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Low-strain interface models for epitaxial graphene on SiC(0001) ☆

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ABSTRACT

A set of low-strain commensurate interface structures for epitaxial graphene on SiC(0001) are obtained by combining rotated graphene supercells with $m\times m$ or $m\sqrt{3}\times m\sqrt{3}R30°$ SiC cells. For two among the interfaces with lowest strain, corresponding to 4×4 and $6\sqrt{3}\times6\sqrt{3}R30°$ SiC periodicities, we analyze the binding energy of the graphene/SiC(0001) interface in terms of bond energies resulting from the (partial) saturation of individual Si dangling bonds by C atoms of graphene. These bond energies are determined as a function of the relative lateral displacement between the surface Si atoms and the graphene honeycomb. We find that this model energy does not explain the variation of the binding energies obtained from direct density functional calculations for the full interfacial systems. Moreover, for a given interface, the lateral rearrangements of the Si and C atomic positions found upon relaxation do not lead to any significant increase of the model binding energy. These results indicate that the deformations of the graphene layer cannot be neglected in the modeling of the binding energy of the graphene/SiC(0001) system.

1. Introduction

The epitaxial growth of graphene on SiC is a rapidly improving technique which offers great perspectives for future implementations of carbon-based electronic devices [1–3]. A single layer or a few layers of epitaxial graphene are formed on the SiC(0001) surface due to Si depletion during thermal graphitization of SiC, either in UHV conditions [1,4,5], or, more recently, in Ar atmosphere yielding larger uniform samples [6,7]. The remarkable electronic properties of ideal free-standing graphene [8,9] are lost at the interface between the epitaxial graphene and the Si-terminated surface of SiC [10], but are recovered in the successive graphene layers, which nevertheless show a residual interaction with the substrate [5,10,11]. The details of the graphene/SiC(0001) interface are still under experimental and theoretical investigation, but there is a broad consensus that a thin carbon layer, often called buffer layer, lies between the SiC substrate and the nearly-unperturbed graphene layers, thus providing an effective decoupling of the latter from the growth template [4,5]. The C atoms in the buffer layer are likely to be arranged in a honeycomb structure as in graphene [10,12], but the covalent bonding of part of them to the underlying SiC surface spoils the characteristic Dirac-like band dispersion of the graphene π electrons. The graphene/SiC(0001) buffer layer is closely related to the $6\sqrt{3}\times6\sqrt{3}R30°$ SiC reconstruction seen during the first stages of the graphitization process, a large super-periodic structure which is commensurate with a 13×13 graphene supercell [1,4,10,12]. The first successive graphene layers display a height modulation in STM maps, following the rippling of the buffer layer [1,12,13], and have the Dirac point at about 0.2–0.4 eV below the Fermi level due to n-doping caused by the substrate [10,11].

Several ab initio studies have addressed the electronic and structural properties of graphene/SiC(0001), either using the very large and computationally expensive $6\sqrt{3}\times6\sqrt{3}R30°$ periodicity [14–16], or, more often, a simplified interface having a much smaller $\sqrt{3}\times\sqrt{3}R30°$ periodicity [17–19]. At variance with the $6\sqrt{3}\times6\sqrt{3}R30°$ interface, the $\sqrt{3}\times\sqrt{3}R30°$ one is noncommensurate and the graphene lattice needs to be stretched by about 8% in order to match the SiC substrate. Some other SiC periodicities, which are nearly commensurate with some graphene supercells but have smaller simulation cells than the $6\sqrt{3}\times6\sqrt{3}R30°$ one, have also been considered, such as 3×3 [20], 4×4 [16], 5×5 [13,21], etc., but rarely or never observed in experiments [5]. Instead, other periodicities have sometimes been reported, such as 9×9 or $2\sqrt{3}\times2\sqrt{3}R30°$ (see Ref. [5] for a detailed list with references), but not addressed by theoretical calculations until now. A comparison of the energetics between different graphene/SiC interfaces has been made for the 4×4 and $6\sqrt{3}\times6\sqrt{3}R30°$ periodicities, indicating that the experimentally observed one is indeed more stable [16]. A clear correlation between the binding energy and the vertical spread of the graphene layer was pointed out [16]. However, the degree of passivation at the SiC(0001) surface due to the formation of covalent C–Si bonds and its role in the interface binding energy have not been addressed.

In this work, we construct commensurate graphene/SiC structures from rotated hexagonal supercells of SiC and graphene and identify those with lowest strain. In particular, we determine a list of candidate structures with smallest unit cells for $m\times m$ and $m\sqrt{3}\times m\sqrt{3}R30°$

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periodicities of SiC. Furthermore, we examine to what extent the binding energy is driven by the (partial) saturation of the Si dangling bonds at the interface through the formation of covalent C–Si bonds. For this purpose, the interaction energy between an ideal graphene layer and a single Si dangling bond is computed in a model system as a function of the relative lateral position of the interacting Si atom and the graphene. This graphene–Si bond energy is then used to build a model binding energy for a given graphene/SiC interface structure by summing the contributions of the individual surface Si atoms. Focusing on two structures with 4×4 and $6\sqrt{3}\times6\sqrt{3}R30°$ periodicities showing different binding energies [16], we find that their energetic stability cannot be explained by this modeling. These results contribute to enhancing our understanding of the bonding at the graphene/SiC(0001) interface.

In the following of this paper, we first describe in Section 2 how the graphene/SiC(0001) interface structures are built and selected according to the lowest graphene strain. Then, in Section 3 we analyze the binding energy of the 4×4 and $6\sqrt{3}\times6\sqrt{3}R30°$ structures in terms of the Si dangling bond saturation and the local graphene–Si interactions. Finally, our conclusions are drawn in Section 4.

2. Construction of graphene/SiC model interfaces

In this section we will put forward a procedure to build graphene/SiC(0001) interface models starting from the basic SiC and graphene unit cells and to identify visually the structures with the lowest strain on the graphene. We restrict ourselves to supercells which can be used in the Bloch theorem framework and are thus suitable for standard electronic structure calculations within periodic boundary conditions. Moreover, we will limit our discussion to hexagonal cells, assuming that the graphene layer is isotropically stretched or compressed in the plane and that the strain on the thicker SiC substrate is negligible. The observed Moiré patterns formed by graphene on SiC(0001) are typically identified by their periodicity, which usually corresponds to a $m\times m$ or a $m\sqrt{3}\times m\sqrt{3}R30°$ SiC cell. Therefore, we will consider here only these two cases, although our procedure can also be applied to other types of SiC cells (e.g., $m\sqrt{7}\times m\sqrt{7}R19.1°$, $m\sqrt{13}\times m\sqrt{13}R13.9°$, ... and so on, see also Ref. [5]).

The honeycomb structure of graphene can be described by a hexagonal Bravais lattice with basis vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ and an atomic basis of two C atoms, as shown in Fig. 1a. A graphene periodic supercell is constructed by selecting a lattice vector, $\mathbf{v}_1 = n_1\mathbf{a}_1 + n_2\mathbf{a}_2$, with n_1 and n_2 integers, and the corresponding vector $\mathbf{v}_2$ forming together with $\mathbf{v}_1$ the basis for a new hexagonal lattice, as exemplified in Fig. 1a for $(n_1,n_2)=(3,2)$ and $(2,1)$. The number of basic graphene units (2 C atoms each) included in this supercell is given by $n_G = n_1^2 + n_2^2 + n_1 n_2$. The length of the new basis vectors can be expressed as $|\mathbf{v}_1| = |\mathbf{v}_2| = a_G\sqrt{n_G}$, with $a_G = |\mathbf{a}_1| = |\mathbf{a}_2|$, and the

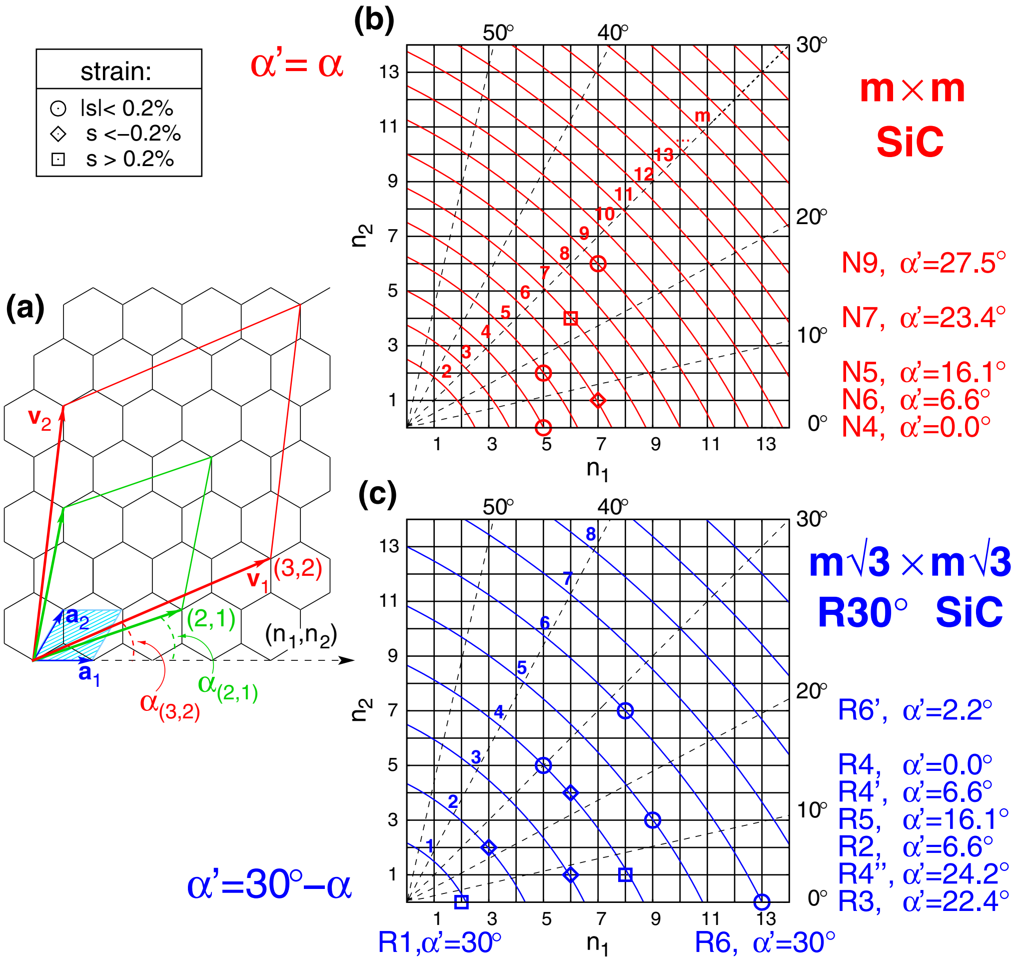

Fig. 1. (a) Construction of the rotated graphene cell, and lattice matching between the rotated graphene layer and (b) the $m\times m$ or (c) the $m\sqrt{3}\times m\sqrt{3}R30°$ SiC cells. In panel (a), the primitive unit cell of graphene and its basis vectors, $\mathbf{a}_1$ and $\mathbf{a}_2$, are indicated in blue, while two supercells with first basis vector $\mathbf{v}_1 = 3\mathbf{a}_1 + 2\mathbf{a}_2$ and $\mathbf{v}_1 = 2\mathbf{a}_1 + 1\mathbf{a}_2$ are shown with red and green lines, respectively. In panel (b) [(c)], the isolines corresponding to the matching conditions in Eq. (2) are shown with solid red [blue] lines for the $m\times m$ [$m\sqrt{3}\times m\sqrt{3}R30°$] SiC cells. The dashed lines correspond to constant values of the graphene rotation angle α (notice that a graphene rotation angle $\alpha > 30°$ is equivalent to a rotation of $60° - \alpha$). Pairs of integers $(\bar{n}_1,\bar{n}_2)$ which give rise to a low-strain commensurate interface are indicated by circles, when the graphene strain is below 0.2%, or by diamonds (squares), when the compressive (tensile) strain is larger. The name of the interface structure (see text and Table 1) and the graphene/SiC relative rotation angle, α', are indicated aside of each symbol.