



# Electronic properties of fluorinated silicon carbide nanowires



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## ABSTRACT

The control and modulation of the electronic properties of silicon carbide nanowires (SiCNWs) are crucial for the obtention of materials with specific electronic features for the design of stable and robust electronic devices. Tuning the band gap by chemical surface passivation constitutes a way for the modification of the stability and the electronic band gap of these nanowires. In this work, the structural and electronic properties of fluorinated 3C-SiCNWs, grown along the [1 1 1] crystallographic direction, are investigated by using the density functional theory within the generalized gradient approximation. We consider nanowires with five diameters, varying from 0.71 nm to 2.13 nm, and six surface covering schemes including fully hydrogen- and fluorine-terminated ones. Relative stabilities and electronic band gaps were calculated for the different surface functionalization schemes and diameters considered. The effects of chemical passivation on the size and nature of the band gap of the various studied nanowires are discussed.

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## 1. Introduction

Silicon carbide (SiC) can crystallize in many different polytypes and the most common of them are wide band gap semiconductors [1]. Their technological importance stems from their high thermal stability and high thermal conductivity, which play a key role in the development of SiC based high temperature applications [2,3]. SiC nanostructures have potential applications as active elements in various nanoscale and electronic devices, including sensitive chemical detectors [4–7], photocatalysts [8–12], nanoscale field-effect transistors [13–16], and optoelectronic devices [17,18]. Different applications demand distinct electronic properties and then it is desirable to identify possible routes to control and adapt the electronic structure of such systems. Theoretical studies of silicon carbide nanowires (SiCNWs) have revealed several factors that may influence the size and character of their band gap. These include surface reconstruction [19], the diameter and cross-sectional shape of the nanowires [20,21], chemical passivation [22,23], impurities [24] and doping [25].

Methods to control the geometry of nanowires have been developed, such as growth based on the vapor–liquid–solid mechanism, the vapor–solid mechanism and the solid–liquid–solid mechanism. These methods yield wires with cubic core along the [100] and [111] crystallographic orientations with diameters ranging from

10 nm to 200 nm [26–32]. Bechelany et al. [29] proposed a vapor–solid-based method without the use of catalysts for the mass production of 3C-SiCNWs with tuneable geometric features and surfaces and that could be chemically modified *in situ*. A facile low pressure annealing route using  $\text{NH}_3$  as a hydrogen source for the structural and chemical modification of SiCNWs has been applied by Rummeli et al. [33]. Moreover, Niu et al. [34] have shown that the SiCNWs can be mixed with other compounds and conveniently coated on desired surfaces. Accordingly, many of the earlier theoretical studies of SiCNWs have addressed hydrogen passivated SiCNWs [20,21,35]. However, there are studies that have shown that the passivation of SiCNWs with hydroxyl and oxygen tends to reduce the band gap and to increase the energetic stability [22,23,36,37]. Furthermore, the effects of fluorine-passivation have been studied in silicon nanowires [38–40], but they have not been addressed for SiCNWs with different radii. Therefore, in this work we study the relative stability and electronic properties of [1 1 1] 3C-SiCNWs passivated with fluorine and hydrogen.

## 2. Nanowires structures and surface covering

We consider 3C-SiCNWs with diameters ( $d$ ) varying from  $d = 0.71$  nm to  $d = 2.13$  nm and grown along the [111] direction (see Fig. 1). Since the thinnest possible SiCNW along this direction has a hexagonal cross section, we only study NWs with this type of cross sections. Moreover, we have verified that both fully-hydrogenated SiCNWs with hexagonal and circular cross

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sections and diameters around 2.13 nm have practically the same energetic stability, but the former has a slightly larger band gap than the latter. Furthermore, for the fully-fluorinated SiCNWs with diameters around 2.13 nm, the NW with hexagonal cross section is slightly more stable than that with nearly circular cross section and, also, the former has a larger band-gap than the latter by 0.11 eV. It is worth mentioning that many theoretical studies of semiconductor NWs, including 3C-SiCNWs, only consider [111] systems with hexagonal cross sections [22,41–45]. In this work, the diameter of the nanowire refers to the distance between atoms located at opposite vertices of the hexagonal cross section of the bare SiC nanowire (see Fig. 1a). The diameters of the nanowires considered were chosen to be sufficiently small in order to exploit quantum confinement and edge chemistry effects on the electronic structure of the systems. We note that at least one size of the nanowires studied here ( $d = 2.13$  nm) is within experimental reach, since SiCNWs with diameters ranging from 2 to 30 nm have been grown with a technique based on CNT solid–vapor reaction with volatile oxide and/or halide species [46].

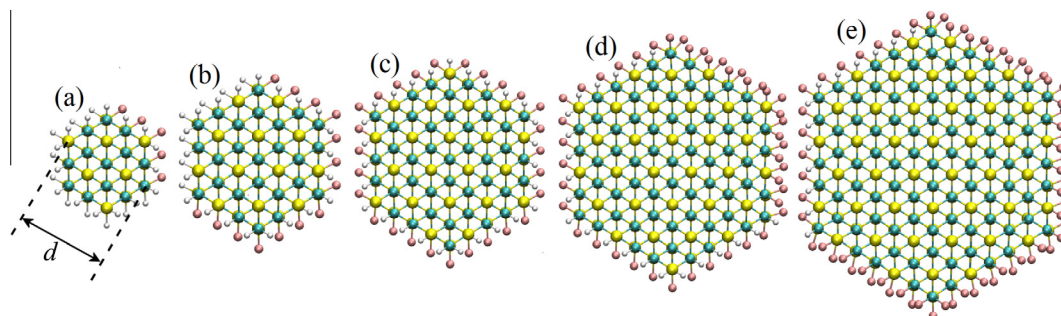
All the 3C-SiCNWs structures considered have a hexagonal cross section cut out of bulk 3C silicon carbide. The dangling bonds of each nanowire were first fully hydrogenated and their structure relaxed using the forces obtained from a DFT calculation. These fully hydrogenated SiCNWs were taken as reference for the subsequent surface covering schemes considered in this paper, where the hydrogen atoms were gradually substituted with fluorine ones. The fluorine atoms were chosen since it is known that they can stabilize silicon nanowires [38–40]. Here,  $f$  will denote the fraction of surface fluorine atoms in an otherwise hydrogen passivated SiCNW. Moreover, for each  $d$  and  $f$ , with  $0 < f < 1$ , we considered four combined (hydrogen and fluorine) covering schemes depicted in Fig. 2(b)–(e) and labeled by NW-I, NW-II, NW-III and NW-IV,

respectively, together with the fully hydrogenated ( $f = 0$ ) and fully fluorinated ( $f = 1$ ) cases, shown in Fig. 2(a) and (f), respectively.

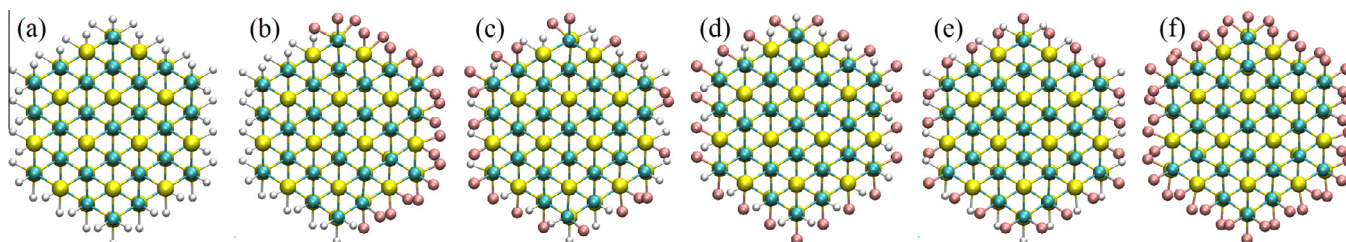
For the NW-I scheme, the surface substitution sites were progressively chosen beginning at a vertex of the hexagonal cross section and crossing the different sides, let's say in the clockwise direction, until getting the desired value of  $f$ . It is worth mentioning that a completely fluorine saturated hexagonal side stands for  $f = 0.16$ . For the NW-II scheme, the substitution sites were randomly determined. Moreover, for the NW-III covering-scheme, only the hydrogen atoms saturating the Si dangling bonds were progressively substituted by fluorine ones in a similar way to the NW-I case, until achieving  $f = 0.5$ . Then, the hydrogen atoms saturating the carbon atoms were progressively substituted by fluorine ones until  $f = 1$ . Finally, for the NW-IV covering scheme, the saturation method is similar to the previous case but we first substituted the hydrogen atoms saturating the C dangling bonds and then those saturating the Si bonds.

### 3. Computational method

All calculations were performed within the density functional theory formalism, as implemented in the SIESTA code [47]. We used the generalized gradient approximation (GGA) with the PBE exchange–correlation functional [48], an optimized double- $\zeta$  basis plus single polarization orbitals for the valence electrons and norm-conserving Troullier–Martins pseudopotentials [49]. The Brillouin zone was sampled with  $1 \times 1 \times 24$   $k$ -points per unit cell and the numerical integrals were performed on a grid sufficiently fine to represent plane waves up to 180 Ry without aliasing. The optimization of atomic positions was allowed to proceed without any symmetry constraints until the force on each atom were less than 0.04 eV/Å.



**Fig. 1.** Top view of the cross sections of decorated [111] 3C-SiCNWs with (a)  $d = 0.71$  nm ( $f = 0.16$ ), (b)  $d = 1.06$  nm ( $f = 0.33$ ), (c)  $d = 1.42$  nm ( $f = 0.5$ ), (d)  $d = 1.77$  nm ( $f = 0.66$ ) and (e)  $d = 2.13$  nm ( $f = 0.83$ ). The surface decorations correspond to the NW-III surface-covering scheme (see text for details). Yellow, cyan, pink and white spheres represent Si, C, F and H atoms, respectively. The definition of the nanowire diameter ( $d$ ) is shown in (a). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



**Fig. 2.** Top view of the cross sections of some 3C-SiCNWs with the surface covering schemes considered in this work. (a) fully hydrogenated ( $f = 0$ ), (b) NW-I ( $f = 0.5$ ), (c) NW-II ( $f = 0.5$ ), (d) NW-III ( $f = 0.5$ ), (e) NW-IV ( $f = 0.5$ ) and (f) fully fluorinated ( $f = 1$ ). All SiCNWs have  $d = 1.06$  nm. Yellow, cyan, pink and white spheres represent Si, C, F and H atoms, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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