Electronic structure of twinned ZnS nanowires*

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The electronic properties of twinned ZnS nanowires (NWs) with different diameters were investigated based on first-principles calculations. The energy band structures, projected density of states and the spatial distributions of the bottom of conduction band and the top of the valence band were presented. The results show that the twinned nanowires exhibit a semiconducting character and the band gap decreases with increasing nanowire diameter due to quantum confinement effects. The valence band maximum and conduction band minimum originate mainly from the S-p and Zn-s orbitals at the core of the nanowires, respectively, which was confirmed by their spatial charge density distribution. We also found that no heterostructure is formed in the twinned ZnS NWs since the valence band maximum and conduction band minimum states are distributed along the NW axis uniformly. We suggest that the hexagonal (2H) stacking inside the cubic (3C) stacking has no effect on the electronic properties of thin ZnS NWs.

Keywords: ZnS nanowires, twin plane, density of states, charge density distribution, density functional theory

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1. Introduction

Zinc sulfide (ZnS) is an important wide band-gap semiconductor, which has been widely investigated as promising electronic and optoelectronic material.[1−4] ZnS has two stable phase structures: the cubic zinc blende (ZB) at low temperatures and the hexagonal wurtzite (WZ) at high temperatures. The structure transformation for single crystal ZnS nanobelts occurs at about 750 °C based on the analysis of scanning electron microscopy and transmission electron microscopy.[5] The structures of nanomaterials also have the size-dependent effect. Akiyama *et al.* found that the wurtzite ZnS nanowires (NWs) are stable for diameters less than 4 nm while the zinc blende NWs are energetically favorable for diameters larger than 24 nm.[6] The twinned II–VI NWs with the mixed ZB/WZ structures are commonly observed along the [111] direction, such as ZnS,[7,8] ZnSe,[9−11] and ZnTe[12] NWs. A twinning is a kind of stacking fault with low formation energy because the energy difference between the two critical nuclei of the ZB and WZ structures is small. The periodically twinned ZnS NWs have been synthesized via a thermal evapouration method.[8] The photoluminescence spectra of the twinned NWs were found to exhibit buleshift compared with that for ZnS nanopower. Hao *et al.*[7] also has successfully fabricated periodically twinned ZnS NWs via an Au-catalyzed vapour–liquid–solid (VLS) process. It was found that the twinned NWs were derived from the periodical fluctuation between diffusion rate inside the catalytic droplet and the growth rate at the liquid–solid interface. Recently, the twinned ZnS nanocables were fabricated by catalyzed and self-catalyzed mechanism.[13] The WZ-phase ZnS NWs was suggested to be the self-catalyzed growth from the surface of the ZB-phase ZnS NWs, which was synthesized by VLS deposition techniques at low temperatures.

Few theoretical researches about the properties of twinned ZnS NWs were carried out, although the ZB- and WZ-phase ZnS NWs were widely investigated by first-principles.[14−17] Akiyama *et al.*[6] studied the size dependence of the average periodicity for the twinned ZnS NWs based on Monte–Carlo simulations. The results showed that the nucleation at the top layer of nanowire markedly affects the periodicity of rotational twinned structures. For the twinned bulk ZnS, Northrup *et al.*[18] studied the electric property using self-consistent pseudopotential method. The results

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showed that the twin plane created a potential barrier of ∼ 0.07 eV and induced the localization of resonances near the top of valence band. To the best of our knowledge, the electronic properties of the twinned ZnS NWs have attracted little attention for experimental and theoretical studies so far. In addition, the stacking fault of a twinning plane may affect the electronic properties, such as minibands formation in the twinning superlattice of InP NWs.[19] Therefore, the electronic properties of the twinned ZnS NWs demand further study. In this paper, we present an extensive study of the electronic structures of the twinned ZnS NWs using first principles density functional theory calculations within the generalized gradient approximation. This method has proved to be useful in calculating the mechanical and electronic properties of nanostructures.[20−25]

2. Computational details

We presented first-principles calculations based on the density functional theory using the VASP code.[26] The ion–electron interaction was described by the projector augment wave method (PAW).[27] Generalized gradient approximation (GGA) approach was used to deal with the energy of exchange-correlation.[28,29] The wave functions have been expanded in plane waves with a cutoff energy of 450 eV. Integration over an irreducible Brillouin zone was carried out using the Monkhorst–Pack grid of 1×1×5. All the geometries were optimized until the forces were less than 0.02 eV/Å (1 Å=0.1 nm). The relaxation was handled by computing the Hellmann–Feynman forces using the conjugate gradient algorithm.

The twinned ZnS nanowires consist of a mixture of hexagonal (2H) and cubic (3C) stacking of Zn–S layers and the corresponding atomic configurations viewed from the ⟨110⟩, ⟨112⟩, and ⟨111⟩ directions are shown in Figs. 1(a), 1(b), and 1(c), respectively. The dangling bonds of the surface atoms are passivated by pseudohydrogen atoms. For simulating nanowires, periodic boundary conditions were applied along the wire axis (noted as z axis) and sufficient vacuum space (up to 2.0 nm) was imposed in radical directions to make sure that there is no interaction between the ZnS NWs. The twinned ZnS nanowires with its axis along the [111] direction surrounded by the {111} side facets are investigated. The twinned ZnS NWs with diameters of ∼ 0.76, 1.54, 2.31 nm and segment thickness (t) of 0.5 nm and with the diameter of 1.54 nm and t = 1.0 nm were studied. The optimized lattice constant for 3C–ZnS is 5.446 Å.

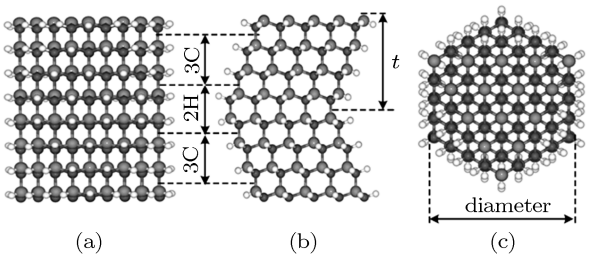


Fig. 1. Representative atomic configurations of the twinned ZnS nanowires with non-parallel {111} side facets viewed from (a) the ⟨110⟩ direction, (b) the ⟨112⟩ direction, and (c) the ⟨111⟩ direction; t represents segment thickness, the bigger balls represent the S atoms, the smaller balls represent the Zn atoms, the smallest balls represent the H atoms.

3. Results and discussions

The twinned ZnS NWs with different nanowire diameters were relaxed using the conjugate gradient method. The results showed that the relaxation is negligible due to passivating the dangling bonds by pseudohydrogen atoms at the surface. The density of states (DOS) of these twinned ZnS NWs was illustrated in Fig. 2. It can be seen that all the nanowires exhibit a semiconducting character with the bottom of conduction band (CBM) and the top of the valence band (VBM) being all located at the Γ point of the Brillouin zone. The band gaps were calculated to be 3.6, 2.87, and 2.54 eV for the twinned NWs having the diameters of 0.76, 1.54, and 2.31 nm, respectively and the segment thickness of 0.5 nm. For the NWs with the diameter of 1.54 nm and the segment thickness of 1 nm, the band gap is 2.79 eV, as shown in Fig. 3. These band gaps are larger than the bulk value (2.2 eV) and the band gaps of the twinned ZnS NWs decrease with the increase of the nanowire size due to quantum confinement effects. From Fig. 2, we also find that the value of the CBM shifts to lower energy with the increase of the diameter, while the VBM almost does not change. In order to compare with the band structures of the ZB and WZ-phase ZnS NWs, we present the band structures for the twinned NWs with the segment thickness of 0.5 nm in Fig. 4. We see that the value of the VBM for the twinned structures shifts to lower energy as compared with that for the WZ-phase ZnS NWs.[15] In contrast to the energy band structures of the ZB-phase ZnS NWs,[14] we find that the curvature of VBM for the twinned NWs is larger. The larger dispersion should exist in the VBM of the twinned NWs. Figure 4 also shows that the

curvature of VBM for the twinned structures becomes smaller as the diameter is increased since the quantum confinement effect is greater for small NWs.

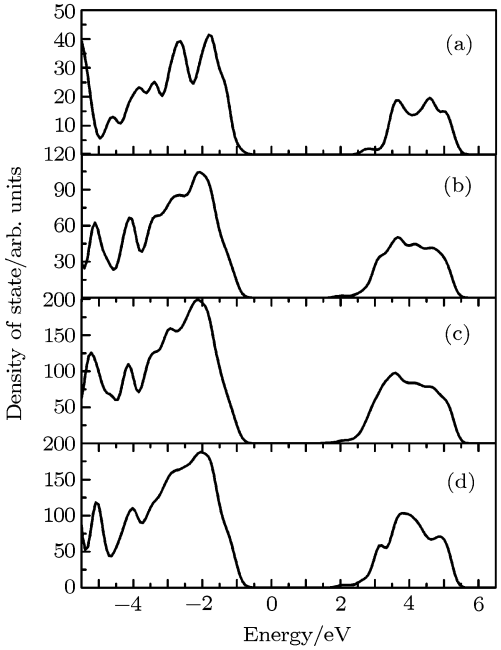


Fig. 2. The total DOS of the twinned ZnS nanowires. The Fermi energy is set to be zero. The diameters of these twinned nanowires are (a) 0.76 nm, (b) 1.54 nm, (c) 2.31 nm, and (d) 1.54 nm and the segment thicknesses are (a)–(c) 0.5 nm and (d) 1 nm.

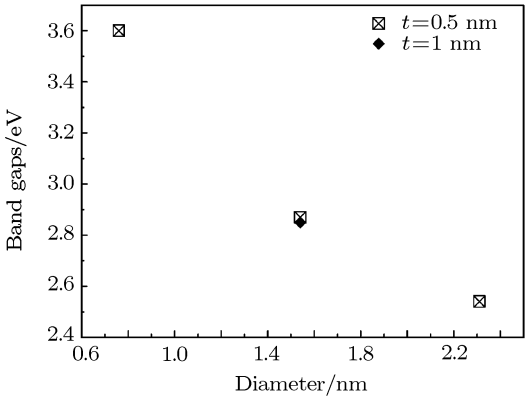


Fig. 3. Band gap for the twinned ZnS nanowires as a function of the nanowire diameter.

In order to understand the contributions of the different atomic orbitals in the electronic levels near the band edges, the projected density of states (PDOS) of surface and core atoms are calculated and the results are shown in Fig. 5. A similar result is obtained for all the simulated nanowires, so we show a representative PDOS of nanowire with diameter of 2.31 nm. As seen from Fig. 4, the VBM and CBM arise mainly from the S-p and Zn-s orbitals at the core of the nanowires, respectively. The results may be confirmed from the spatial distribution of the charge density of the levels near the energy band gap edges. From Fig. 6, it is observed that the VBM and CBM for the twinned ZnS NWs are mainly localized in the central region of the wires. The distribution of the charge density for the twinned ZnS NWs is different from that for the hydrogen-passivated

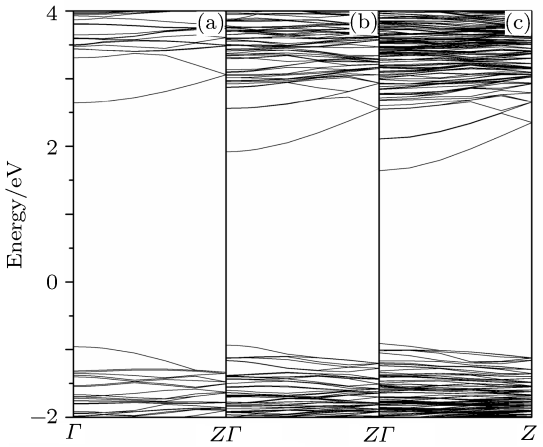


Fig. 4. Calculated band structures for the twinned ZnS nanowires with the segment thickness of 0.5 nm. The diameters are (a) 0.76 nm, (b) 1.54 nm, (c) 2.31 nm.

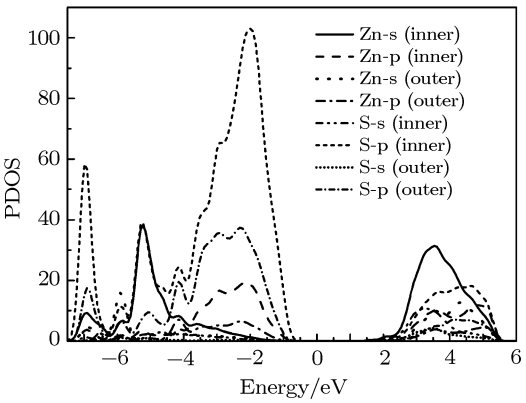


Fig. 5. Projected density of states for the twinned ZnS nanowire with a diameter of 2.31 nm and a segment thickness of 0.5 nm.

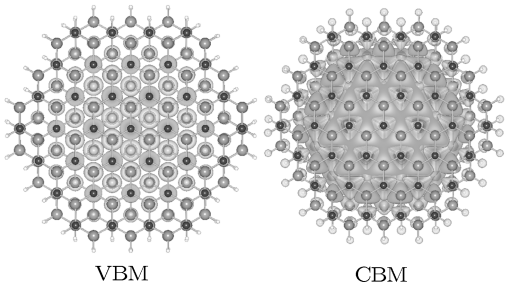


Fig. 6. Wave function square contour plots of the VBM and CBM states for the twinned ZnS nanowire with a diameter of 2.31 nm and a segment thickness of 0.5 nm

WZ-phase ZnS NWs.[15] For the WZ-phase ZnS NWs, the CBM is localized mostly on the core of the NWs while the VBM is delocalized and distributed from the centre to the surface.

To obtain deeper insight into whether a heterostructure can be formed from the 2H and 3C stacking in the twinned ZnS nanowires, we investigate the VBM and CBM distribution along the wire axis. If type-II heterostructure is formed, the electrons and holes will separate from each other and the nanowires are not good candidates for applications in optoelectronic device as the recombination efficiency is reduced. The VBM and CBM distributions of the twinned ZnS NWs with a diameter of 1.54 nm and a segment thickness of 1.0 nm are shown in Figs. 7(a), 7(b), and 7(c) that are viewed from the ⟨110⟩, ⟨112⟩, and ⟨111⟩ directions. It can be seen that the VBM and CBM are distributed along the nanowire axis uniformly, indicating that no heterostructure is formed in the twinned ZnS NWs. The results show that the twinned ZnS NWs has great potential applications in realizing nano-optoelectronic devices.

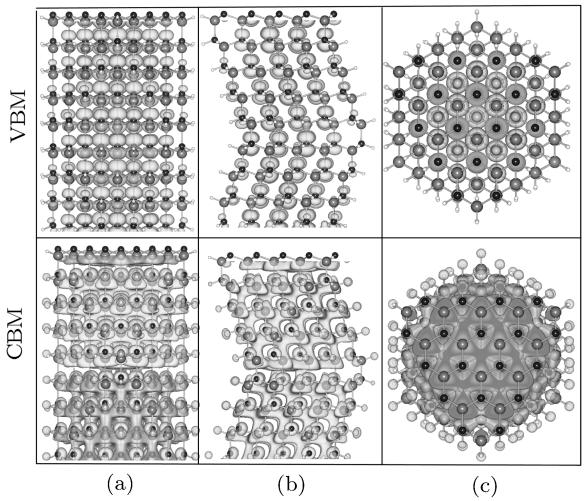


Fig. 7. Wave function square contour plots of the VBM and CBM states for the twinned ZnS nanowire with a diameter of 1.54 nm and a segment thickness of 1.0 nm viewed from (a) the ⟨110⟩ direction, (b) the ⟨112⟩ direction, and (c) the ⟨111⟩ direction.

4. Conclusions

DFT–GGA method has been used to study the electronic properties of the twinned ZnS NWs with different diameters grown along [111] direction and surrounded by {111} side facets. The analysis of energy band structures showed that the twinned nanowires exhibit a semiconducting character and the band gap decreases with increasing nanowire size due to quantum confinement effects. The value of the CBM shifts to lower energy with the increase of the diameter, while the VBM almost does not change. The VBM and CBM originate mainly from the p-orbitals of the S atoms and s-orbitals of the Zn atoms inside the nanowires, respectively. This was confirmed by spatial distribution of the charge density of the VBM and CBM states. The results showed that the hexagonal (2H) stacking inside the cubic (3C) stacking has no effect on electronic properties of the thin ZnS nanowires. The VBM and CBM states distributed along the nanowire axis uniformly, indicating the twinned SiC nanowires are a good candidate in realizing nano-optoelectronic devices.

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