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Energy gap of extended states in SiC-doped graphene nanoribbon: Ab initio calculations

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ABSTRACT

The energy gap of extended states in zigzag graphene nanoribbons (ZGNRs) was examined on the basis of density-functional theory. In isolated ZGNRs, the energy gap is inversely proportional to the width of ribbon. It agrees well with the results from the Dirac equation in spin-unpolarized ZGNRs, although the considered ZGNRs have spin-polarized edges. However, the energy gap in SiC-doped ZGNRs cannot be modeled by effective width approximation. The doping also lifts the spin-degenerate of edge states and results in a metallic-like band structure near the Fermi level in SiC-doped ZGNRs. Our calculations may be helpful for understanding the origin of the reported single-channel ballistic transport in epitaxial graphene nanoribbons.

1. Introduction

Graphene has attracted extensive attention in recent years due to its unique and remarkable electronic properties, such as the gapless-semiconductor band structure, existence of pseudospin, and the high electronic mobility at room temperature [1–3]. These features are desirable for the development of the next-generation microelectronic and spintronic devices [4,5]. When the gapless graphene is patterned into a narrow ribbon [6], one would expect the opening of an energy gap due to the lateral confinement of charge carriers [7,8]. The electronic structures of graphene nanoribbons can be modeled by imposing appropriate boundary conditions on tight-binding approximation [9] or on Dirac's equation [10]. Theoretical studies show that the energy gap depends on the width and geometry of graphene nanoribbons [10–12]. In experiment, an energy gap near the charge neutrality point was measured in lithographically patterned graphene nanoribbons [7,13]. It scales inversely with the ribbon width, consistent with theoretical studies [9,14].

However, it is puzzling that exceptional ballistic transport was measured in epitaxial graphene nanoribbons [15,16]. It was reported that 40-nanometer-wide graphene nanoribbons epitaxially grown on silicon carbide are single-channel room-temperature ballistic conductors [15]. Theoretically, the zigzag graphene nanoribbons (ZGNRs), which are studied in the recent experiment [15], should have spin-polarized edges, band gap and spin-degenerate channels [17]. None of these theoretical predictions can match the recent experimental observations [18].

In this work, we use the first-principles calculation based on density-functional theory (DFT) [19] to study the energy gap of extended states in ZGNRs. In isolated ZGNRs, the energy gap is inversely proportional to the width of ribbons. It agrees well with the results from the Dirac equation in isolated ZGNRs with appropriate boundary conditions [10]. The effective width of ZGNRs is slightly larger than the width of ribbons. However, the energy gap in SiC-doped ZGNRs [15,20] cannot be modeled by effective width approximation. It is not only from the quantum-confinement effect [21,22] but also from the new boundary condition. In a 40 nm-wide ZGNR with SiC-doped boundary, the energy gap would be about 100 meV, which is several times larger than the gap in an isolated 40 nm-wide ZGNR. The doping also lifts the spin-degenerate of edge states and results in a metallic-like band structure near the Fermi level in SiC-doped ZGNRs. The spin-polarized and metallic-like band structure may be used to understand the origin of the reported single-channel ballistic transport behavior [15].

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2. Method and computational details

The electronic structures were calculated on the basis of DFT at the level of local spin-density approximation (LSDA) [23]. Although there may be some limitations within local density approximation (LDA) method, conventional LDA is usually used in the calculations about graphene and graphene-based structures [24–26]. In this work, the considered electronic structures are spin-dependent. Therefore, LSDA is used in all our calculations. The projector-augmented wave (PAW) pseudopotentials were employed to describe the effect of core electrons. The energy cutoff in the calculations was set to be 400 eV, and the total energy was converged to better than 10^{-5} eV. The equilibrium structures were obtained through structural relaxation until Hellmann–Feynman forces were less than 0.02 eV/Å. The *k*-point grid of $1 \times 15 \times 1$ was employed to sample the Brillouin zone.

The atomic structure of the SiC-doped ZGNRs is shown in Fig. 1. The structure was modeled by a periodic slab geometry, with a vacuum of at least 9.4 Å between two neighboring slabs in *x* and *z* direction. The ZGNRs are assumed to be infinite along the *y*-direction with a lattice constant of 0.492 nm. The edges of ZGNRs in *x*-direction are terminated with H atoms. As for the SiC-doped ZGNRs, the location of SiC is close to the rightmost edge, leading to an asymmetric boundary in *x*-direction. The Si-terminated SiC is stretched, its $\sqrt{3} \times \sqrt{3}R30^{\circ}$ cell corresponds to a 2×2 graphene cell [27]. The dangling bonds of SiC are saturated by hydrogen atoms, except for the lonely Si atom [28] shown in Fig. 1. It makes the structure more stable. Besides, when graphene is grown on the Si-terminated SiC(0001) surface, the substrate (SiC) has a strong effect on graphene [29–31]. The epitaxial graphene would be highly distorted because of strong covalent bonding to the SiC-substrate. In our model, there is also a strong SiC-ZGNR interaction. In Fig. 1(c), obvious deformation of ZGNR near SiC can also be found due to the strong SiC–graphene interaction. Their binding energy is about 2.48 eV each unit cell (0.83 eV each Si atom in SiC surface). The large binding energy between SiC and graphene also suggests a stable interface structure.

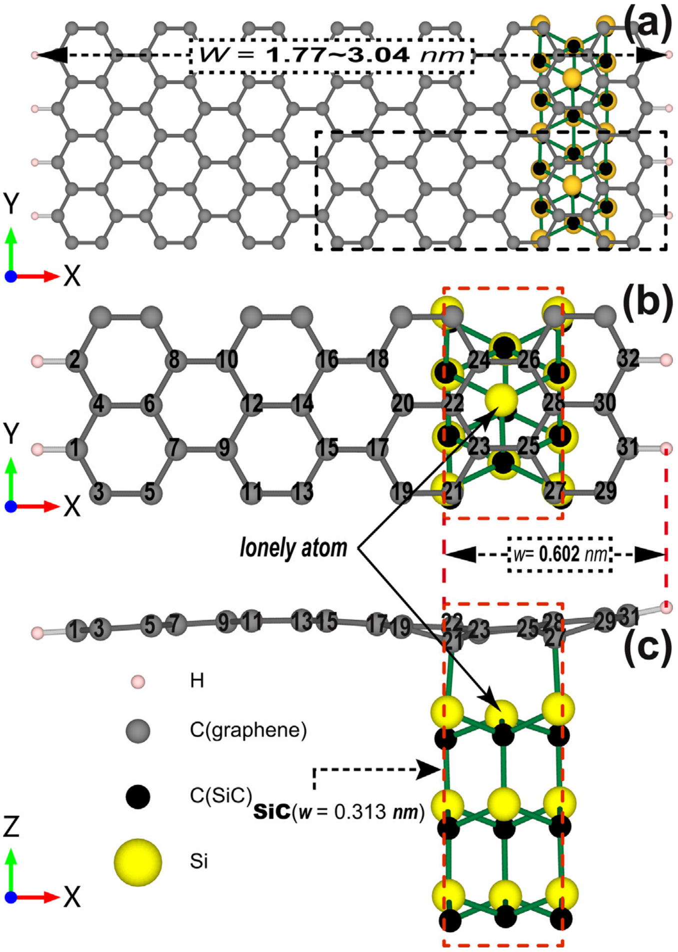

Fig. 1. (a) Top view of SiC-doped zigzag graphene nanoribbon (ZGNR) with 14 zigzag chains (14-ZGNR). The width of 14-ZGNR is about 3.04 nm. The width of ZGNRs considered in this work is from 1.77 nm (8-ZGNR) to 3.04 nm (14-ZGNR). (b) Top view of SiC-doped 8-ZGNR [the dashed box in (a)]. The width of 8-ZGNR is about 1.77 nm. (c) Side view of SiC-doped 8-ZGNR. The Si-terminated SiC is stretched, its $\sqrt{3} \times \sqrt{3}R30^{\circ}$ cell corresponds to a 2×2 graphene cell. The ZGNRs are assumed to be infinite along the *y*-direction with a lattice constant of 0.492 nm. The edges of ZGNRs in *x*-direction are terminated with H atoms. The length of C–H bond is about 0.11 nm. The location of SiC is close to the rightmost edge. The distance, from the leftmost of SiC to the rightmost of ZGNR, is about 0.602 nm. The width of SiC is about 0.313 nm. The dangling bonds of SiC are saturated by hydrogen atoms (no shown), except for the lonely Si atom. The carbon atoms in graphene ribbons, from left to right and from bottom to top in unit cell, are labeled with numbers as shown in (b).

In experiment [15], the width of the SiC-doped region is hundreds of nanometer. The large SiC-doped region is unable to be simulated in DFT calculations due to the limitation of computational resources. Fortunately, the width of the SiC-doped region has little influence on the electronic structure of the free graphene region near Fermi level due to the strong and localized SiC-graphene interaction. Considering the limitation of computational resources and the lattice mismatch between SiC and graphene, the width of the SiC-doped region is set to be about 0.3 nm in this work. Moreover, in order to make the free graphene region as long as possible, SiC is located near the rightmost edge. We would focus on the free graphene region with leftmost H-terminated edge and SiC-doped boundary.

3. Results and discussion

The spatial distribution of charge density difference, between spin up and spin down, in isolated and SiC-doped ZGNRs is shown in Fig. 2. In isolated ZGNRs, the two edges are spin-polarized with opposite spin. In comparison, the charge density difference is almost zero at the SiC-doped edge due to the strong SiC–graphene interaction [29–31], while it is almost unchanged by the doping at another edge. It suggests that the rightmost spin-polarized edge states of isolated ZGNRs may be destroyed by SiC. Moreover, it is expectable that the leftmost spin-polarized edge state can survive in the SiC-doped ZGNRs. Therefore, the spin-degenerate of edge

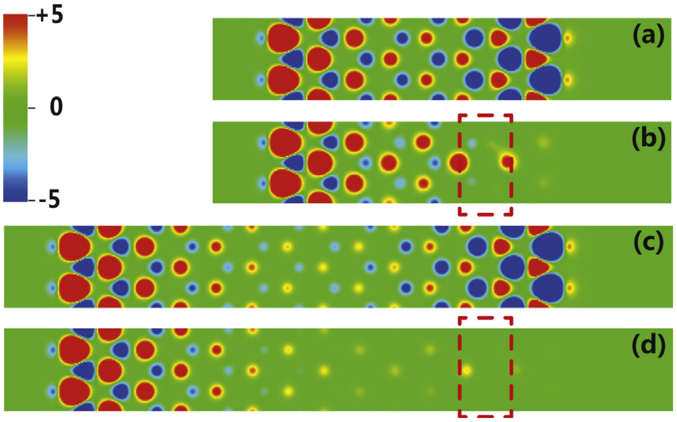

Fig. 2. The spatial distribution of charge density difference, between spin up and spin down, on graphene ribbon in 8-ZGNR (a, b) and 14-ZGNR (c, d) without (a, c) and with (b, d) SiC. The scale bar is in the unit of $10^{-3}|e|\text{Å}^{-3}$. The dashed box in (b) and (d) shows the location of SiC.