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Recovery of the Dirac states of graphene by intercalating two-dimensional traditional semiconductors

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Abstract

The epitaxial growth of graphene on transition-metal substrates has proved to be an efficient method to synthesize high-quality large-area graphene. However, due to the interaction between graphene and the transition-metal substrate, the electronic structure of the as-fabricated graphene is distorted. Here, using density functional theory calculations, we investigated the effect of intercalating two-dimensional (2D) silicon and III–V materials, such as double-layer honeycomb AlAs, into the graphene-metal interface. We found that the intercalation of these 2D materials significantly reduces the interaction between graphene and the transition-metal substrate. The Dirac state is largely restored. The doping level of graphene induced by 2D intercalated material and the metal substrate is proportional to the work function difference between graphene and 2D materials/metal. This work provides a way for the formation of freestanding graphene and further fabrication of graphene-based devices.

Keywords: semiconducting materials intercalation, graphene, first-principles calculations

(Some figures may appear in colour only in the online journal)

1. Introduction

Monolayer graphene is a two-dimensional (2D) arrangement of sp^2 -bonded carbon atoms in a honeycomb lattice, which has a linear energy dispersion at its Dirac point and exhibits an extremely high carrier mobility exceeding 200000 cm² (V · s)⁻¹ [1–6]. Graphene is a fascinating material to investigate various interesting physical phenomena. One example is van der Waals heterostructures consisting of monolayer graphene on top of hexagonal boron nitride, which exhibit a Hofstadter butterfly spectrum of electrons owing to relatively weak interlayer interactions [7, 8]. Moreover, graphene-based devices are also promising for next-generation electronics [9].

The epitaxial growth of graphene on a single-crystal transition-metal (TM) substrate has been proved to be an efficient method to fabricate large-area and high-quality graphene [10– 17]. However, the presence of the substrate affects the electronic properties of graphene. For example, while epitaxially grown on Ru, Ni, and Pd, the Dirac cone of graphene is severely distorted [18–20], which not only lowers the carrier mobility but also causes difficulties in the applications of graphene in electronic devices. The distortion of Dirac cone has been restored by intercalating hetero-atoms underneath graphene. Previous studies have shown that the intercalation of Pt or Au leads to a decrease in the interaction between graphene and a Ru substrate, making the graphene layer quasi-freestanding [21–27]. However, after metal intercalation, the whole system is still metallic, which hinders applications in electronic devices. Recently, the intercalation of silicon, ranging from monolaver silicene to multilayer silicene has been successfully achieved [28–31]. A rectifying device has also been fabricated in this system [31]. After silicon intercalation of graphene nanoislands on an Ir substrate, the edge state of nanoislands with zigzag edges is restored [30]. Besides silicon, 2D III-V GaN



Figure 1. A schematic structure of Gr/2D-materials/Ni heterostructure. The blue, violet, dark cyan, purple, orange, aqua, light blue, light sea green, light coral, mint, yellow, represent Si, As, Ga, I, Cu, Ag, Al, Mg, Se, Zn, S, respectively.

Table 1. Calculated lattice paraments, strain (compressive, -; tensile, +), and h_1, h_2, d .

	AlAs	MgSe	ZnS	CuI	AgI	GaAs	Monolayer silicon
Free-standing lattice constant (Å)	4.02	4.32	3.89	4.11	4.45	4.05	3.84
Strain (%)	+6.0	-1.4	+9.5	+3.6	-4.3	+5.2	+11.0
h_1 (Å)	3.52	3.52	3.41	3.67	3.57	3.58	3.67
h_2 (Å)	1.86	2.04	1.71	2.00	2.30	2.07	1.87
d (Å)	2.88	3.14	2.71	4.49	4.57		

has also been successfully intercalated into graphene and metal interface [32]. These experimental achievements inspire us to investigate the effect of semiconducting materials intercalation between graphene and TM substrates.

In this paper, using quantum mechanical calculations based on density functional theory (DFT), we investigate intercalating 2D silicon and III-V materials between graphene and a Ni(111) substrate. Various types of semiconducting 2D III-V materials were studied, ranging from theoretically predicted 2D double-layer honeycomb (DLHC) [33] to single-layer honeycomb (SLHC) materials [34]. A schematic structure is shown in figure 1. Calculations show that all 2D binary semiconducting materials and monolayer silicon decouple the graphene from the Ni(111) surface and restore the Dirac state of graphene. The shift of the Dirac point, which is an indicator of the doping level, is proportional to the work function difference between graphene and the 2D materials on Ni(111). The doping of graphene is also sensitive to the thickness of the 2D silicon and semiconducting materials, which is due to the change of the work function for different thicknesses. These results indicate that intercalating 2D silicon and semiconducting III–V materials is an effective way to achieve quasifree-standing graphene and tailor the electronic structures for potential applications.

2. Methods

We use quantum mechanical calculations based on density functional theory (DFT) to investigate the atomic structures and electronic properties of graphene/2D materials/Ni(111) heterostructures. All DFT calculations are carried out using the Vienna *ab initio* simulation package [35] with the projector augmented wave (PAW) method [36]. A generalized gradient approximation (GGA) in the form of Perdew–Burke– Ernzerhof (PBE) is adopted for the exchange-correlation functional [37]. It is well known that PBE functional underestimates the band gap in semiconductors. However, the occupied states and work functions are reasonably good comparing with higher level calculations, such as random phase approximation and GW approximation [38]. The DFT-D3 method is used to correct for van der Waals (vdW) interactions [39].

Considering the lattice constants of graphene, Ni(111), and different semiconducting layers, we chose a supercell containing a ($\sqrt{3} \times \sqrt{3}$) graphene on a ($\sqrt{3} \times \sqrt{3}$) Ni(111) slab for the intercalation of 2D semiconducting materials and a (3 × 3) graphene on a (3 × 3) Ni(111) supercell for the intercalation of silicon. Lattice constants and the lattice mismatch of 2D materials and graphene are listed in table 1. Fouratomic-layer slabs are used to model the Ni(111) surfaces.

We employ a plane-wave basis set with a 550 eV energy cutoff. The convergence criterion for electronic relaxation is 10^{-5} eV. A Γ -centered $24 \times 24 \times 1$ *k*-point sampling in the 1st Brillouin zone (BZ) is used for $(\sqrt{3} \times \sqrt{3})$ supercell and $15 \times 15 \times 1$ *k*-point sampling for the (3×3) cell. With this set of parameters, the binding energy is converged to 1 meV. Atomic positions are full optimized until the forces are less than $0.01 \text{ eV} \text{ Å}^{-1}$, except the bottom two-layers of the Ni(111) substrate.

3. Results and discussions

We start from the intercalation of recently predicted 2D DLHC semiconducting materials with sizable band gaps, including AlAs, MgSe, ZnS, CuI, and AgI. We choose a typical Gr/



Figure 2. The atomic structures and PDOS of typical Gr/2D-materials/Ni structures. (a) Gr/DLHC AlAs/Ni, (c) Gr/SLHC GaAs/Ni and (e) Gr/monolayer silicon/Ni systems. The red hexagons are the unit cells. h_1 and h_2 are the vertical height differences between graphene and 2D materials, 2D materials and Ni(111) surface, *d* is the thickness of 2D materials. (b), (d) and (f) Projected density of states (PDOS) on C atoms in (a), (c) and (e), respectively.

AlAs/Ni system as an example. We first search for the most stable relative position of DLHC AlAs on Ni(111), which gives clues for the possible intercalation site. According to the symmetry, there are three possible relative positions, namely fcc, hcp, and top sites, which are named according to the relative positions between AlAs layer and the Ni(111) substrate. For the fcc site, the atoms in AlAs layer are placed directly above the Ni atoms of the third layer. A similar terminology is used for the other two situations. The binding energy for fcc site is 18 (746) meV higher than that of hcp (top) site. Therefore, the fcc site is the most stable relative position for AlAs/Ni(111). Compared to the freestanding AlAs structure, AlAs is less buckled after its adsorption on Ni(111). The bond length of Al–As is stretched by 1% comparing to that in the freestanding form.

We then searched for the most stable configuration of the Gr/AlAs/Ni system. Different graphene/AlAs and AlAs/ Ni(111) relative positions were considered. The most stable configuration is shown in figure 2(a). For this configuration, C atoms of graphene prefer to adsorb on top-fcc site relative to Ni(111) substrate and Al and As atoms of AlAs layer adsorb on fcc site. The average vertical distance between graphene and AlAs, h_1 , is 3.52 Å. The average vertical distance between the bottom of AlAs and Ni substrate, h_2 , is 1.86 Å.

The electronic structure of Gr/AlAs/Ni(111) was calculated in order to evaluate the effect of DLHC AlAs intercalation. Figure 2(b) shows the density of states (DOS) projected on C atoms. The projected density of states (PDOS) shows a linear feature around its minimum (the Dirac point), which characterizes the electronic structure of graphene in a freestanding form. This feature is absent in the Gr/Ni(111) without AlAs intercalations due to the strong interaction between graphene and Ni(111) [18]. The energy position of the Dirac point, E_D (which is reflected by the V-shape in the PDOS plot), is located at -0.294 eV (below Fermi level, E_F) in the Gr/AlAs/Ni system, which reflects electron doping of graphene. The intact Dirac point of graphene proves a good decoupling between graphene and Ni(111) after DLHC AlAs intercalation.

In addition to DLHC AlAs intercalation, we also investigated the atomic structure and electronic properties after intercalating other DLHC semiconductors, including MgSe, ZnS, CuI, and AgI.

The vertical distance between graphene and 2D DLHC semiconducting materials top surface (h_1) , the vertical distance between DLHC bottom surface to Ni (h_2) , and the thickness of 2D semiconducting materials (d) are listed in table 1. It is found that in all of these systems, except ZnS, the PDOS on graphene exhibits an intact Dirac point, which means that the 2D DLHC semiconducting materials intercalation restores the electronic properties of graphene. The Dirac state is still absent in the Gr/ZnS/Ni system due to the hybridation of the p_z orbitals of graphene and the *s* orbitals of ZnS.

GaAs in an SLHC structure has been theoretically predicted to be stable and has a band gap of 2 eV [34]. We investigated the intercalation of SLHC GaAs into a Gr/Ni(111) interface. We compared different relative positions of SLHC GaAs. Similar as the intercalation of DLHC semiconducting layers, Ga and As atoms of SLHC GaAs prefers to adsorb on fcc site on Ni(111) and C atoms of graphene sits on top-fcc site of GaAs. The most stable configuration is shown in figure 2(c). As shown in figure 2(d), the PDOS on C atoms also shows a



Figure 3. Electronic properties of Gr/2D-materials/Ni structures. (a) Dirac point position (E_D) as a function of the workfunction difference (ΔW) between graphene and the 2D materials-on-Ni. The insets illustrate the position of the Dirac point with respect to the Fermi level, orange and blue colors represent p-type and n-type doped graphene, respectively. (b) The electrostatic potential for the AlAs/Ni heterostructure. The vacuum level is set to zero. The workfunction is derived from the difference between the vacuum level and the Fermi level. (c) The in-plan integration and isosurfaces of electron density difference in graphene–AlAs–Ni(111) heterostructure. The yellow and light blue colors represent the charge accumulation and depletion, respectively. $|\Delta \rho| = 0.047$ e Å⁻³.

intact Dirac point with a $E_{\rm D}$ at $-0.135 \,\mathrm{eV}$ relative to the Fermi level.

The intercalation of 2D Si, has also been considered. Recent results show that for silicon intercalation in Gr/ Ru(0001), silicon atoms first form silicon honeycomb structures at the atop regions of the moiré pattern and then gradually extend to silicene [31]. As the distance between graphene and Ni(111) is similar as that in the atop regions of graphene/ Ru(0001), we consider a silicon honeycomb structure for the silicon intercalation in graphene/Ni(111). We have tested the monolayer silicon, bilayer silicon, and multi-layer silicon in both planar and buckled form. The most energetic favour configurations were considered here. The most stable configuration after silicon intercalation is shown in figure 2(e). Si atoms prefer to adsorb on hcp site. The monolayer silicon is flat. Comparing to the freestanding monolayer silicene [40], the bond length of this flat silicon monolayer is 8% longer. PDOS of C atoms in Gr/monolayer silicon/Ni system is shown in figure 2(f). The Dirac state is restored and the Dirac point $E_{\rm D}$ is found at 0.206 eV above the Fermi level indicating hole doping of graphene.

We then analyzed the position of Dirac point for different intercalations. It has been reported that the doping level of graphene is related to the work function difference between graphene and the underlying substrate [18]. So we plotted the position of Dirac point (E_D) as a function of ΔW . ΔW is the the work function difference between graphene (W_{Gr}) and the 2D materials-on-Ni ($W_{M/Ni}$) in figure 3(a). The calculated work function of graphene is 4.23 eV, consistent with previous reports [41]. As shown in figure 3(b), the work function of 2D materials-on-Ni (AlAs on Ni as an example here), $W_{M/Ni}$, is defined as $E_{vac} - E_F$, where E_{vac} is the energy of a stationary electron in the vacuum nearby the surface, and E_F is the fermi level in the system [42].

It is clear that the Dirac point shift downwards from E_F for the intercalations of MgSe, AlAs and GaAs, which is indicative of electron doping (n-type). On the other hand, for the intercalation of AgI, monolayer silicon, and CuI, the Dirac point shift upwards from E_F , which is indicative of hole doping (p-type). The position of Dirac point (E_D) is nearly

proportional to ΔW . It is worth to mention that the crossover point from n-type to p-type doping is not at $W_{M/Ni} = W_G$. This is due to dipole formation between 2D materials/Ni interface and graphene, as explained by Giovannetti *et al* [18].

To further understand the doping effect, we plotted the electron density difference of the intercalated system. Take AlAs intercalation as the example, the electron density difference is defined as follows: $\Delta \rho = \rho_{\text{Gr/AlAs/Ni}} - \rho_{\text{Gr}} - \rho_{\text{AlAs}} - \rho_{\text{Ni}}$, where $\rho_{\text{Gr/AlAs/Ni}}$, ρ_{Gr} , ρ_{AlAs} , and ρ_{Ni} are the electron densities of the Gr/AlAs/Ni heterostructure, graphene, DLHC AlAs, and Ni substrate, respectively. The in-plane intergration of $\Delta \rho$ is plotted in the left panel of figure 3(c). Isosurfaces with $|\Delta \rho| = 0.047$ e Å⁻³ are plotted in the right panel of figure 3(c). Yellow and light blue represent electron accumulation and depletion respectively. We can see that, after AlAs intercalation, there are charge reconstribution only at AlAs/Ni interface, which means that AlAs intercalation effectively decouples the interaction between graphene and the Ni substrate.

We then checked how the thickness of the intercalated 2D semicondcting layers affects the doping level of graphene. We still use DLHC AlAs as the example. As shown in figure 4(a), the amount of n-type doping increases when the thickness of AlAs buffer layer increases. Top inset of figure 4(a) are the side views after intercalating 1, 2, and 3 layer DLHC AlAs, respectively. The work functions of 1L DLHC, 2L DLHC, and 3L DLHC on Ni are shown in figure 4(c). The work function decreases while increasing the thickness of AlAs. It is found that the n-type doping level of graphene increases with increasing the thickness of the intercalated DLHC AlAs.

For silicon intercalation, the relation between doping level and intercalation thickness is not simple. The positions of Dirac point for different intercalation thickness is shown in figure 4(b). For monolayer silicon intercalation, graphene is hole doped. For two-layer and three-layer silicon intercalations, however, graphene switched to electron doping. When increasing silicon intercalation thickness to four and five layers, graphene becomes hole doped again. The corresponding work function is shown in figure 4(d). The work



Figure 4. The effect of intercalation thickness. The positions of Dirac point (E_D) for different layers of AlAs intercalation (a) and silicon intercation (b), respectively. Figures (c) and (d) are the workfunctions corresponding to the intercalating materials-on-Ni in (a) and (b), respectively.



Figure 5. The electronic properties of DLHC AlAs with different thickness. (a)–(c) Atomic structures of 1L, 2L, and 3L DLHC AlAs on Ni. (d)–(f) Projected density of states of the top-double-layer AlAs in the three systems.

function has the same trend of doping level with increasing intercalation thickness.

We now go beyond graphene and investigate the influence of the Ni substrate on the electronic properties of the semiconducting layers. Figures 5(a)–(c) are side views of 1L, 2L, and 3L DLHC AlAs on Ni(111), respectively. The PDOS of the top-double-layer AlAs are plotted in figures 5(d)–(f), respectively. Though freestanding DLHC AlAs is has a band gap of 1.36 eV (PBE level) [33], 1L DLHC AlAs on Ni(111) is metallic. Starting from 2L DLHC, the top-double-layer AlAs becomes semiconducting. The energy gap in the top-double-layer is 1.40 eV for the 2L DLHC case. The bottom-double-layer plays the role as a buffer layer. For 3L DLHC, the energy gap of top-double-layer AlAs is 1.31 eV. These results indicate that there should be at least one buffer layer to decouple the interaction between DLHC semiconducting layers and transiton-metal substrate to use the semiconducting properties of DLHC semiconducting layers such as AlAs.

4. Conclusions

We have investigated the several 2D materials intercalation at Gr/Ni(111) interface. We show that 2D semiconducting materials and silicon can effectively decouple the strong interaction between graphene and Ni(111) surface. The doping level of graphene has a nearly linear relation of the work function difference between graphene and 2D materials-on-Ni. We also provide a method to tune the doping of graphene with different layers of 2D materials. These results indicate that the intercalating 2D silicon and semiconducting materials from III–V groups may be useful in the development of next generation graphene-based devices.

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