Quantum confinement effects on electronic properties of hydrogenated 3C–SiC nanowires

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ABSTRACT

In this work, the effect of the morphology on the electronic band structure and density of states of hydrogenated silicon carbide nanowires is studied by using a semiempirical sp^3s^* tight-binding (TB) approach applied to the supercell model, where the Si- and C-dangling bonds are passivated by hydrogen atoms. The TB results are compared with those of ab-$initio$ density functional theory within the local density approximation, showing that this method gives systematically larger energy gaps than the TB one. As expected, hydrogen saturation induces a broadening of the band gap energy due to quantum confinement effect.

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1. Introduction

Silicon carbide (SiC) nanostructures have very unique properties which bode well for applications in microelectronics and optoelectronics and have thus attracted much interest from the materials and device communities. In the microelectronics industry, SiC is regarded as a promising substitute for silicon, especially in high power, high temperature, and high frequency devices. Recent advances in the preparation of ultra-high quality SiC single-crystals have in fact paved the way for wider uses of SiC in microelectronic devices.

On the other hand, nanoscale materials are expected to possess different electronic properties compared to their corresponding bulk crystals; in particular, one-dimensional nanostructures deserve special attention, as they are expected to play a crucial function as building blocks of molecular electronic devices [1].

From the theoretical point of view, there are many approaches which allow the investigation of the optical and electronic properties of materials. Ab-$initio$ methods have been widely used, due to the possibility of giving a fully atomistic description of these systems. They have become very efficient thanks to the continuous increasing of both computer performance and algorithm speed. Nevertheless, semiempirical methods remain a powerful tool, giving the chance to simulate real crystals. The tight-binding (TB) method has the advantage of being simple, suitable for large systems, and its experimentally determined parameters frequently include many-body correlation effects, otherwise difficult to be considered in ab-$initio$ calculations.

However, these TB parameters are usually fitted to the bulk properties of the system and their applicability at the atomic and nano scales is not clear.

The applications of SiC for microelectronic and optoelectronic devices require the knowledge of the electronic band structure and the optical properties caused by electronic transitions between the interband states. In this work, we use a sp^3s^* TB model to study the electronic structure of hydrogenated cubic (β) SiC nanowires (SiC-NW). The results are compared with those obtained from the density functional theory (DFT) calculations within the local density approximation (LDA).

2. Model

Free standing, infinitely long and homogeneous SiC-NW of different cross sections with the wire axis along the [0 0 1] direction are considered. Each surface-dangling bond is saturated with a hydrogen atom. The system has translational symmetry along the z-axis with a period equal to a lattice constant a. In the TB approach, we suppose that the nanostructures have the same lattice structure and the same interatomic distance as bulk SiC and that all the dangling bonds are saturated with hydrogen atoms described by the 1s orbital. For simplicity, is assuming also that, there is no hydrogen–hydrogen interaction. These atoms are used to simulate the bonds at the surface of the wire and sweep surface states out of the energy band gaps. It is well known that within the TB approximation sp^3s^* reproduce the bulk indirect band gap. The Vogl parameters [2] used in this work reproduce an indirect-gap of 2.329 eV for bulk crystalline β-SiC. In addition, the H on-site energy of -3.4 eV [3] and H–C orbital interaction

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parameters of $ss\sigma_{H-C} = -4.81$ and $ss\sigma_{H-C} = 5.32$ eV are employed, which are obtained by fitting the energy levels of CH_4 [4], where the C–H bond length is considered as 1.125 Å. Also, the H–Si orbital interaction parameters are taken as $ss\sigma_{H-Si} = -4.075$ and $ss\sigma_{H-Si} = 4.05$ eV, which are obtained again by fitting the energy levels of silane [5]. The Si–H bond length is taken as 1.51 Å. All calculations are done without spin-orbit coupling.

The electronic states of β-SiC are determined by diagonalizing the TB Hamiltonian matrix, whose dimension is $5(N_{Si}+N_C)+N_H$, with N_{Si}, N_C, and N_H being the numbers of Si, C, and H atoms in the supercell, respectively, and the DFT-LDA calculations are performed by using the CASTEP code [6]. A full geometry optimization is performed using norm-conserved, nonlocal, Troullier-Martins pseudopotentials. The electronic wave functions were expanded in a plane wave basis set with periodic boundary conditions and a plane wave energy cut-off of 900 eV, due to the presence of hydrogen atoms. The Monkhorst–Pack method has been used to select the **k** points set, with a $4 \times 4 \times 4$ grid. In order to overcome the semiconductor band gap underestimation of DFT, a scissors operator of 1.029 eV was introduced.

3. Results

Fig. 1 shows the electronic band structures and density of states (DOS) of crystalline β-SiC, obtained from TB (solid lines) and DFT-LDA (open circles) calculations. An elemental cell of eight SiC-atoms was used. Notice the good agreement around the band gap between these two approaches, except for conduction bands.
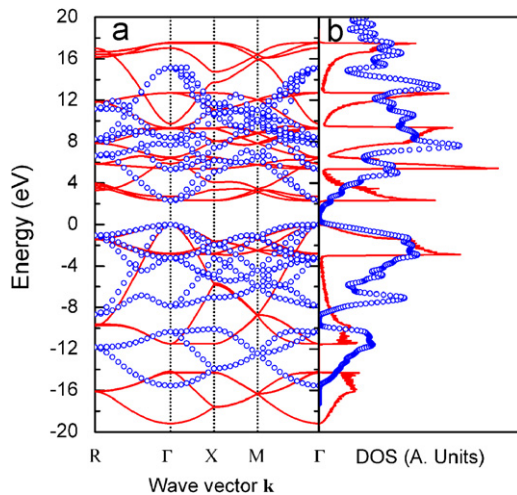

Fig. 1. (a) Electronic band structure and (b) DOS of bulk β-SiC, calculated by means of TB (solid line) and DFT-LDA (open circles) methods. A unit cell of 8-SiC atoms was used.

The difference between the conduction bands could be due to that the s^* orbital has non d-wave symmetry and additionally the geometry optimization is absent in the TB calculations.

Fig. 2 shows the structures of the hydrogenated SiC-NW studied in this work. A full geometry optimization is performed in order to lead the atoms to their minimal energy positions. In Fig. 3, the corresponding electronic band structures calculated within the TB (solid lines) and DFT-LDA (open circles), are shown. The calculated energy gaps are presented in Table 1. Notice that, as expected within the quantum confinement scheme, both TB and DFT-LDA calculations predict a clear broadening of the electronic band gap. Moreover, for SiC-NW, the DFT-LDA approach gives systematically larger gaps than the TB method, contrary to what happens in porous semiconductors [7].

Direct band gap energy is seen in all calculations. This feature of the band structures can be explained by a zone-folding argument of the bulk β-SiC bands onto the one-dimensional Brillouin zone of nanowires.

In Fig. 4, we show the calculation of electronic density of states from both TB (solid lines) and DFT-LDA (open circles) approximations. It can be seen that the gap broadening and the cleaning of
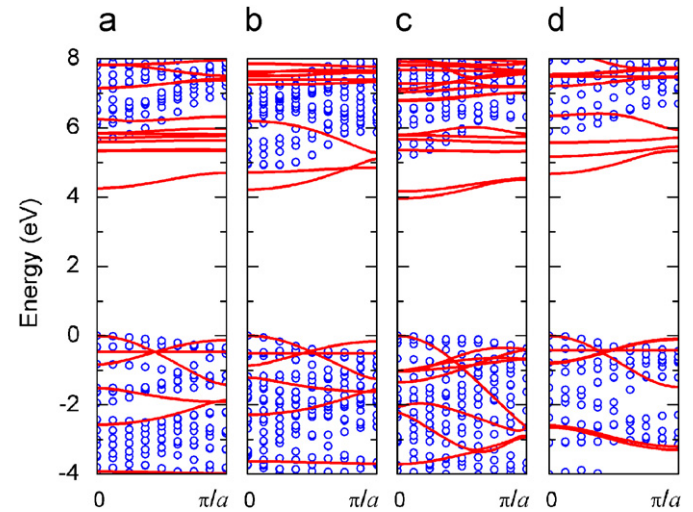

Fig. 3. Electronic band structures of SiC-NW calculated from TB-sp^3s^* (solid line) and DFT-LDA (open circles) corresponding to the structures of Fig. 2.

Table 1
Energy band gaps of SiC-NW in eV.

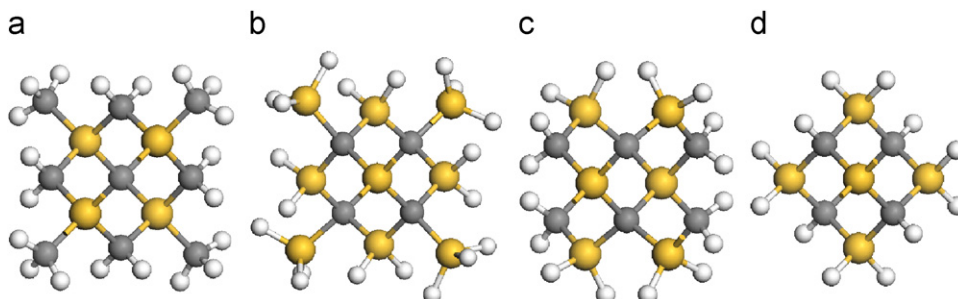| Structures of Fig. 2	a	b	c	d
DFT-LDA	5.65	4.93	5.18	5.9
TB-sp^3s^*	4.25	4.22	3.95	4.67

Fig. 2. Relaxed structures of hydrogenated SiC-NW projected along the [0 0 1] direction. The yellow, black and white spheres represent, respectively, the silicon, carbon and hydrogen atoms.
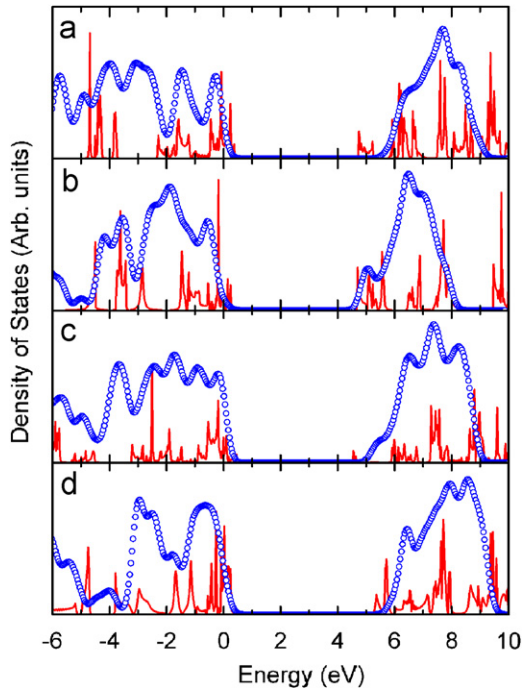
Fig. 4. DOS obtained from TB (solid line) and DFT-LDA (open circles) approaches corresponding to the nanowires of Fig. 2.

the gap due to hydrogen surface passivation. This hydrogen surface passivation is a good model of all those experimental cases in which the formation of new surface states is prevented, e.g., oxidation, and coverage with amorphous layers.

4. Conclusions

In summary, we have presented a comparative study of the semiempirical TB and *ab-initio* DFT-LDA approaches applied to hydrogenated β-SiC nanowires. The supercell model has the advantage of being suitable for calculations of their electronic even using *ab-initio* methods. On the other hand, both DFT and TB approximations confirm the quantum confinement effects on the electronic properties, but the first method systematically gives a larger energy gap than the second one. As expected, hydrogen saturation induces a broadening of the band gap energy due to quantum confinement effect.

Acknowledgments

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