First-principles study of the doping effects in bilayer graphene

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Abstract. We used first-principles calculations to study the doping effects in bilayer graphene, focusing on Au substitute doping in the upper layer of graphene. We found that Au doping in the upper layer maintains the lattice structure of the lower graphene layer. Our study on binding energy shows that the Au-doped bilayer structure is stable with Au atom tightly confined in a small region between the upper and lower layers. Charge density analysis indicates that charge is transferred from the Au donor to the carbon atoms in the lower layer, increasing the carrier density in the lower graphene.

Graphene, a two-dimensional (2D) hexagonal lattice of carbon atoms, has attracted considerable attention [1]–[3] due to its unusual electronic properties [4] characterized by massless Dirac fermions [5]. It was first produced by micromechanical cleavage of graphite with immediate confirmation of the half-integer quantum Hall effect [6, 7]. In addition to graphene, fewlayer graphene films can also be produced [8]. Of particular interest is the bilayer graphene, where two carbon planes lie on top of each other according to the AB (Bernal) stacking. Most notably, bilayer graphene is a gapless semi-metal with the quadratic dispersion [9]. Theoretical [10, 11] and experimental [12]–[15] works have shown the gap opening in exfoliated bilayer graphene by applying an external electric field. Ohta et al [16] demonstrated that by controlling the carrier density in a bilayer of graphene, the occupation of electronic states near the Fermi level and the magnitude of the gap could be manipulated. Indeed, a band gap has also been observed in bilayer graphene epitaxially grown on SiC substrate [17]. Zhong et al [18] reported theoretically that the
one-layer-doping bilayer graphene behaves remarkably different from the conventional ordered or disordered electron systems, exhibiting metal–insulator transitions with persistent mobility edges and superdiffusive anomalous quantum diffusion. Recently, Castro et al [19] examined the magnetic properties of the localized states induced by lattice vacancies in bilayer graphene and showed that magnetic switching between an unpolarized and a fully polarized system could be created. We have investigated the manganese doping bilayer graphene [20] and found that manganese doping leads to a highly spin polarized state, which was regarded as groundbreaking for spintronics in carbon-based devices [21].

The knowledge of the bonding between metal and carbon atoms and of the location and diffusivity of metal atoms in graphene layers is central to realizing future electronics based on carbon [22, 23]. The first-principles calculations of Charlier and coworkers [24] have been used to investigate the nature of gold–graphene interactions. Their calculations revealed that this interaction was quite weak, allowing Au migration at the graphene surface. Defects (or ‘active sites’) such as oxygenated vacancies or divacancies may trap these diffusive Au atoms and play the role of nucleation centers for a future gold cluster, which will be stabilized by the stronger Au–Au interaction. A recent interesting experiment by Gan et al [25] monitored individual Au and Pt atoms in layers consisting of one or two graphene planes using TEM and also measured the rate for metal atom diffusion. Although no clear indications for an off-layer position were seen in their study, they predicted that a slight off-layer position of metal atoms would be expected when the metal atoms occupied single vacancies in graphene. Using density functional theory (DFT), Malola et al [26] have supplied a theoretical support for the above main results found in Gan et al’s experiment. In order to fully understand and control the electrical properties of bilayer graphene, a careful consideration of doping effects of the Au atom is necessary. Important questions are: how does the doping in the upper layer affect the geometrical configuration and electronic properties in bilayer graphene? Can the symmetry of the bottom layer be well maintained in order to keep the feature of the 2D electron gas (2DEG) with significant charge transfer from Au dopant in the upper layer? In this paper, using first-principles calculations, we show that Au doping in the upper layer of bilayer graphene keeps well the 2D lattice structure of the lower graphene layer. Importantly, there is a high-energy barrier between the two graphene planes, which prevents the thermal diffusion of Au dopant to the lower graphene layer. Moreover, electrons are transferred from the Au donor to the lower graphene layer, increasing the charge density in the bottom graphene layer. Our findings help us to understand the mechanism of controllable doping in the graphene-based system.

To investigate the doping effects of Au in the upper layer of bilayer graphene, we construct a $4 \times 4$ supercell structure. The supercell parameters are set to be the same as $a = b = 9.84$ Å in the $xy$-plane ($a$ and $b$ refer to the crystal lattice constants). The relaxed C–C bond length in the perfect bilayer graphene is 1.408 Å. Two kinds of typical doping sites, named H site (above the center of a carbon hexagon of the lower graphene layer) and T site (directly on the top of a carbon atom of the lower graphene layer) in the upper layer of bilayer graphene, are schematically shown in figures 1(a) and (c), respectively. The calculations were performed in the framework of DFT with the local density approximation (LDA) and ultrasoft pseudopotentials as implemented in the CASTEP simulation package [27]. Because generalized gradient approximation (GGA) calculations give essentially no bonding between graphene planes and lead to excessively large values of $c$ [28] (we find an interlayer distance of 4.125 Å between the graphene layers), we perform the structure relaxation calculations within...
Figure 1. The top and side views of final relaxed configurations for the two doping cases: (a, b) for the H site doping and (c, d) for the T site doping. Values of optimized bond length are labeled in the plot. Insets at the top right corner in (a) and (c) indicate the relaxed lattices in the H site and T site doping, respectively.

the LDA. Nevertheless, GGA was shown to produce a band structure identical to LDA [29] and was also proved accurate in our previous calculations of the band structures and magnetic properties of the metal-doped graphene system [3, 20]. We used an energy cut-off of 600 eV for the plane wave basis functions. The size of the supercells in the lateral plane was adjusted to maintain a sufficiently large separation between adjacent bilayer graphene (>20 Å from...
Table 1. Summary of results of the optimized structures of Au-doped bilayer graphene with H site and T site doping. The interlayer distance (Å) refers to the average distance from the upper layer to the bottom layer. The bond length (Å) refers to the length of the bond Au–C (C1, C2 and C3) as indicated in figure 1(a) for the H site doping and in figure 1(c) for the T site doping. The charge (e) means the atomic Milliken charge of the Au atom after doping.

|                      | H site doping         | T site doping         |
|----------------------|-----------------------|-----------------------|
| Total energy (eV)    | $-1.070\,8862 \times 10^{4}$ | $-1.070\,8830 \times 10^{4}$ |
| Relaxed lattice parameters (Å) and supercell angles (°) | $a = 9.787$ | $a = 9.780$ |
|                      | $b = 9.787$           | $b = 9.780$           |
|                      | $c = 21.620$          | $c = 21.219$          |
|                      | $\alpha = 78.834$    | $\alpha = 90.002$    |
|                      | $\beta = 101.178$    | $\gamma = 21.219$    |
|                      | $\gamma = 120.211$   | $\gamma = 119.999$   |
| Layer distance (Å)   | 3.781                 | 3.798                 |
| Bond length (Å)      | 2.06 (C1-Au)          | 2.06 (C1-Au)          |
|                      | 2.06 (C2-Au)          | 2.06 (C2-Au)          |
|                      | 2.06 (C3-Au)          | 2.06 (C3-Au)          |
|                      | 2.24 (C4-Au)          | 2.22 (C4-Au)          |
| Bond angle (°)       | 82.527(C1-Au-C2)      | 80.959(C1-Au-C2)      |
|                      | 77.723(C1-Au-C3)      | 80.957(C1-Au-C3)      |
|                      | 82.590(C2-Au-C3)      | 80.966(C2-Au-C3)      |
| Charge (e)           | +1.60                 | +1.62                 |

surface to surface). We used $4 \times 4 \times 2 \times$ points in the Brillouin zone. Calculations with more $k$ points and larger energy cut-offs indicated that total energies converge to the values smaller than $1.0 \times e^{-4}$ meV cell$^{-1}$ with these parameters. Atomic positions were optimized for all configurations with a criterion that requires the maximum force on all atoms to be smaller than 0.01 eV Å$^{-1}$.

The top and side views of fully relaxed structural configurations of H site and T site doping are shown in figure 1. Figures 1(a) and (b) are for the H site doping and figures 1(c) and (d) are for the T site doping. A summary of the results for the optimized structures is given in table 1. Comparing the total energy of the two configurations, we find that two doping configurations have a minor difference of about 0.03 eV in total energy. Interestingly, for H site doping, severe lattice transition from the hexagonal system to the triclinic one takes place (as shown in the inset of figure 1(a)). In table 1, we can find that, although one of the super-cell angle $\gamma$ (120.211°) remains near the hexagonal lattice angle of 120°, the other lattice angles $\alpha = 78.834°$ and $\beta = 101.178°$ are not close to the angle 90° as that in hexagonal supercell. Moreover, the bilayer graphene with H site doping stays as a 2D layer structure as the undoped bilayer graphene does. In this particular case, six possible initial sites are equivalent for Au to bond to the lower graphene layer. As shown in figures 1(a) and (b), the final relaxed position of Au atom in H site doping now changes to stay directly above a carbon atom (denoted as C4) of the lower graphene layer due to the lattice transition. For the optimized structure of T site
Figure 2. Binding energy curves for the Au atom approaching the lower graphene layer along three different diffusion paths denoted by the arrows in the inset of the plot.

doping (see figures 1(c) and (d)), however, the bilayer structure keeps the hexagonal lattice (as shown in the inset of figure 1(c)). Relevantly, as indicated in table 1, one of the supercell angles is close to 120° and the other two supercell angles are close to 90°, which is similar to that of undoped bilayer graphene. The optimized interlayer distances of bilayer graphene in H site doping and T site doping have a similar value (about 3.8 Å), which is larger than 3.338 Å in the ideal bilayer graphene. There are two sets of bonds between the Au atom and carbon atoms for the two relaxed configurations, one with an equal bond length of 2.06 Å to the C1, C2 and C3 carbon atoms on the upper layer, and the other with a bond length of 2.24 Å in H site doping and 2.22 Å in T site doping to the nearest-neighboring carbon atom on the lower graphene plane. In both the doping cases, there is a concave geometry around the doping Au atom for the upper layer (see figures 1(a) and (c)). The C–C bonds directly below the Au atom undergo a slight change of length of 0.012 and 0.02 Å, respectively, and other C–C bonds in the lower graphene nearly remain unchanged. Because the C–C bond length in the lower graphene layer only has minor changes (smaller than 1.5%), the lower graphene layer keeps the original graphene structure.

The mobility of the Au dopant to the lower layer is a key fact to determine the property of bilayer graphene. For monolayer graphene, Malola et al [26] studied the bonding and diffusion of Au in the plane of single layer graphene vacancies using DFT. Their energetic calculations showed that all diffusion barriers for the complex of Au in double vacancy of the plane are above 4 eV, whereas the barriers for larger vacancies are below 2 eV. To examine the possibility of the Au dopant diffusing to the lower graphene layer, we calculated the binding energy of the Au atom along different paths from the upper layer to the lower layer in bilayer graphene, as shown in figure 2. In general, the diffusion barrier is about one-third of the absolute values in
The binding energy ($E_b$) for a given position of Au atom was calculated as the total energy difference

$$E_b = E_{(\text{doped})} - E_{(\text{undoped+vacancy})} - E_{(\text{Au})},$$

where $E_{(\text{doped})}$ is the total energy of the doped bilayer graphene with Au, while $E_{(\text{undoped+vacancy})}$ represents the total energy of the relaxed doped bilayer structure without Au at the substitution point, and $E_{(\text{Au})}$ is the total energy of the isolated Au atom. Figure 2 displays the calculated binding energy for an Au atom at different positions along three typical paths between the two graphene layers. One finds that the bind energy $E_b$ is positive and increases rapidly when Au atom approaches the upper or lower layer. It reaches the same minimum close to about 2.2 Å along three different diffusion paths. This indicates that the Au atom prefers to stay on a plane with a height of about 2.2 Å above the lower graphene layer. The lowest binding energy that occurs at this distance is $-4.84$ eV in path 1, $-3.06$ eV in path 2 and $-2.45$ eV in path 3. In the region near the upper or lower layer, the binding energy has a finite positive value, which indicates that the interaction between the Au atom and the graphene layer is repulsive. Our results show that the Au-doped bilayer structure is stable with Au atom tightly confined in a small region between the upper and lower layers. This indicates that a high-energy barrier must be overcome for the Au dopant to diffuse to the lower graphene layer, which is determined by the repulsive interaction between the Au atom and the carbon atoms in the lower graphene layer. This high-energy barrier prevents destruction of the lower layer. Further spin-polarized calculation on the binding energy of magnetic dopant such as 3d transition metal (TM) manganese has been done to examine the accuracy of our energy barrier estimation. Our spin-polarized calculation indicates that the trend of Mn diffusion is similar to Au atom, except for the value of $E_b$, which is $-8.26$ eV in path 1, $-6.08$ eV in path 2 and $-4.07$ eV in path 3, respectively (not shown here).

Figure 3(a) shows the band structure and corresponding density of states (DOS) of bilayer graphene in the built $4 \times 4$ supercell. Apparently the two bands touch together at K point and the corresponding DOS at the Fermi level has a zero value. This indicates that the bilayer graphene is semi-metallic, which is consistent with the conclusion in the literature [9]. In the band structure and corresponding DOS of H site doping (see figure 3(b)) and T site doping (see figure 3(c)), two typical doped configurations exhibit similar behavior. The $\pi-\pi^*$ band crossing of the pure bilayer graphene is disturbed by the presence of Au impurity. As clear evidence of the interaction between Au dopant and the bilayer graphene, the Fermi level is now moved to the conduction band, making the bilayer graphene $n$-doped. Especially in the region above or below the Fermi level, the bands have noticeable modifications by the Au dopant. Detailed analyses indicate that the band of $E_f$ at gamma is localized on Au in a 6s-orbital but around K point (just below $E_f$) is localized on graphene. The corresponding DOS of H site and T site doping plotted in the right panels of figures 3(b) and (c) display a sharp peak at the Fermi level. Therefore, the doping of Au in the upper layer makes the bilayer graphene metallic.

Distributions of charge density on planes that pass through the carbon atoms in the upper graphene layer, lower graphene layer and Au atom along the z-direction are shown in figure 4. Because two typical doping sites exhibit similar charge density distributions, we only show the contour plots of charge density for the T site doping. In the Au-doped upper layer plane, electrons around the Au atom in graphene show localized characteristics (see figure 4(a)). In contrast, the electron density on the lower graphene layer (see figure 4(b)) is delocalized. Recently, Castro et al [31] addressed the character of vacancy-induced electronic states in
Figure 3. The band structure and corresponding DOS of pure bilayer graphene (a), Au H site doping bilayer graphene (b) and Au T site doping bilayer graphene (c). The Fermi level is indicated by the dotted line.

bilayer graphene. They demonstrated that the wave function was quasi-localized in one layer and totally delocalized in the other. They commented that the delocalization was due to the spread of the wave function in the opposite layer where the vacancy resided. The physics in their theorem calculations accords well with our charge analysis for localized and delocalized states due to the upper-layer doping by Au atom in bilayer graphene. Furthermore, as can be seen in figure 4(c), the Au–C interaction features larger values of the charge density between the doped Au atom and the carbon atoms in the upper graphene layer, indicating a clear covalent-bonding character. This covalent-binding also occurs between Au atom and the carbon atoms of the lower graphene directly below the Au atom. Atomic Milliken charges (the sum of the atomic Milliken charges in the case of doped bilayer graphene) reflect the nature of chemical bonds. For H and T site doping, Milliken charges are all $-0.2e$ for the C1, C2 and C3 atoms in the upper graphene layer and $-0.15e$ for the carbon atom directly below the Au atom in the lower graphene layer.

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Figure 4. The charge density isoface of the upper graphene layer (a), lower graphene layer (b) and the Au dopant between the two layers along the z-direction (c).

We find that the Milliken charges of the Au atom itself is +1.6e in H site doping and +1.62e in T site doping. As a result, there are net charges of −0.85e and −0.87e transferred from Au to the bilayer graphene for the H site and T site doping, respectively. Experiment has been carried out on metallic doping on single-layer graphene [32]. There is charge transfer and hence doping but the mobility is catastrophically reduced because of Coulomb scattering. Our calculations on charges in one-layer doping bilayer graphene prove that electrons are transferred from the Au donor on the upper layer to the carbon atoms in the lower layer, increasing the charge density in the lower graphene.

In conclusion, we have conducted first-principles calculations to investigate the effects of Au doping on the upper layer of bilayer graphene. One of our main findings is that the graphene structure in the lower layer of bilayer graphene has only minor changes. Our study on binding energy shows that the Au-doped bilayer structure is stable with the Au atom tightly confined in a small region between the upper and lower layers. The Au-doped bilayer graphene exhibits metallic electric property. Moreover, charge is transferred from the Au donor to the carbon

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atoms in the lower layer, increasing the carrier density in the lower graphene. Our results suggest that the one-layer-doped bilayer graphene is an ideal system to realize the thinnest ordered–disordered separated quantum films [18] only with two layers of atoms.

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References

[1] Geim A K and MacDonald A H 2007 Phys. Today 60 35
[2] Geim A K and Novoselov K S 2007 Nat. Mater. 6 183
[3] Mao Y L, Yuan J M and Zhong J X 2008 J. Phys.: Condens. Matter 20 115209
[4] Saito R, Dresselhaus G and Dresselhaus M S 1998 Physical Properties of Carbon Nanotubes (London: Imperial College Press)
[5] Novoselov K S, Geim A K, Morozov S V, Jiang D, Katsnelson M I, Grigorieva I V, Dubonos S V and Firsov A A 2005 Nature 438 197
[6] Zhang Y, Tan Y W, Stormer H L and Kim P 2005 Nature 438 201
[7] Novoselov K S, McCann E, Morozov S V, Fal’ko V I, Katsnelson M I, Zeitler U, Jiang D, Schedin F and Geim A K 2006 Nat. Phys. 2 177
[8] Novoselov K S, Jiang D, Schedin F, Booth T J, Khotkevich V V, Morozov S V and Geim A K 2005 Proc. Natl Acad. Sci. USA 102 10451
[9] McCann E and Fal’ko V I 2006 Phys. Rev. Lett. 96 086805
[10] Nilsson J and Castro Neto A H 2007 Phys. Rev. Lett. 98 126801
[11] McCann E 2006 Phys. Rev. B 74 161403
[12] Castro E V, Novoselov K S, Morozov S V, Peres N M R, Lopes dos Santos J M B, Nilsson J, Guinea F, Geim A K and Castro Neto A H 2007 Phys. Rev. Lett. 99 216802
[13] Oostinga J B, Heersche H B, Liu X L, Morpurgo A F and Vandersypen L M K 2008 Nat. Mater. 7 151
[14] Zhang Y B, Tang T T, Girit C, Hao Z, Martin M C, Zettl A, Crommie M F, Shen Y R and Wang F 2009 Nature 459 820
[15] Mak K F, Lui C H, Shan J and Heinz T F 2009 Phys. Rev. Lett. 102 256405
[16] Ohta T, Bostwick A, Seyller T, Horn K and Rotenberg E 2006 Science 313 951
[17] Zhou S Y, Gweon G H, Fedorov A V, First P N, De Heer W A, Lee D H, Guinea F, Castro Neto A H and Lanzara A 2007 Nat. Mater. 6 770
[18] Zhong J X and Stocks G M 2007 Phys. Rev. B 75 033410
[19] Castro E V, López-Sancho M P and Vozmediano M A H 2009 New J. Phys. 11 095017
[20] Mao Y L and Zhong J X 2008 Nanotechnology 19 205708
[21] Stöberl U, Wurstbauer U, Wegscheider W, Weiss D and Eroms J 2008 Appl. Phys. Lett. 93 051906
[22] Rutter G M, Crain J N, Giusinger N P, Li T, First P N and Stroscio J A 2007 Science 317 219
[23] Girit C O et al 2009 Science 323 1705
[24] Charlier J-C et al 2009 Nanotechnology 20 375501
[25] Gan Y J, Sun L T and Banhart F 2008 Small 4 587

New Journal of Physics 12 (2010) 033046 (http://www.njp.org/)
[26] Malola S, Häkkinen H and Koskinen P 2009 Appl. Phys. Lett. 94 043106
[27] Segall M D, Lindan P L D, Probert M J, Pickard C J, Hasnip P J, Clark S J and Payne M C 2002 J. Phys.: Condens. Matter 14 2717
[28] Ooi N, Rairkar A and Adams J B 2006 Carbon 44 231
[29] Mao Y L, Yan X H and Xiao Y 2005 Nanotechnology 16 3092
[30] Venables J A, Spiller G D T and Hanbucken M 1984 Rep. Prog. Phys. 47 399
[31] Castro E V, Lopez-Sancho M P and Vozmediano M A H 2010 Phys. Rev. Lett. 104 036802
[32] Chen J H, Jang C, Adam S, Fuhrer M S, Williams E D and Ishigami M 2008 Nature Phys. 4 377