SCF calculations are performed with a convergence criterion of 10^{-6} hartree on the total energy. All structures are fully optimized without any symmetry constraint, with a convergence criterion of 0.002 hartree/Å for the forces and 0.005 Å for the displacement.
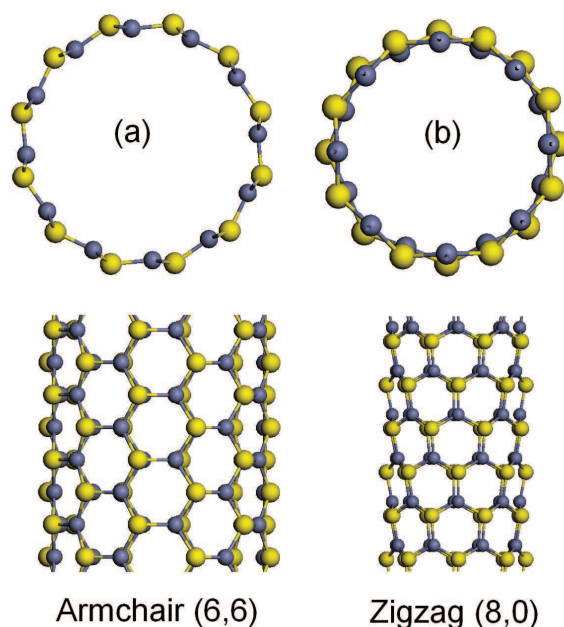
Figure 1: The top-view and side-viewof the relaxed structures of the armchair (6,6) (a) and zigzag (8,0) (b) SW-ZnS NTs. The gray (small) and yellow (big) balls represent Zn and S atoms.

3   Results and discussions

3.1   Structural properties and stability

The optimized geometry of armchair (6, 6) and zigzag (8,0) SW-ZnS NTs are shown in Fig. 1. Different from Single-walled C NTs in which all of carbon atoms lie on a cylindrical surface, after geometry optimization, Zn atoms move inward whereas S atoms move outward, with respect to their initial position. Thus, the fully relaxed ZnS NTs can be characterized by two coaxial cylindrical tubes, with an outer S cylinder and an inner

Table 1: The average diameters of S and Zn atoms at two different coaxial cylindrical surfaces (d_S, d_{Zn}, in nm), and the radial buckling (δ, in nm) of armchair and zigzag ZnSNTs. The common diameters (d, in nm) are also shown.

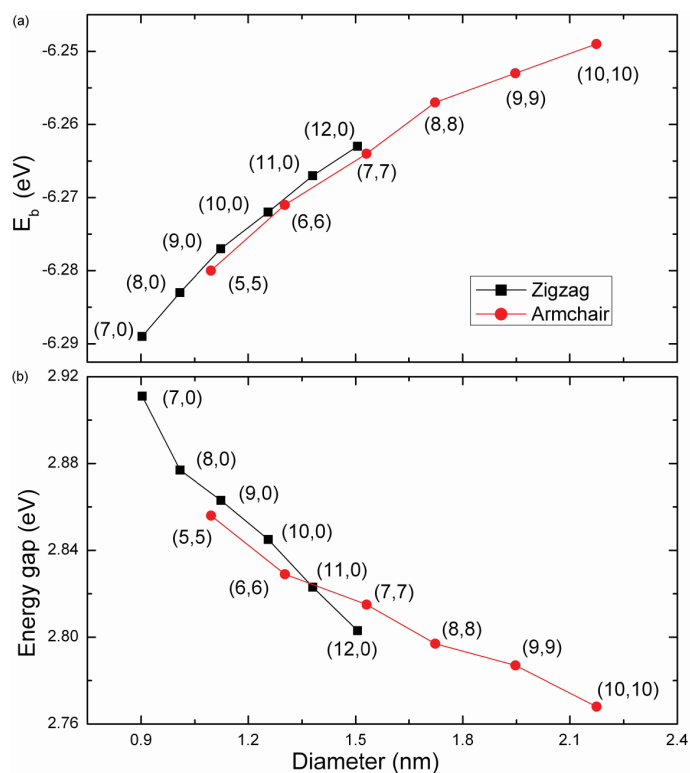| Zigzag	d_S	d_{Zn}	δ	d	Armchair	d_S	d_{Zn}	δ	d
(7,0)	0.95	0.85	0.10	0.90	(5,5)	1.14	1.05	0.09	1.10
(8,0)	1.05	0.97	0.08	1.01	(6,6)	1.34	1.26	0.08	1.30
(9,0)	1.17	1.08	0.09	1.13	(7,7)	1.57	1.49	0.08	1.53
(10,0)	1.3	1.22	0.08	1.26	(8,8)	1.76	1.69	0.07	1.72
(11,0)	1.42	1.34	0.08	1.38	(9,9)	1.98	1.91	0.07	1.95
(12,0)	1.54	1.47	0.07	1.51	(10,10)	2.21	2.14	0.07	2.17

Figure 2: The binding energy (a) and energy gap (b) of SW-ZnS NTs as a function of diameter.

Zn cylinder, forming a buckle of the Zn-S dimer. This reduces the total energy of the system since the electron-electron repulsion is lowered. The average diameters of Zn and S atoms (d_S, d_{Zn}) at two different coaxial cylindrical surfaces, and the radial buckling δ are all listed in Table 1. It can be seen that the buckling decreases with increasing tube diameter. This feature is the same as those observed in ZnS quantum dots [32], ZnS nanotubes [14], and ZnS nanowires [33].

In order to analyze the energetic stability of the SW-ZnS NTs, the binding energy of per pair of ZnS atoms, E_b, is defined as $E_b = E_t/N - E_{Zn} - E_S$, where E_t is the total energy of the ZnS atoms in a nanotube and N is the number of the pair Zn and S atoms. E_{Zn} and E_S is the energy of the single Zn and S atom respectively.

Fig. 2(a) shows the size dependence of the binding energy for fully relaxed SW-ZnS NTs. It is seen that a strong size effect is evident for both types of nanotubes. By comparison of binding energies, SW-ZnS NTs of armchair form is found to be more stable than those of zigzag form. The binding energies of armchair and zigzag NTs increase monotonically with increasing diameter, indicating their less stability with increased diameter. This feature is on the contrary to that of single-walled ZnO NTs [28]. It suggests that we can obtain stable SW-ZnS NTs with small diameter.
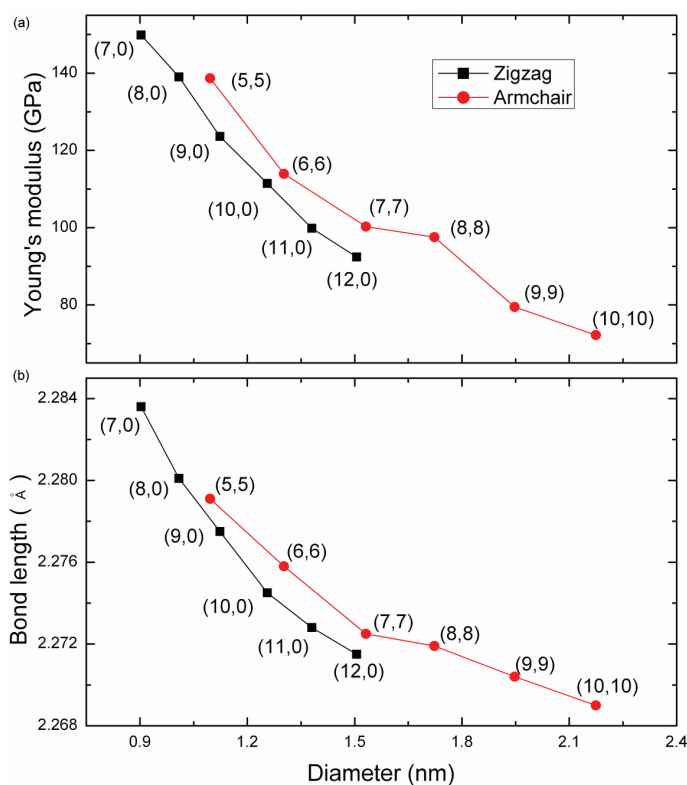
Figure 3: The dependence of Young's modulus of SW-ZnSNT (a) and bond-length (b) as a function of diameter.

3.2 Electronic properties

In the following, the electronic properties of these SW-ZnS NTs are calculated.

Fig. 2(b) shows the size dependence of energy gap. The energy gaps of armchair and zigzag NTs both decrease monotonically with increased diameter. The gaps of zigzag NTs are larger than those of armchair ones at small diameter, but the armchair ones have larger gaps with increasing diameter.

The calculated results are different from the previous theoretical research, in which zigzag NTs are always smaller than armchair ones [14]. All the gap values are much larger than the bulk value (2.15 eV). This trend is understandable in terms of the quantum confinement effect.

3.3 Elastic properties

To characterize the elastic properties of SW-ZnS NTs, we investigate the Young's modulus of two types of SW-ZnS NTs. The Young's modulus is calculated as the second derivative of the total energy with respect to the strain at the equilibrium, i.e., $Y = V_0^{-1} \partial^2 E / \partial \varepsilon^2|_{\varepsilon=0}$ where V_0 is the equilibrium volume, E is the total energy, and ε is the strain. The unit

cell equilibrium length L_0 is determined from finding the minimum L by using a second order polynomial fit of total energy versus cell length. The fully relaxation is followed for each elongation or compression axially around its equilibrium. In the regime of relative low applied strain, the mechanical behavior of SW-ZnS NTs can be characterized by linear elastic response without noticeable plastic structural deformation [34]. The Young's modulus for each nanotube is determined by applying a quadratic polynomial fit to the corresponding $E-\varepsilon$ data within a low strain (-2 $\sim$ 2%).

For comparison of SW-ZnS NTs with different sizes and structures, a common diameter is defined as $d = \frac{d_{Zn}+d_S}{2}$, where dZn and dS are the average diameters of Zn and S atoms at two different coaxial cylindrical surfaces. The common diameters d are also shown in Table 1.

Fig. 3(a) shows the size dependence of Young's modulus. Clearly, for a given diameter, the Young's modulus of armchair nanotube is slightly larger than that of zigzag one. For both types of tubes, the elastic modulus is decreased with increasing diameter, similar to that of ZnS nanowires [26,27].

Since the Young's modulus characterizes the strength of the forces between atoms that varies with the type of their bonding in a given material, it is relatively sensitive to the change of interatomic distance. As we know, the Young's modulus of nanowires has connection with both the surface relaxations and the core nonlinear effect [26,35]. Therefore, the Young's modulus of NTs should be expected to be closely associated with the bond length of this material. To explore the origin of size dependence of the elastic modulus of SW-ZnS NTs, we have calculated Zn-S bond lengths. Note that the Zn-S bond lengths in each ZnS nanotube are not equal but their differences are small. Therefore, the average bond length is introduced to characterize the bonding strength between Zn and S atoms in the SW-ZnS NTs. Fig. 3(b) shows the size dependence of the average Zn-S bond length. The average Zn-S bond length in two types of NTs are slightly shorter than in bulk ZnS (2.387 Å). It is seen that strong size effects are also evident for both types of SW-ZnS NTs. Their bond lengths are decreased with increased diameter, showing a strengthening bond in the tubes with larger diameters. Furthermore, the bond length of the armchair tube is clearly larger than that of zigzag tube.

By comparing of Fig. 2(a) and Fig. 3(a), it reveals that the binding energy of SW-ZnS NTs is inversely proportion to the bond-length. Although the Zn-S bond was strengthened with increasing diameters, the stability of SW-ZnS NTs was reduced.

By comparing of Fig. 3(a) with Fig. 3(b), one can see that there is a clear correlation between the Young's modulus and the bond length: the larger the bond length, the higher the Young's modulus. It reveals that the Young's modulus is proportional to the bond length. This finding has further demonstrated that the elastic modulus is closely associated with the interatomic bonding strength.

4   Conclusion

In summary, we have investigated the structural, stability and elasticity of SW-ZnS NTs using first-principles approaches. We consider two types of tubes, namely armchair and zigzag forms. It is demonstrated that the stability and Young's modulus of both types of SW-ZnS NTs are decreased with increasing tube diameter and proportional to the Zn-S bond length.

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