Theoretical study of the electronic band gap in β-SiC nanowires

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The structure and electronic properties of β-SiC nanowires in the directions of growth [111] and [001] are carried out by means of density functional theory (DFT) based on the generalized gradient approximation (GGA). The dangling bonds of the surface atoms in the quantum wires are passivated using hydrogen atoms. The calculations show that both nanowires exhibit a direct energy band gap at center of Brillouin zone. The electronic band structure and band gaps show a significant dependence on the diameter, orientation and surface passivation.

Keywords: Density functional theory; nanowires; silicon carbide.

La estructura y las propiedades electrónicas de nanoalambres de β-SiC crecidos en las direcciones [111] y [001] son calculadas a través de la teoría del funcional de la densidad (DFT) basada en la aproximación de gradiente generalizado (GGA). Los enlaces rotos de los átomos de la superficie en los alambres cuánticos son pasivados usando átomos de hidrógeno. Los resultados muestran que ambos tipos de nanoalambres presentan una brecha de energía directa en el centro de la zona de Brilllouin. La estructura de bandas electrónica y la brecha de energía muestran una significativa dependencia del diámetro, orientación y pasivación de la superficie.

Descriptores: Teoría del funcional de la densidad; nanoalambres; carburo de silicio.

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1. Introduction

The study of low-dimensional quantum structures has attracted great attention recently in the field of semiconductors research [1–3]. Nanowires are one of the most common one-dimensional (1-D) structures and many kinds of materials can be synthetized into nanowires structures. They present remarkable different properties and applications from their corresponding bulk forms [4]. An example, of these 1-D systems are SiC nanowires (NWs), due to their wide band gap with high electron mobility, SiCNWs would be favorable for applications in high temperature, high power, and high frequency nanoscale devices [5, 6]. In recent years SiC have been intensively studied for their potential applications in electronic devices and sensors [7]. In this work, we study the hydrogen-passivated β-SiC NWs oriented along both [001] and [111] directions [Figs. 1(a) and 1(b), respectively] using the density functional theory (DFT) based on the pseudopotential plane-wave approach with the supercell technique. The generalized gradient approximation (GGA) exchange-correlation functional used is a revised version of Perdew, Burke, and Enzerhof (RPBE) [8]. We are focusing on the electronic structure and energy gap and their dependence on wire diameter and orientation. Also, the total and partial density of states (DOS) as well as the total electron density are calculated.

2. Calculation procedure

As we have mentioned above, our calculations were performed in the framework of DFT-GGA utilizing the RPBE exchange and correlation functional. The core electrons are described using ultrasoft Vanderbilt pseudopotentials [9] within the CASTEP code [10, 11], as implemented in the Materials Studio software suite. The kinetic energy cutoff for the plane-wave basis set is 280 eV. The Brillouin zone has been sampled with a highly converged set of **k** points, using grids up to (1×1×6) points according to the Monkhorst Pack scheme [12], the initial bond lengths of Si-H and C-H are 0.147 nm and 0.107 nm, respectively. Nanowires are then placed in a cubic simulation cell with periodic boundary conditions. The size of the simulation cell is chosen so that

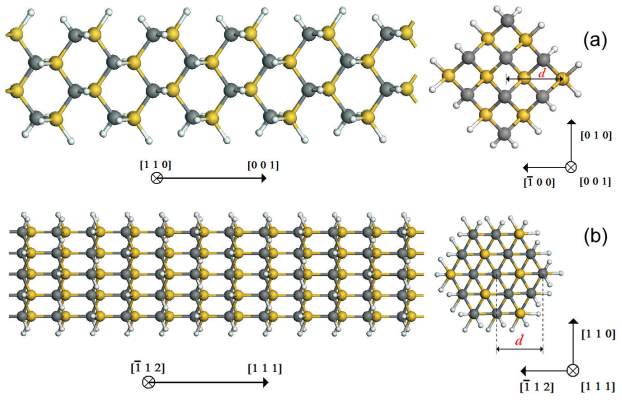

FIGURE 1. Side and top view of relaxed structural models grown in the directions (a) [001] and (b) [111] SiCNWs passivated with H (small spheres). C and Si are represented by dark and light gray spheres.

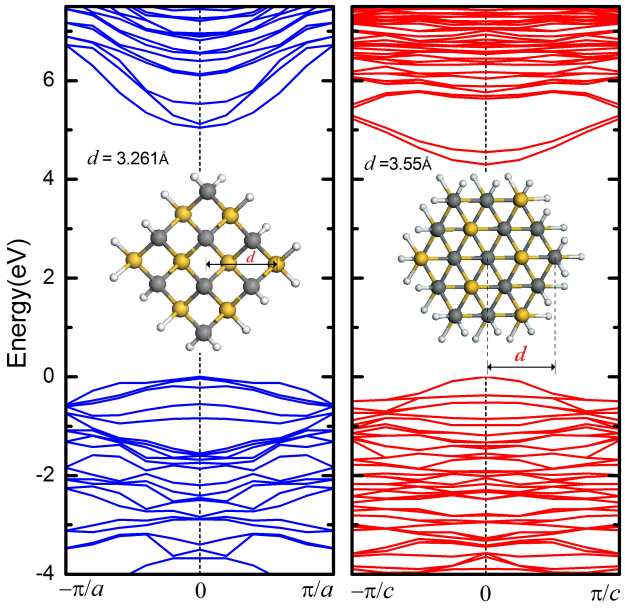

FIGURE 2. Energy bands for the SiCNWs grown in the directions [001] and [111], respectively. The calculated gaps are 5.04 and 4.3 eV for the diameters 3.261 and 3.55 Å, respectively. The maximum value of the valence band energy, at the Γ point, was taken as the (zero) reference.

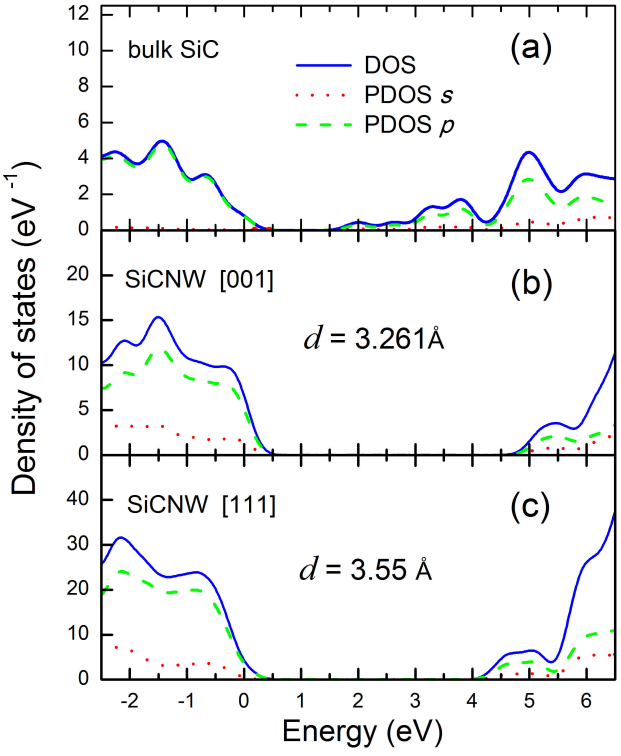

FIGURE 3. Calculated density of states (DOS, solid line) and partial density of states (PDOS) projected onto *s* (dotted line) and *p* (dashed line) orbitals. (a) Bulk β-SiC, (b) [001], and (c) [111] SiCNWs.

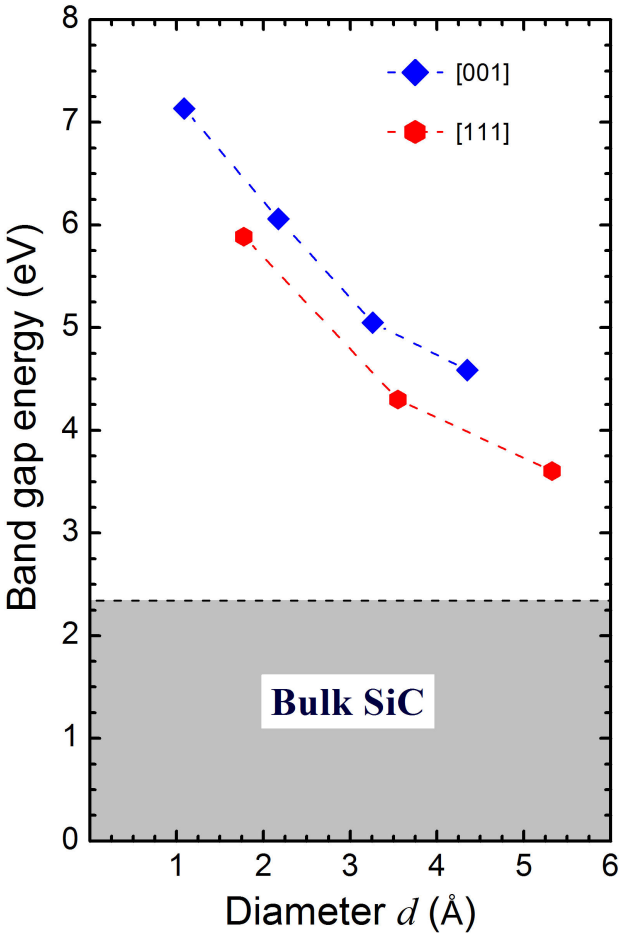

FIGURE 4. Band gap energy of hydrogenated SiCNWs as a function of diameter. (a) [001] SiCNW (solid diamonds) and (b) [111] SiCNW (solid hexagons). The dash line is a guide for the eyes.

the distance between the cluster and its replica (due to the periodic boundary conditions) is more than 12 Å. Under this consideration, the interactions between the nanowires and their replicas are negligible. Finally all the wires are relaxed to minimize the total energy using the conjugate gradient algorithm [13]. The local minimum is achieved when all residual forces acting on the atoms are less than 0.03 eV/Å. It is known that DFT systematically underestimates the semiconductor band gap energy [14]. A scissors operator of 0.97 eV has been considered, which is corresponding to the difference between experimental (2.34 eV) [15] and our calculated value (1.37 eV) for the energy bandgap of bulk crystalline β-SiC.

3. Results

We present here the electronic band structure for β-SiC nanowires (SiCNWs) oriented along the [001] and [111] directions. The atomic positions of all atoms were fully relaxed using the first principles methods described above. Calculation of electronic properties performed in one-dimensional Brillouin zone along the wires axis. Figures 2(a) and 2(b) shows the band dispersion along the

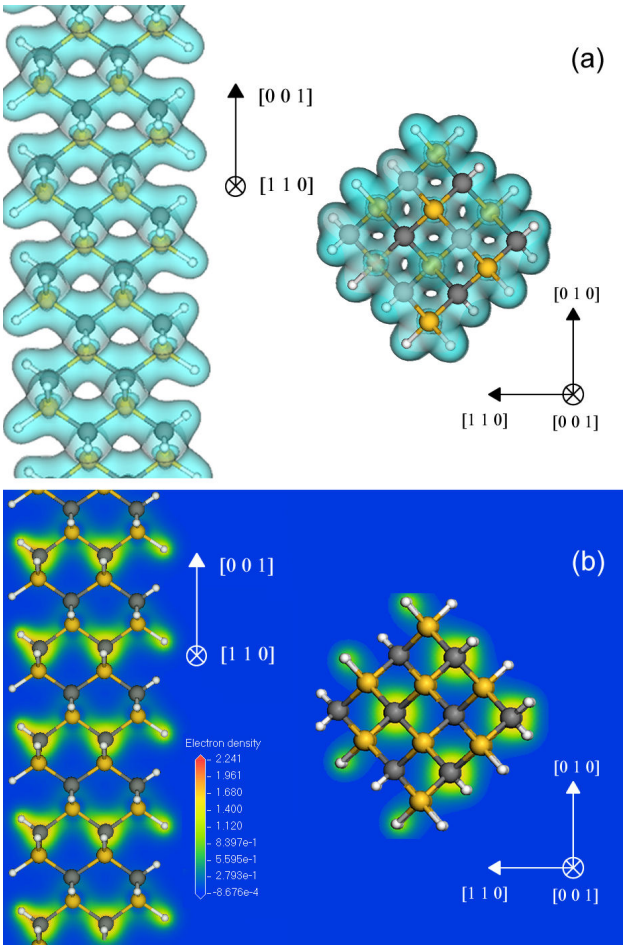

FIGURE 5. (a) Longitudinal and cross sectional view of [001] relaxed SiCNWs showing the total electron density, the isosurface value used was 0.2 Å^{-3}. (b) Electron charge density in a (110) plane through only C atoms of bulk, showing the ropelike structure resulting from the relaxation.

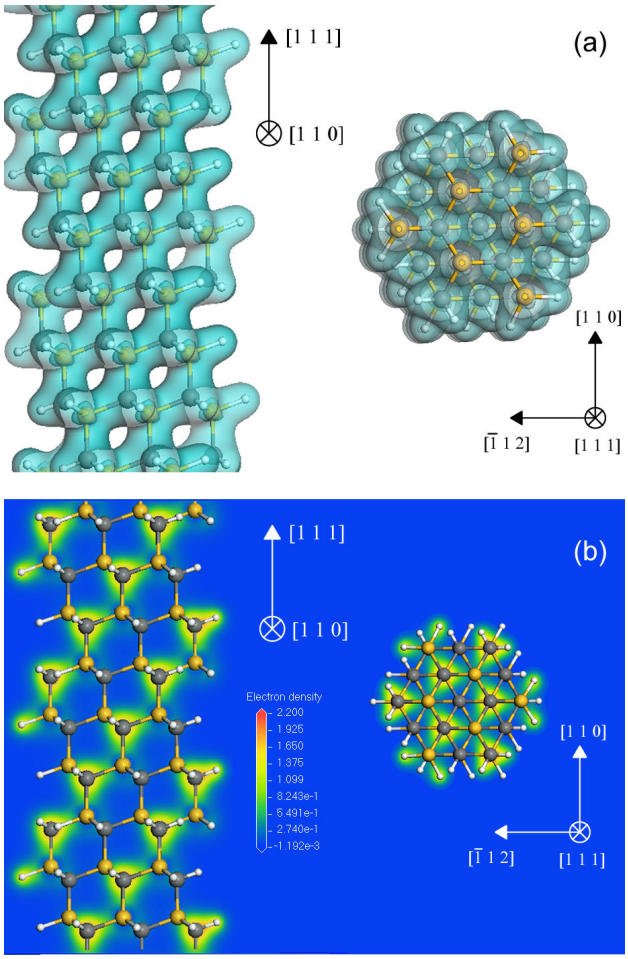

FIGURE 6. (a) Longitudinal and cross sectional view of [111] relaxed SiCNWs showing the total electron density. The isosurface value used was 0.2 Å^{-3}. (b) Electron charge density in a (110) plane through only C atoms of bulk, showing the ropelike structure resulting from the relaxation.

nanowire direction for SiCNWs with similar width d. Notice that in both cases the SiCNWs have a direct band gap. This is true for all NWs widths considered here. It is worth noting that dangling bond-like states do not appear within the energy band gap region for SiCNWs in the two directions. This is an indication of hydrogen passivation of the surface dangling bonds that provides a smooth termination of the orbitals.

Figure 3 shows the calculated total density of states (DOS) and partial density of states (PDOS) corresponding to electronic band structure of Fig. 2. An analysis of the orbital contributions shows that the eigenvalue near the valence-band maximum are pure carbon atom p states. Notice that in all cases, (a)-(c), the conduction band edge near the Brillouin zone center is primarily formed by p states, the contribution of s states being negligible.

As expected from quantum size effects, we observed that the absolute value of the conduction band minimum increases in energy as the thickness of the wire decreases. This effect of quantum confinement of electron is observed all widths we studied. This leads to an increase in the electronic energy band gap (Eg) with decreasing NWs diameter.

For NWs with similar diameter but different orientation we observed, in Fig. 4, that E_g is greater for wires along [001] and lower for wires along [111] directions. Besides this dependence of E_g on the diameter d and the orientation of growth axis, other ways for modifying the electronic properties would be important for applications. The orientation anisotropy in Eg reduces with the nanowire width and is expected to disappear for very thick wires when the Eg approaches that of the bulk material.

Figures 5 and 6 show the isosurface (a) and the contour map (b) for the total electron density of the two kinds of nanowires [001] and [111], respectively. The electron densities cover regions in the [001] nanowire only for carbon atoms in transversal planes (observed from the [110] perspective) of growth direction. The substantial difference with [111] nanowire is the orientation of these planes, which is diagonal (observed from the same perspective) to the growth direction. In the contour maps, the lighter regions

are associated with higher field values. In the isosurfaces, the darker values correspond to more populated regions. This information could be corroborated observing the contour maps for both wires. As was expected the greater magnitude values are associated with the nearest regions of the more electronegative nucleus (carbon atoms). Consistently, partial density of states [Fig. 3 (a)-(c)], for the superior edge of valence band has a primordial *p* character contribution, which are related with carbon atoms shown in the electron density maps. Similarly, the partial density of states for the lower edge of conduction band has a *p* character, we suppose that these are related with unoccupied *p* orbitals of Si atoms.

4. Conclusions

In summary we have studied, in the framework of density functional theory within the generalized gradient approximation, the structures of β-SiC nanowires oriented in the [001] and [111] and their electronic band structure as a function of diameter. These properties are strongly influenced by quantum confinement. Direct fundamental band gaps are found at Gamma point for both wires, which enlarge as diameter shrinks. It is also found that [001] wires have overall a larger gap than [111] wires. SiC nanowires with direct band gap are promising candidates for optoelectronics applications such as light emitting devices and photodetectors. The wave length of the emitted or detected light can be tuned through the choice of the NWs width.

Acknowledgments

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