

Charge neutrality in epitaxial graphene on 6H-SiC(0001) via nitrogen intercalation

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(Received 20 May 2015; published 21 August 2015)

The electronic properties of epitaxial graphene grown on SiC(0001) are known to be impaired relative to those of freestanding graphene. This is due to the formation of a carbon buffer layer between the graphene layers and the substrate, which causes the graphene layers to become strongly *n*-doped. Charge neutrality can be achieved by completely passivating the dangling bonds of the clean SiC surface using atomic intercalation. So far, only one element, hydrogen, has been identified as a promising candidate. We show, using first-principles density functional calculations, how it can also be accomplished via the growth of a thin layer of silicon nitride on the SiC surface. The subsequently grown graphene layers display the electronic properties associated with charge neutral graphene. We show that the surface energy of this structure is considerably lower than that of others with intercalated atomic nitrogen and determine how its stability depends on the N₂ chemical potential.

DOI: [10.1103/PhysRevB.92.081409](https://doi.org/10.1103/PhysRevB.92.081409)

PACS number(s): 73.20.At, 68.65.Pq, 71.15.Mb, 73.22.Pr

The thermal decomposition of silicon carbide (SiC) is one of the most promising methods to produce high-quality epitaxial graphene on a wafer scale, directly on a semiconducting surface. However, the electronic properties of the resultant graphene have been shown to depend intimately on the chosen SiC surface. When graphene is grown on the Si-rich SiC(0001) surface, the first carbon layer is covalently bonded to the surface Si atoms, with only subsequent layers displaying the characteristic electronic features of graphene. Furthermore, these graphene layers are heavily doped, due to charge transfer from the surface, and have a considerably reduced electron mobility compared to freestanding graphene [1–3].

Several attempts have been made to electronically decouple the so-called carbon buffer layer or “zeroth layer” graphene (OLG) from the substrate and thereby reduce the intrinsic electron doping. A promising technique to do so is by intercalating atoms or molecules between the OLG and the SiC substrate [4–8]. Hydrogen intercalation has been shown to reproducibly decouple the buffer layer from the substrate [9], increasing the carrier mobility to more than 11000 cm² V⁻¹ s⁻¹ at 0.3 K [10]. However, the resulting quasifreestanding monolayer graphene is slightly *p*-doped [11] due to the intrinsic spontaneous polarization of hexagonal SiC [12,13].

Attaining charge neutrality is vital to achieve the high electron mobilities associated with freestanding or suspended graphene [14]. The intercalation of highly electronegative atoms, such as N, O, and F, could be expected to reduce or even eliminate the intrinsic *n*-type doping of graphene. However, F intercalation results in strong *p*-doping [15], while O intercalation is difficult to control [16–18]. The effect of nitrogen intercalation on the electronic structure of graphene on SiC has only recently been addressed. Wang *et al.* [19] showed that, after thermal treating with NH₃, dissociated N species intercalate between the OLG and the substrate, weakening the interaction between the two. Moreover, there

have been several reports of the formation of a silicon nitride interface between SiC and the carbon layers [20–22], which serves to passivate the SiC surface. Masuda *et al.* showed that even a single atomic Si-N layer increases the mobility of the subsequently grown graphene layers [23].

In this Rapid Communication, we determine the effect of such a nitrogen layer on the electronic structure of graphene using first-principles calculations. When considering a thin nitride interface, we show that, although the OLG layer remains coupled to the substrate, the next carbon layer behaves as charge neutral graphene, with its Dirac point coinciding with the Fermi level of the system. This is due to a complete passivation of the silicon dangling bonds on the SiC(0001) surface. To this, we compare the effect of simple atomic nitrogen intercalation and show that, by a similar process of eliminating the Si dangling bonds, the OLG can be completely decoupled from the surface. This first layer of carbon atoms is already charge neutral or slightly *p*-doped, depending on the N concentration. The relative stability of these structures is addressed from *ab initio* thermodynamics where temperature and pressure are taken into account via the nitrogen chemical potential.

Density functional theory calculations are performed using the VASP code [24–26]. The Perdew-Burke-Ernzerhof (PBE) [27] parametrization of the generalized gradient approximation (GGA) is employed. The plane-wave basis set is converged using an 800 eV energy cutoff. Structural relaxations of the cell are carried out using a 9 × 9 × 1 *k*-point Monkhorst-Pack mesh [28] to sample the three-dimensional Brillouin zone. van der Waals interactions are included using the semiempirical approach of Grimme [29,30]. The SiC(0001) substrate is modeled using an asymmetric slab consisting of six bilayers of SiC(0001), arranged in the ABCACB stacking associated with the 6H polytype. A bulk termination is assumed. The GGA calculated lattice constant of bulk SiC is 3.09 Å, in good agreement with the experimental value of 3.08 Å. A vacuum layer of at least 15 Å is included in the direction normal to the surface to ensure no spurious interactions between repeating slabs and the dipole correction is applied to cancel the artificial

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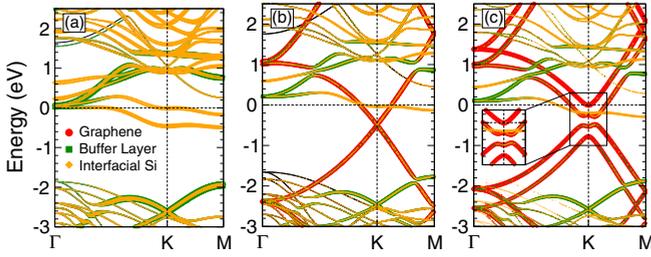


FIG. 1. (Color online) Electronic band structure of (a) the 0LG/SiC(0001) system, (b) the 1LG/SiC(0001) system, and (c) the 2LG/SiC(0001) system.

electric field which would arise due to the application of periodic boundary conditions [31,32]. The dangling C bonds on the SiC(000 $\bar{1}$) surface are passivated with H atoms. The positions of the top two bilayers of SiC(0001), as well as the H-terminating atoms, the N atoms, and all carbon layers, are optimized until all residual forces are less than 0.01 eV \AA^{-1} . The remaining atoms are held fixed at their bulk positions.

Experimentally, the growth of graphene on SiC(0001) has been shown to proceed via a $(6\sqrt{3} \times 6\sqrt{3})R30^\circ(6R3)$ surface reconstruction [33–36]. This is composed of a single layer of carbon atoms arranged predominantly in the honeycomb structure associated with graphene. We model this using the simplified $\sqrt{3} \times \sqrt{3}R30^\circ$ cell ($R3$) which corresponds to a 2×2 graphene cell. Such an approximation was shown to be adequate to correctly describe the interaction between the SiC(0001) surface and the carbon layers [37]. Figure 1(a) shows the electronic band structure of the system that includes only the 0LG on SiC(0001), for comparison with later calculations. The “fat-bands” technique was used to illustrate the character of each band, whereby a weight is given to each eigenvalue proportional to the amount of character of that particular atom in the corresponding Bloch function. The almost flat bands evident at E_F originate from the spin-split dangling Si bonds at the surface. Because of the strong covalent bonding between the Si atoms and the C atoms, the linear dispersion associated with graphene is not present at the K point. Figure 1(b) then shows the electronic properties of the same system when a second carbon layer is included. As this top layer of carbon atoms is bonded via the van der Waals interaction to the 0LG, it has an electronic structure similar to a freestanding graphene layer with a well-defined Dirac point located 0.45 eV below E_F . Such structures that include the buffer layer as well as a second carbon layer will be referred to subsequently as 1LG structures. Figure 1(c) finally shows the energy spectrum of a structure that includes a third layer of carbon atoms arranged in an ABC stacking [38], i.e., the 2LG structure. The almost quadratic dispersion of the bands in the vicinity of the K point is evidence of bilayer graphene, while the small gap of approximately 0.25 eV and the “Wizard hat” shape, points to the asymmetry between the two graphene layers induced by the presence of the surface.

Figure 2(a) shows the relaxed structure of the 2LG/Si-N/SiC(0001) slab. The Si-N layer has a structure reminiscent of the well-studied oxynitride layer on SiC [39–41]. The optimized Si-N bond is 1.76 \AA . The distance between the 0LG and the 1LG is 3.27 \AA , while the interlayer spacing between

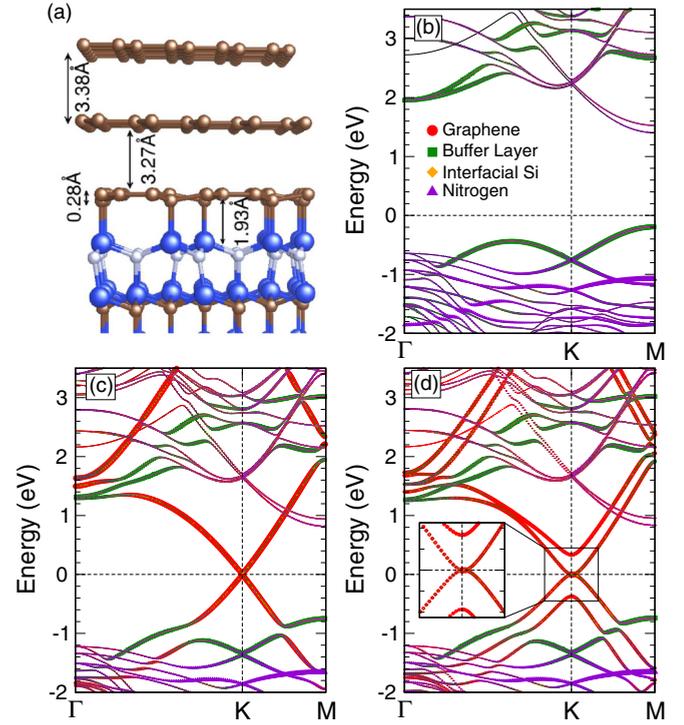


FIG. 2. (Color online) (a) Relaxed structure of the 2LG/Si-N/SiC(0001) system showing optimized interlayer distances. The dark blue spheres represent Si, the light gray spheres represent N, while the brown spheres represent carbon. Electronic band structure of the (b) 0LG/Si-N/SiC(0001), (c) 1LG/Si-N/SiC(0001), and (d) 2LG/Si-N/SiC(0001) systems.

1LG and 2LG is 3.38 \AA . We note the distance measured by Masuda *et al.* [23] is much bigger than this, at 4.4 \AA . As this value is considerably larger than the typical interlayer distance in bilayer graphene, one possibility is that N_2 molecules become trapped between the carbon layers [42].

The band structure of the 0LG/Si-N/SiC(0001) system is shown in Fig. 2(b). The Si-N layer does not decouple the 0LG from the substrate, as the C atoms in this layer are still required to satisfy the remaining Si dangling bonds; each Si atom is bonded to three N atoms in the Si-N layer and one C atom in the 0LG. In this way, the Si dangling bonds are eliminated, leaving no unsaturated bonds in the unit cell. Bader charge analysis [43] shows that the C atoms of the 0LG gain 0.16 electrons each from the interfacial Si atoms. The binding energy between the carbon layer and the substrate [44] is 169 meV \AA^{-2} , providing evidence of the strong interaction between the two. Figure 2(c) then shows the band structure of the 1LG system. The interaction between the top layer of carbon atoms and the 0LG is now minimal with a binding energy of only 14 meV \AA^{-2} and the charge transferred between the substrate and this graphene layer is negligible. As a result, the Dirac point and the Fermi level are coincident. Figure 2(d) finally shows the band structure of the 2LG system. The bands at the K point, as projected onto the top two carbon layers, show the symmetric, gapless and parabolic dispersion associated with charge neutral bilayer graphene. Furthermore, the work functions of the 1LG and 2LG structures are almost

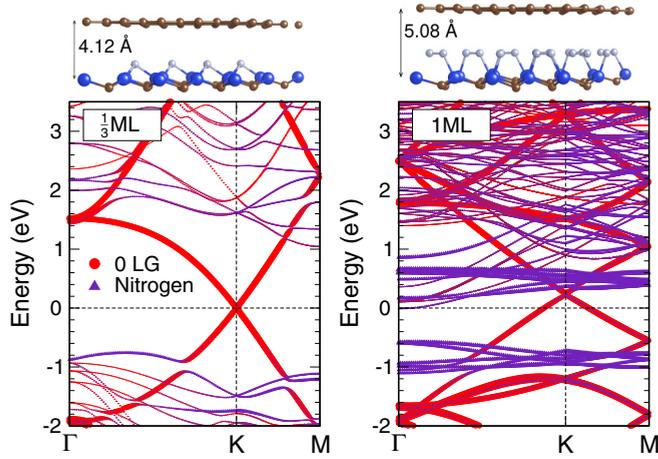


FIG. 3. (Color online) Electronic structure of the 0LG/SiC(0001) structure including (left) $1/3$ ML and (right) 1 ML nitrogen atoms at the interface. Note the in-plane unit cell of the 1 ML structure is four times that of the $1/3$ ML structure.

equal and close to that of freestanding graphene at the same strain (4.9 eV). This is in contrast to that found for graphene grown on the clean SiC(0001) surface [45], where the work function increases by 135 meV when moving from the 1LG to the 2LG surface, which can be attributed to an electrostatic origin [46].

As the decoupling of the 0LG is not achieved via a Si-N interlayer, two carbon layers are required to obtain charge neutral graphene. The growth conditions necessary to create a second carbon layer, such as higher temperatures, often result in a higher density of defects as well as a smaller degree of control over the number of layers grown. It is often preferable to grow only one layer of carbon atoms which is then decoupled from the substrate. We consider the possibility of achieving this by passivating the SiC(0001) surface using simple atomic nitrogen adsorption. One-third of a monolayer of nitrogen atoms is sufficient to passivate the SiC(0001) surface [47,48] (where coverages are given with respect to the number of Si surface atoms). The N atoms sever the bonds between the substrate and the carbon layer, resulting in a decoupling of the 0LG. This can be seen in the left panel of Fig. 3 which shows a distinct Dirac cone with its point 20 meV beneath the Fermi energy. The right panel of Fig. 3 shows the effect of increasing the concentration of nitrogen to 1 ML. Due to the less ideal bonding configuration, p -doping of the decoupled 0LG occurs, with the Dirac point located 0.24 eV above the Fermi energy. Increasing the N concentration to 2 ML (not shown), further increases the p -doping to 0.3 eV.

In order to determine the relative stability of these nitrogen intercalated structures, we calculate the surface energy of the 0LG systems as a function of temperature and pressure. This is defined here as [49]

$$\gamma(T, P) = \frac{1}{A} (E_{\text{comb}} - n_{\text{Si}} \mu_{\text{Si}} - n_{\text{N}} \mu_{\text{N}_2}),$$

where A is the surface area of the unit cell, E_{comb} is the energy of the combined system including nitrogen, $n_{\text{Si(N)}}$ are the number of additional Si(N) atoms in the intercalated structure, μ_{Si} is the chemical potential of Si and is given by the energy

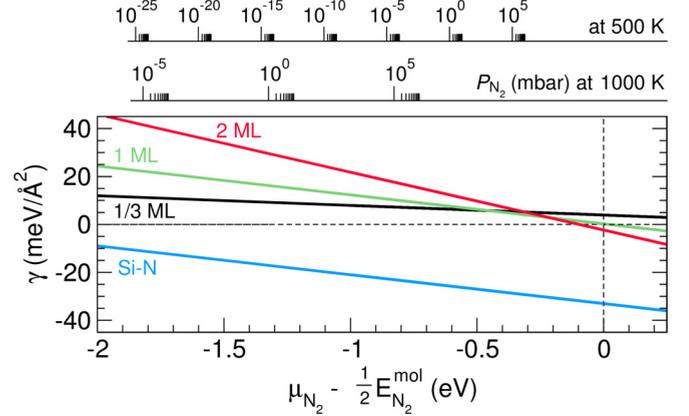


FIG. 4. (Color online) The surface free energies of the intercalated N systems relative to the clean surface which includes only the 0LG, as a function of the N_2 chemical potential. The relationship between the chemical potential and the N_2 pressure is shown on the top axis for two fixed temperatures, 500 K and 1000 K.

of a single atom in bulk Si, and μ_{N_2} is the chemical potential of N_2 , given by $\frac{1}{2} [E_{\text{N}_2}^{\text{mol}} + \tilde{\mu}_{\text{N}_2}(T, p_0) + k_B T \ln(P_{\text{N}_2}/p_0)]$. For a standard pressure, $p_0 = 1$ atm, the values of $\tilde{\mu}_{\text{N}_2}(T, p_0)$ are tabulated in thermochemical tables [50]. The results are shown in Fig. 4.

Over the entire range of chemical potential considered here, the intercalated Si-N structure is the most stable by a considerable margin. At 0 K it has a surface energy $30 \text{ meV } \text{\AA}^{-2}$ lower than that of the next most stable structure. Of the three structures involving intercalated atomic nitrogen, the $1/3$ ML structure is the most stable at low values of chemical potential, where $\mu_{\text{N}_2} < -0.45$ eV. This corresponds to low values of N_2 pressure. Higher concentrations of N are stabilized with increasing pressure.

In summary, although the intercalation of many elements between the buffer layer of carbon atoms and the SiC(0001) surface has been suggested and implemented, only hydrogen, to date, has succeeded in reducing the intrinsic n -doping of the as-grown graphene layers. We demonstrate, using first-principles calculations, that nitrogen intercalation is another promising route to access charge neutral graphene on a semiconducting surface. An atomically thin silicon nitride layer succeeds in satisfying all the surface Si dangling bonds, thereby eliminating charge transfer across the buffer layer to the subsequent graphene layers. These layers then display all the hallmarks of charge neutral mono- and bilayer graphene, exhibiting a Dirac cone with its point at the Fermi energy of the system. This nitride layer is shown to be stable across a wide range of pressure and temperature, in particular when compared to intercalated atomic nitrogen. Achieving charge neutrality in epitaxial graphene layer on SiC(0001) would be hugely beneficial for device performance. For instance, the performance of graphene-based molecular sensors depends sensitively on the number of graphene layers present when grown on clean SiC due to differing amounts of charge transferred to the two layers. Eliminating this difference would result in a more uniform interaction between the sensing device and the gas molecules. Likewise, the concomitant expected increase in carrier mobility due to charge neutrality is a

promising step towards including graphene in future electronic devices.

The research leading to these results has received funding from the European Union Seventh Framework Programme under Grant Agreement No. 604391 Graphene Flagship. The authors also wish to acknowledge the Swedish Research Council (VR) Grant No. 621-2011-4426 and the Swedish Foundation for Strategic Research (SSF) program SRL Grant No. 10-0026. R.A. acknowledges financial support from VR Grant No. 621-

2011-4249 and the Linnaeus Environment at Linköping on Nanoscale Functional Materials (LiLi-NFM) funded by VR. I.A.A. acknowledges the support from the Grant of Ministry of Education and Science of the Russian Federation (Grant No. 14.Y26.31.0005) and Tomsk State University Academic D. I. Mendeleev Fund Program (Project No. 8.1.18.2015). All calculations were performed using the supercomputer resources of the Swedish National Infrastructure for Computing (SNIC), National Supercomputing Center (NSC), and PDC Centre for High Performance Computing (PDC-HPC).

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