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A route to strong *p*-doping of epitaxial graphene on SiC

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(Received 25 August 2010; accepted 23 October 2010; published online 9 November 2010)

The effects of Au intercalation on the electronic properties of epitaxial graphene grown on SiC{0001} substrates are studied using first principles calculations. A graphene monolayer on SiC{0001} restores the shape of the pristine graphene dispersion, where doping levels between strongly *n*-doped and weakly *p*-doped can be achieved by altering the Au coverage. We predict that Au intercalation between the two C layers of bilayer graphene grown on SiC{0001} makes it possible to achieve a strongly *p*-doped graphene state, where the *p*-doping level can be controlled by means of the Au coverage. © 2010 American Institute of Physics. [doi:10.1063/1.3515848]

Graphene is a two-dimensional gapless semiconductor, in which the low-energy excitations are massless, chiral, Dirac fermions.¹ Epitaxial graphene always shows *n*-type behavior due to the interaction with the substrate. The Dirac point is found to be ~ 0.4 eV below the Fermi level.² However, for metal-oxide-semiconductor (MOS) applications, it is of great importance to induce *p*-type doping in epitaxial graphene. Recently, the study of Au adatoms on graphene has raised much interest. On one hand, unlike other transition-metal adatoms, such as Fe, Co, and Ni, Au adatoms cause no destruction of the graphene layer because Au adatoms have little effects on the characteristics of the vacancies.³ On the other hand, Au adatoms are expected to induce *p*-type doping.^{4,5} Recent work by Premlal *et al.*⁴ has shown that an Au layer (AuL) deposited on a graphene monolayer (GML) develops into an intercalation layer between the GML and the Si-terminated SiC substrate when the system is annealed at 800 °C for 5 min. Within the GML, a *p*-doping effect is observed. Furthermore, Gierz *et al.*⁵ reported that by controlling the Au coverage level, GMLs ranging from strongly *n*-doped to weak *p*-doped can be formed. However, it is still a problem to achieve a strongly *p*-doped GML by AuL intercalation.

In the present work, we investigate the influence of an intercalated AuL on the electronic structure of epitaxial graphene grown on SiC{0001} substrates by first principles calculations. We find that the intercalation of the AuL restores the pristine graphene band dispersion of the GML. We propose a method for achieving strongly *p*-doped graphene and controlling the *p*-doping level, which is desirable for MOS applications.

Our calculations use density functional theory⁶ and the generalized-gradient approximation⁷ of the exchange correlation functional with ultrasoft pseudopotentials,⁸ as implemented in the QUANTUM-ESPRESSO package.⁹ This approach enables us to interrelate the crystal structure to the corresponding electronic structure. A high cutoff energy of 80 Ry and a precise k-point sampling in an $8 \times 8 \times 4$ mesh are employed to achieve a high accuracy in the calculations. The SiC substrate is described by a slab of four SiC bilayers with hydrogen-saturated dangling bonds on the second slab surface. In order to avoid any drawback of the periodic bound-

ary conditions, vacuum layers of thicknesses between 10 and 15 Å are included.

On both the Si- and C-terminated faces of a SiC substrate, graphene is commonly grown by thermal graphitization in ultrahigh vacuum. An annealing temperature of about 1000 °C for 5 min is sufficient for forming the first graphene layer on SiC{0001} substrates.^{2,4,5} The surface of a GML intercalated by an AuL on Si-terminated SiC is subject to a $(2\sqrt{3} \times 2\sqrt{3})R30^\circ$ -Au(111) surface reconstruction.⁴ However, this pattern is too complicated to be computationally feasible. As the best possible approximation of the real structure, we thus use the $(\sqrt{3} \times \sqrt{3})R30^\circ$ -Au(111) unit cell. Figure 1 shows schematic diagrams of GML [Fig. 1(a)], bilayer graphene [Fig. 1(b)], GML intercalated by AuL [Fig. 1(c)], and bilayer graphene with AuL intercalation between the two graphene layers [Fig. 1(d)], on SiC{0001} substrates.

The band structures of GMLs on Si- and C-terminated SiC are shown Figs. 2(a) and 2(b), respectively. For both terminations, the band structure shows a large energy gap. The Fermi level is pinned by a state with a small dispersion. These facts are consistent with previous experiments⁵ and results from first principles calculations.¹⁰ The pinning state is related to the dangling bonds of the Si/C atoms in the top layer of the substrate. A conventional method to restore the main features of the graphene band structure is to form further graphene layers by annealing at 1150 °C for 5 min, which works for both the Si- and C-terminated surfaces.^{5,10} The structural setup is shown in Fig. 1(b). The first GML may be viewed as a buffer layer because the pinning state remains unchanged for bilayer graphene on SiC{0001}.¹⁰ Bilayer graphene on either Si- or C-terminated SiC is *n*-doped,

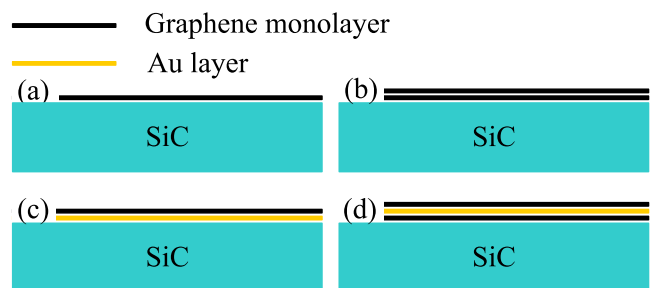


FIG. 1. (Color online) Schematic diagrams of (a) GML, (b) bilayer graphene, (c) GML intercalated by AuL, and (d) bilayer graphene with AuL intercalation between the two graphene layers on SiC{0001} substrates.

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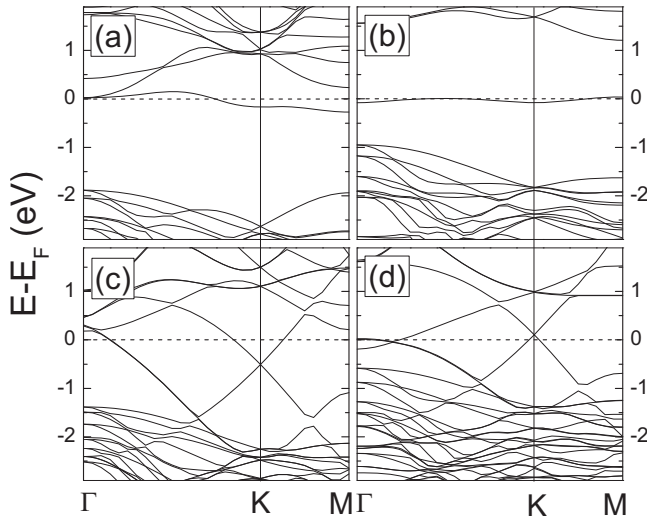


FIG. 2. Band structure obtained for a GML on a SiC surface without [(a) and (b)] and with [(c) and (d)] an intercalated AuL. Panels (a) and (c) correspond to the Si-terminated surface, whereas panels (b) and (d) correspond to the C-terminated surface.

where the upper GML is stronger *n*-doped for the Si- than for the C-terminated substrate.¹⁰ The strong influence of the substrate reduces the carrier mobility in the upper GML considerably.^{11,12} Therefore, careful consideration of the underlying substrate is required also for achieving *p*-doping and for optimizing the performance of devices in electronic applications.

To introduce holes in epitaxial graphene grown on SiC, it has been demonstrated that Au is a suitable element to extract electrons.^{4,13–15} Recent angle resolved photoemission spectroscopy measurements performed on epitaxial graphene with Au atoms deposited on top reveals hole doping with a shift of the Dirac point to ~ 0.1 eV above the Fermi level.¹³ Moreover, to saturate the dangling bonds on top of the substrate, Au atoms are deposited on top of the GML and the sample is annealed at about 800 °C.^{4,5} This results in an AuL intercalated between the GML and the Si-terminated SiC substrate, as shown in Fig. 1(c). Scanning tunneling spectroscopy shows that the Dirac point shifts to an energy of 0.2 eV above the Fermi level.⁴ Beyond, a strong *n*-doping is found for a coverage of about one third AuL, while weak *p*-doping is found for a complete AuL.⁵ The weakly *p*-doped GML is expected to be subject to a considerable increase in carrier mobility. Its transport properties therefore should be close to those of multilayer graphene on the C-terminated surface of SiC. Thus, the introduction of an AuL below the GML should *p*-dope the GML for both Si- and C-terminated SiC substrates and consequently increase the carrier mobility in the GML.

From Figs. 2(c) and 2(d), we find that the intercalation of the AuL removes the pinning states caused by the Si(C) dangling bonds, for the Si-(C)-terminated surface, and that the graphene dispersion is restored. On the Si-terminated surface, the Fermi level is located 0.5 eV above the Dirac point [Fig. 2(c)], which means that the GML stays *n*-doped, resembling bilayer graphene on SiC. However, for the C-terminated surface, the GML is *p*-doped with the Fermi level 0.1 eV below the Dirac point.

We next study the charge density difference isosurface of the GML intercalated by an AuL on C-terminated SiC, as

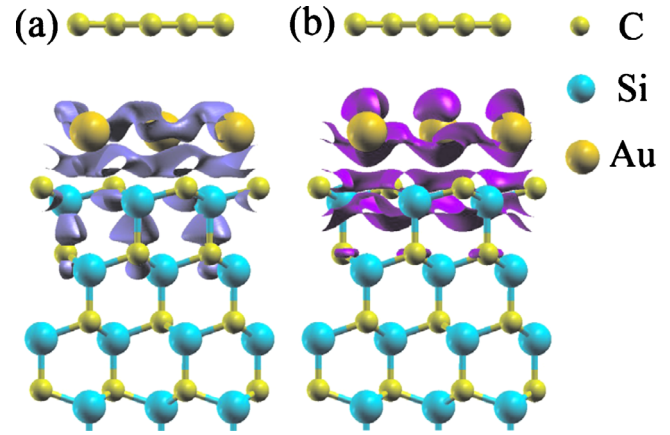


FIG. 3. (Color online) Charge density difference isosurfaces of a GML intercalated by an AuL on a C-terminated SiC substrate. The isosurfaces shown correspond to the small isovalues (a) -5×10^{-5} and (b) $+5 \times 10^{-5}$ electrons.

shown in Fig. 3, as an example to address the reason why the pinning states are removed under AuL interaction. The nearest neighbor Au–Au distance is 3.10 Å, the distance between the AuL and the GML is 3.97 Å, and the distance between the AuL and the SiC substrate is 2.08 Å. The GML is almost flat and far away from the AuL, which implies it resembles a pristine graphene layer. The AuL is so close to the SiC substrate that the interaction between them is strong, i.e., covalent bonds are formed. The isovalues are set to -5×10^{-5} and $+5 \times 10^{-5}$ electrons in Figs. 3(a) and 3(b), respectively. The charge density difference isosurfaces imply that the GML exchanges very few charge with the AuL. Charge transfer mainly occurs between the AuL and the upper two SiC bilayers. The introduced AuL saturates the C bonds and therefore weakens the chemical interaction between the GML and the substrate. Hence, the GML, in a good approximation, can be viewed as a freestanding pristine graphene layer. The linear dispersion around the Dirac point consequently is visible in Figs. 2(c) and 2(d).

Even though *n*-doping as well as weak *p*-doping of graphene can be achieved by controlling the Au coverage, there are two problems to achieve stronger *p*-type doping for a GML intercalated by an AuL on SiC{0001}. First, a high Au coverage level of 1 ML is needed to achieve *p*-type doping, while, on the other hand, a high Au coverage level will cause Au clusters on top of the GML, which has drawbacks on the experimental characterization. Second, as the achieved *p*-type doping is weak (the Dirac point is only about 0.2 eV above the Fermi level), it is difficult to control the doping. We therefore propose a modified method to achieve this control.

Since the number of graphene layers grown on SiC{0001} substrates can be controlled in experiment,¹⁶ we can grow epitaxial bilayer graphene in the first step. In the second step, Au atoms can be deposited on top of the bilayer graphene. Afterward, the sample is annealed at a proper temperature. For bilayer graphene on SiC{0001}, the interaction between the upper layer and the buffer layer is much smaller than between the buffer layer and the substrate.¹⁰ As a consequence, an AuL can be intercalated between the two GMLs of bilayer graphene for an annealing temperature below 800 °C. Bilayer graphene on both Si- and C-terminated SiC is *n*-doped, where the upper GML shows stronger doping for

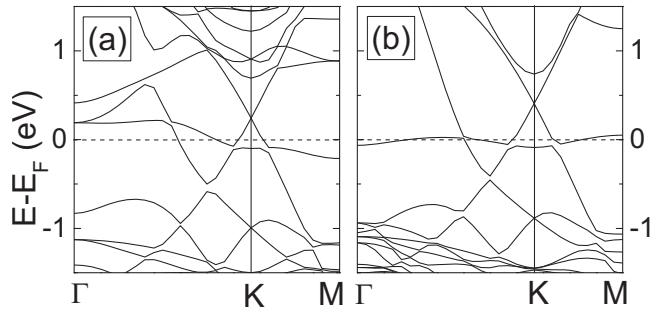


FIG. 4. Band structure obtained for a graphene bilayer on SiC with an AuL intercalated between the two GMLs which the graphene bilayer consists of. Panels (a) and (b) correspond to Si- and C-terminated surfaces, respectively.

Si- than for C-termination of the substrate.¹⁰ After intercalation of the AuL between the two GMLs, the upper GML acts as pristine graphene, whereas the lower GML still acts as buffer layer.

The Fermi level is found to be 0.24 and 0.41 eV below the Dirac point in the band structures obtained for the Si- and C-terminated surfaces [see Figs. 4(a) and 4(b)], respectively. The figures clearly show a stronger *p*-type doping than in the case of monolayer graphene intercalated by an AuL with the same Au coverage. The lower GML (buffer layer) in bilayer graphene saturates the dangling bonds of the surface Si/C atoms of the substrate. Therefore, the intercalated AuL becomes a more efficient hole dopant for the upper GML, as compared to the case where the AuL is in direct contact to the substrate. In particular, the magnitude of the *p*-doping in the upper GML now can be modulated directly by controlling the Au coverage.

In conclusion, we have studied the effects of intercalating an Au monolayer into systems consisting of either a graphene monolayer or a graphene bilayer grown on SiC{0001} substrates. In contrast to the monolayer system, the bilayer system makes it possible to obtain strongly

p-doped epitaxial graphene on SiC, which is needed for MOS applications.

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