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Quantum confinement effect in silicon carbide nanostructures: a first principles study

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Based on the density functional theory (DFT) within local-density approximations (LDA) approach, we calculate the electronic properties of SiC nanowires and nanodots. The saturated nanowires exhibit semiconducting characteristics with a direct band gap and the band gaps decrease with increasing the diameters of the nanostructures due to quantum confinement. The difference of between the band gap of nanowires and that of bulk SiC evolves as $\Delta E_g^{wire} = 0.51/d^{1.245}$ as the diameter *d* decreases, while $\Delta E_g^{dot} = 2.18/d^{0.85}$ for the case of nanodots.

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1. Introduction

One-dimensional semiconductor nanostructures are receiving ever-increasing attention because of their potential applications in single-electron memories, nanowire laser, and single molecule sensors [1-3]. Silicon carbide (SiC) is an important wide band-gap semiconductor with superior properties, such as high break down field strength, high thermal conductivity, high saturation drift velocity, and excellent physical and chemical stability. Bulk SiC is not a good candidate for application in optoelectronic integration on account of its indirect band gap. However, SiC nanorods and nanowires have been shown to exhibit more superior properties. SiC nanostructures show semiconducting with direct band gaps. Considerable efforts have thus been made to fabricate SiC nanostructures via several methods, such as nanotube-conversion reaction [4], carbon-thermal reduction [5], chemical vapor deposition [6], and chemical solution routes [7]. Most SiC nanowires are cubic zinc-blend structure grown along the [111]-direction and exhibit mechanical properties superior to other forms of SiC [8-10]. Many research results indicate that the electrical properties of nanostructures depend on their size, geometry, and also on whether the dangling bonds of surface atoms are passivated or not. The SiC nanoscale materials are also expected to possess different electronic properties compared to their corresponding bulk crystals. So, it is important to theoretically study the electronic properties of SiC nanostructures, which would provide a better understanding of their electronic and structural properties.

Density functional theory (DFT) methods are known to be more accurate to predict the electronic prosperities of nanostructures. In this study, we employ DFT to study the electronic properties of SiC nanodots and nanowires. It is essential to provide a detailed analysis the dependence of electronic properties on the size and dimensionality, which is important to understand the electronic properties for practical applications.

2. Simulation details

All the calculations were performed using SIESTA code [11] within the local-density approximation for the exchange-correlation term [12], as proposed by Perdew and Zunger[13]. The interaction between ions and electrons is described using the norm-conserving Troullier-Martins pseudopotentials factorized in the Kleinman-Bylander form. An energy cutoff of 90 Ry is sufficient to converge the grid integration of the charge density. The valence electron wave functions were expanded by using double-ζ basis set plus polarization functions (DZP). The Brillouin zone was sampled by (1×1×6) and (1×1×1) mesh points in the K-space within the Monkhorst-Pack scheme for the nanowires and nanodots, respectively. The structure of the nanostructures were relaxed using conjugate gradient (CG) coordinate optimization until the forces on each atom were less than 0.02 eV/ Å.

The structure optimizations are first performed for bulk 3C-SiC. The calculated lattice parameter, a_0=4.36 Å, and the bulk modulus, *B*=226 GPa, are found to be in good agreement with the experimental values of 4.36 Å and 224 GPa, respectively [14]. We find an indirect band gap (ΓX) of 1.24 eV, which is smaller than the experimental value of 2.4 eV, expected since the conduction states are not accurately described within the DFT approach [15].

3. Results and discussion

Fig. 1 shows cross section of SiC nanostructures in [111] direction. The big, middle and small spheres represent silicon, carbon and hydrogen atoms, respectively. The surfaces of the SiC nanostructures are saturated by hydrogen atoms. Comparison of the different shaped (hexagonal, rectangular, triangular, rhombodedral, octagonal and circular) nanowires with the same size shows that the nanowires with a hexagonal cross-sectional shape have the minimum potential energy, indicating that these nanowires are the most stable [16]. These results agree with experimental results that demonstrate the most stable and natural cross-sectional configurations. So the nanowires with hexagonal cross-section are considered. The diameters of the SiC nanowires are about 0.33, 0.66, 0.99, and 1.33 nm. The diameter of the nanowires is defined as an average of two radial dimensions: corner to corner and edge to edge distances. The diameters of the SiC nanodots are 0.62, 1.26, 1.54, and 1.88 nm.

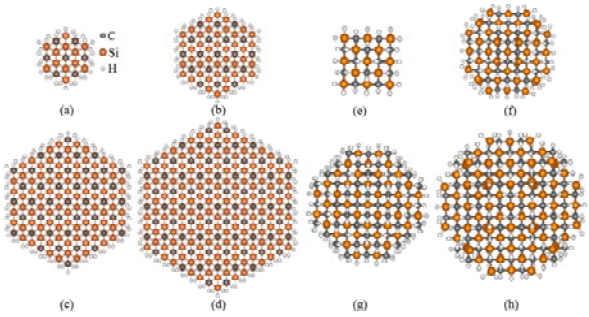

Fig.1. (Color online) Cross-section of SiC nanowires in the [111] direction with diameter of (a) 0.33, (b) 0.66, (c) 0.99, (d) 1.33nm, and nanodots with diameter of (e) 0.62, (f) 1.26, (g) 1.54, and (h) 1.88 nm.

The calculated electronic band structures along the Γ-X direction (parallel to the growth direction of the nanowire) of hydrogen saturated SiC nanowires with four diameters are shown in Fig. 2. Unlike the bulk 3C-SiC, all the nanowires exhibit semiconducting character, with a direct band gap at the Γ point, which suggests that these nanowires may preserve strong electroluminescence, and thus, have high potential for full-color display applications. It is should be noted that according to the effective masses approximation, [111]-oriented 3C-SiC nanowires are expected to have indirect band gaps. However, the DFT calculations clearly show that the nanowires have direct band gaps at the Γ point. The direct band gaps of [111]-oriented nanowires arise from the quantum-confinement effects in these nanowires. Furthermore, the band gaps of SiC nanowires generally decrease with increasing nanowires diameters. The band gaps are 3.28, 2.15, 1.80, 1.60 eV for the SiC nanowires with the diamaters of 0.33, 0.66, 0.99, 1.33 nm, respectively.

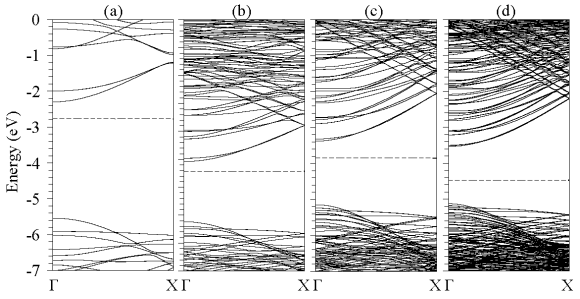

Fig. 2. The band structures of hydrogen saturated SiC nanowires with diameter of (a) 0.33, (b) 0.66, (c) 0.99, (d) 1.33nm. The Fermi energy is denoted by the dash line.

To gain more insight into the detailed characteristics for the top of the valence bands and the bottom of the conduction band, the projected density of states (PDOS) onto the C and Si atoms of hydrogen passivated SiC nanwires are shown in Fig. 3 (a)-(d), and that of the SiC nanodots are shown in Fig. 3 (e)-(h). We can see the top most filled valence state and the lowest state in the conduction band arise from the states of C and Si atoms, respectively. The band gap of the SiC nanostructures increase in energy with decreasing nanostructures diameter, which is associated with quantum confinement effects.

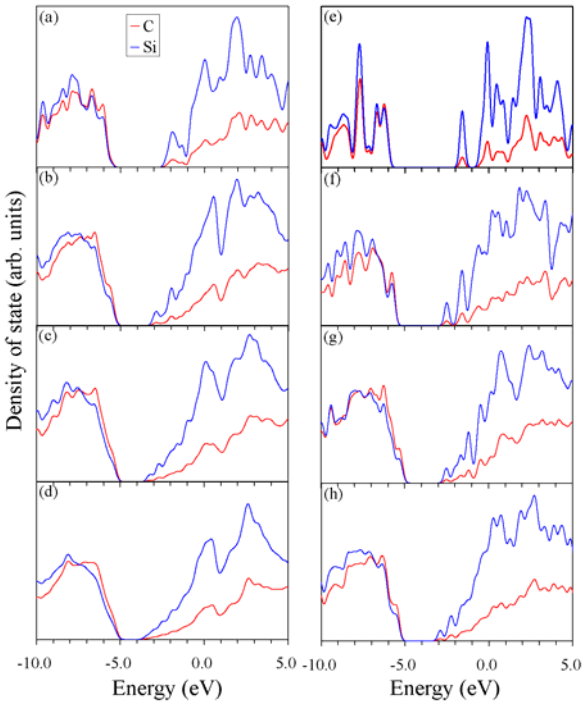

Fig. 3. (Color online) Partial density of states (PDOS) of SiC nanowires with diameter of (a) 0.33, (b) 0.66, (c) 0.99, (d) 1.33nm and nanodots with diameter of (e) 0.62, (f) 1.26, (g) 1.54, and (h) 1.88 nm projected onto Si and C atoms.

The diameter dependence of the band gap for the SiC nanostructures is shown in Fig. 4. It is clearly seen that the band gap of SiC nanostructures decrease with increasing diameter. Compared with bulk band gap of 1.24 eV, there exists a remarkable quantum confinement effect in the nanostructures. The band gap can be fitted using the following expression: $E_g = E_g^{bulk} + \beta / d^{\alpha}$, where E_g is the band gap value of bulk 3C-SiC, α and β are fit parameters, and *d* is the diameter of the nanostructures.

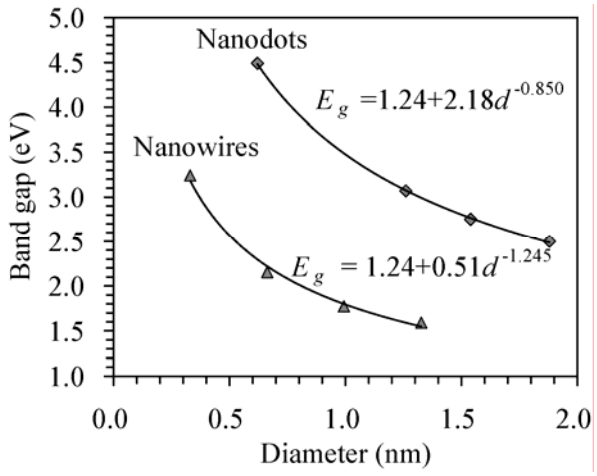

Fig. 4. Band gaps of SiC nanostructures as a function of diameter.

The fit parameters are: α=1.245 and β=0.51 for the [111]-oriented nanowires and α=0.85 and β=2.18 for the nanodots. Using a simple effective-mass approximation, particle-in-a-box model for confinement in planar wells, cylindrical wires, and spherical dots, the band gap of these nanostructures compared to the bulk value depends linearly on $1/d^2$ [17]. Such a simple description should be regarded as only a first approximation of quantum confinement in semiconductors; as the dimension of the nanostructures becomes very small, this relationship can be expected to break down.

4. Conclusions

In summary, we have performed first-principles calculations on SiC nanowires in [111] direction and nanodots with different diameters. All the nanowires exhibit semiconducting character, with a direct band gap at the Γ point ,which suggests that these nanowires may preserve strong electroluminescence, and thus, have high potential for full-color display applications. It demonstrates that the VBM comes mainly from the states of C atoms; whereas CBM is highly localized to Si atoms. Furthermore, the band gaps of SiC nanostructures generally decrease with increasing nanostructures diameters.

Acknowledgments

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