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Intercalation of H at the graphene/SiC(0001) interface: Structure and stability from first principles

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ABSTRACT

We investigate the intercalation of hydrogen at the graphene/SiC(0001) interface through atomistic models characterized by very low strains both in the epitaxial graphene and in the SiC substrate. Adsorption of H at the interface is always stable but shows energy variations larger than 1 eV between different locations of the interface. An interface model presenting a strong interaction of graphene with the substrate, corresponding to the experimental situation, shows that adsorption at the interface is on average 0.75 eV less stable than at the surface of the buffer layer. At variance, a model having a much weaker graphene/SiC interaction results in hydrogenation energies that are comparable in the two cases. The structural modifications occurring upon H intercalation show a partial conversion of the buffer layer into quasi-free standing graphene, accompanied by a marked downward relaxation of the hydrogenated Si atom and a local steric repulsion between the latter and the overlying graphene.

1. Introduction

Epitaxial graphene can be grown by thermal decomposition of SiC, a wide band gap semiconductor [1,2]. From the application point of view, this substrate has the great advantage of avoiding any transfer of the graphene after growth, thus providing a ready-to-use template for future electronics [3–5]. On the (0001) polar surface of SiC, the epitaxial growth can be finely controlled to give a uniform thickness of high-quality graphene on the micrometer scale [6]. This achievement was obtained by performing the graphitization process of SiC under an inert atmosphere [6,7], rather than in ultra-high vacuum conditions. High-quality uniform graphene layers can be grown on both the Si-face and the C-face of single crystal SiC also through a confinement-controlled sublimation method, as recently reviewed by Heer et al. [8].

The highly ordered phase on the Si-face is partly due to the preferential orientation of graphene with respect to the SiC(0001) substrate, as opposed to the rotational stacking seen on the C-face [1] or the rotational disorder of graphene grown by chemical vapor deposition on a number of transition metals [9]. This is in turn related to the occurrence of a thin carbon layer, often called "layer 0" or "buffer layer", at the interface between the SiC(0001) surface and the epitaxial graphene. The buffer layer has been characterized by several experimental works, which showed that it is closely related to the $6\sqrt{3}\times6\sqrt{3}R30^\circ$ SiC reconstruction seen during the first stages of graphitization, a large periodic super-structure commensurate with a 13×13 graphene cell [2,10,11]. The C atoms in the buffer layer are mainly threefold coordinated and form a sp^2 bonding network as in graphene [12,11], but about one out of three C atoms makes a covalent bond to a Si atom of the SiC surface [13–15].

The strong interface bonding is characteristic of the Si-face of SiC{0001} and is related to the rotation angle between graphene and SiC lattices, which corresponds to 30° for the commensurate graphene 13×13/SiC $6\sqrt{3}\times6\sqrt{3}R30^\circ$ interface [1]. Rotations away from this angle would correspond to commensurate interface structures with surface periodicities other than the $6\sqrt{3}\times6\sqrt{3}R30^\circ$, such as 5×5 SiC, for instance [1,2,16]. These are rarely observed [1,2,17] and, indeed, they have been shown to be energetically less favorable [18]. The sp^2-to-sp^3 rehybridization (pyramidalization) of the Si-bonded C atoms is the main mechanism governing the interface stability and results in the atomic-scale buckling of the buffer layer [18], superimposed to the well-known long-range rippling [14]. Because of this departure from ideal graphene, which was recently confirmed by X-ray photoelectron diffraction [19], the π-electrons in the buffer layer do not show the typical Dirac-like band dispersion of graphene [12,15], making this layer unsuitable for electronic transport. The subsequent graphene layers above the buffer are instead electrically active and show the linear dispersion of the π-electrons. However, electron mobilities are not as high as in free-standing graphene produced by exfoliation [5].

Recent experiments showed that it is possible to convert the buffer layer into an electrically active graphene layer by performing a hydrogen intercalation step after the preparation of the buffer

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layer on SiC(0001) [20]. When the system is annealed at high temperatures under a hydrogen flux, H atoms penetrate beneath the buffer layer breaking the covalent bonds to the substrate and saturating all Si dangling bonds at the interface [20,21]. The resulting graphene monolayer, designated “quasi freestanding monolayer graphene” (QFMLG), is efficiently decoupled from the substrate and shows significantly higher electron mobilities, as well as a weaker temperature dependence with respect to standard epitaxial graphene on SiC(0001) [21]. The importance of buffer elimination was recently demonstrated through the realization of a transistor prototype attaining enhanced performances thanks to the superior electrical quality of QFMLG [4].

While a consensus on the electronic properties of QFMLG has already built, the precise intercalation mechanism is still an open question and has not been addressed sufficiently in the literature. Very recently, Deretzis and La Magna performed simulations of the hydrogenation process through Monte Carlo techniques using a sophisticated kinetic model which allowed them to address the nucleation process at atomic resolution [22]. They found that the nucleation proceeds through the formation of QFMLG islands as soon as the H densities become high enough to make the Si—H bonding on the SiC(0001) surface energetically favorable. The input parameters of the model (such as adsorption energies, adsorption/desorption barriers, ...) were mainly taken from *ab initio* calculations of interface models with unrealistic strains in the graphene or in the SiC substrate [23]. Only in selected cases these values were validated by calculations on a more realistic model [14,15]. For general modeling purposes, it would be more desirable to get such values from a strain-free model of tractable size, so that all the quantities could be computed with comparable accuracies within the same framework at a reasonable cost. Indeed, as Bocquet and coworkers pointed out [24], the preparation of QFMLG on SiC by hydrogen intercalation results from the subtle interaction of several competing processes, such as hydrogen chemisorption on the buffer layer, hydrogen intercalation below the buffer layer, and hydrogen desorption from the intercalation sites. On the experimental side, this delicate interplay severely limits the usable temperature window for a complete buffer layer conversion, while on the theoretical side it poses a great challenge and calls for more accurate evaluations of the energetics involved in the process.

In this work, we perform density functional simulations of atomic H at the graphene/SiC(0001) interface using previously developed atomistic models of this system [16]. These atomistic models do not introduce large artificial strains in the graphene layer or in the SiC substrate, at variance with other models used in previous studies [23,25]. The bonding of H on the interfacial Si atoms is addressed through two models of tractable size, which were also used to study H adsorption at the surface of the buffer layer [26]. In this way, binding energies of H at the surface of the buffer layer and at the interface with the underlying SiC(0001) substrate are obtained within the same framework. The surface periodicity of the largest model used here ($4\sqrt{3}\times4\sqrt{3}R30^\circ$) is smaller than the experimentally observed $6\sqrt{3}\times6\sqrt{3}R30^\circ$, but large enough to describe the local variation of the graphene-SiC interaction related to the moiré and to study its effects on the energetics of H adsorption. In particular, we compare binding energies of a single H atom on different interfacial Si atoms in order to investigate possible nucleation sites in the early stages of QFMLG formation. For the most favorable Si site, we discuss the structural modifications of the interface geometry occurring after H adsorption.

In the paper, we first describe the computational parameters and models in Section 2. Then, in Section 3 we report and discuss the binding energies of H at the interface and the structural modifications of the latter. Finally, in Section 4 we draw some conclusions and give an outlook.

2. Methods

The simulations are performed within density functional theory (DFT) using the QUANTUM ESPRESSO package for electronic structure calculations [27], which is based on plane-wave basis sets and pseudopotentials. The PBE gradient-corrected functional [28] is used to approximate the exchange and correlation energy. Basis set cutoffs are chosen as in Ref. [29], while the *k*-point sampling, the thickness of the slab (four SiC bilayers) and of the vacuum region (15 Å) are as in Ref. [26]. The reference energy for the hydrogen atom is obtained from a spin polarized calculation, while all the other calculations are spin-unpolarized, as justified in Ref. [26]. The graphene/SiC interfaces are generated by overlaying a rotated graphene layer on a SiC(0001) surface supercell and slightly stretching or compressing the graphene lattice constant to match the lateral size of the SiC supercell [16]. The SiC lattice constant is fixed to the experimental value at a temperature of 0 K (3.081 Å) [30], which is just 0.7% smaller than our theoretical equilibrium value at the DFT-PBE level.

The first interface model (R4″) considered here has a SiC $4\sqrt{3}\times4\sqrt{3}R30^\circ$ periodicity and a graphene/SiC rotation angle $\alpha'=24.2^\circ$, close to the value of 30° seen in the experiments. The graphene is stretched by about 1.4% to match the SiC substrate. We showed that this level of strain modifies the H binding energies by less than 0.1 eV compared to unstrained graphene [26]. The combined effect of strain and rotation angle gives a graphene/SiC interaction energy of −0.34 eV per Si atom, very close to that of the realistic $6\sqrt{3}\times6\sqrt{3}R30^\circ$ interface model (−0.32 eV) [18]. The second interface (R2) has a smaller periodicity ($2\sqrt{3}\times2\sqrt{3}R30^\circ$) and a smaller rotation angle ($\alpha'=6.6^\circ$), which are less representative of the experimental situation even if the graphene is here compressed by only 0.6%. In the R2 model, the calculated interaction energy (−0.16 eV per Si atom) is about half that of the realistic model [18]. Therefore the R2 model is used here for comparison with the R4″ one and to account for the hypothetical case of a weakly bound interface. The latter could be representative for a class of recently observed graphene/SiC interfaces on low-index SiC surfaces other than the (0001) one [31].

3. Results

We start by analysing the intercalation of atomic H in the R4″ interface system. Infrared absorption measurements showed that the hydrogenated SiC(0001) surface below QFMLG is highly ordered with all Si—H bonds perpendicular to the surface [21], hence H is expected to adsorb atop Si atoms uniquely. Since we are mainly interested in the very early stage of QFMLG formation, we consider the case of a single H atom at the interface, rather than the fully hydrogenated case or other intermediate coverages. Previous DFT calculations showed that H atop Si atoms is the only stable site at the graphene/SiC interface also at very low coverage [23]. Therefore, we will focus on this type of adsorption site.

In Fig. 1a, we present the distribution of the binding energy E_{bind} of one H atom on top of a Si atom for all the interfacial Si atoms in the R4″ unit cell. All these intercalation sites are stable, but E_{ads} can vary by about 1.5 eV from one site to the other. In the same figure, we also report the distribution of H binding energies atop the C atoms of the buffer layer as obtained in a previous study [26]. The two distributions have almost the same spread, but the adsorption at the surface of the buffer layer is about 0.75 eV more favorable than on the intercalation sites at the interface. At first glance, this seems in contrast with the experimental estimates of H desorption temperatures, which are much higher for the Si sites beneath the buffer (1100 K) than for the C site on the buffer (750 K) [24]. However, the former must be strongly limited by the barrier of penetration