Effect of iron intercalation on graphene/SiC electronic structure

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Abstract. Graphene-based materials are of great interest for spintronics devices. In the present paper, the effect of intercalated iron on the electronic structure of the graphene/4H-SiC(0001) system has been studied in the frame of density functional theory. It is shown that the most energetically favorable position of intercalated Fe atoms corresponds to their location between the buffer layer and the top Si layer of the substrate. Insertion of Fe atoms into the system leads to the spin polarization of the electronic states of carbon. Another effect is that the buffer layer becomes flat and bilayer graphene forms in the system.

1. Introduction

Graphene, which is a monatomic layer of carbon arranged in a honeycomb structure, was the first obtained two-dimensional crystal. Due to the high mobility of charge carriers, mechanical strength and outstanding optical properties it remains one of promising materials for future electronics [1]. In particular, for the development of spintronics study of graphene-based ferromagnetic heterostructures is especially important. One of possible approaches for obtaining such interfaces consists in introduction of transition metal atoms into the interlayer space between graphene and the substrate. Synthesis of graphene by thermal decomposition of silicon carbide allows obtaining high-quality graphene of a large area on a dielectric substrate and is suitable as an initial stage for creating graphene/ferromagnetic/dielectric structures [2]. An important feature of graphene grown by this method is the presence of a buffer layer consisting of carbon atoms arranged in a graphene-like structure. The buffer layer is strongly coupled with the substrate, which causes a high rate of carrier scattering and hence negatively affects graphene transport characteristics. One of suggested methods for the illuminating the effects of buffer layer includes intercalation of other species under the graphene. To date, the possibility of synthesizing graphene/Fe/SiC(0001) structure using introduction of iron atoms under graphene, obtained on silicon carbide by thermal decomposition, has been demonstrated [3]. It is shown that the deposition of iron on the graphene/SiC (0001) structure and the subsequent annealing leads to a growth of the iron film under graphene, and the iron atoms are introduced into the space between the buffer layer and the substrate [4]. The question of the effect of intercalated iron on the electronic structure of the system remains open. Thus, it is unclear whether the introduction of iron contributes to the weakening of the interaction of the buffer layer and the substrate and how it affects the magnetic properties of the system. Therefore, the purpose of present work was the theoretical study of the graphene/Fe/SiC(0001) structure.
2. Calculation details

_Ab initio_ calculations were performed using the density functional theory (DFT). The open source software Quantum ESPRESSO [5] was used. For self-consistent calculations, the PBE pseudopotentials and the generalized gradient approximation (GGA) were used. The cutoff energy of wave functions was chosen equal to 200 eV. The Monkhorst-Pack algorithm was used to generate the mesh of 8×8×1 k-points for integration in the reverse space. Dispersion interaction was taken into account for the geometry optimization of the cell.

3. Geometry optimization

The supercell for the calculation of the initial graphene/SiC system is shown on figure 1. It consisted of four bilayers of SiC (three carbon and silicon atoms per layer), a buffer carbon layer (eight C atoms) and graphene (eight C atoms). The Bravias hexagonal lattice with a constant 5.31 Å was used for the translation of the supercell. The structural optimization parameters were chosen in such a way that the resulting distances were in accordance with the literature data [6]. The optimization has shown that graphene in this system is a flat layer of carbon atoms, while the buffer layer turns out to be corrugated: some atoms strongly interact with silicon atoms of the substrate. The distance between graphene and the "top" atoms of the buffer layer is 3.15 Å, while the ones between the "top" atoms of the buffer layer and the substrate and between the "lower" atoms of the buffer layer and the substrate are 2.25 Å and 1.98 Å respectively.

![Figure 1. Supercell for the initial system graphene/SiC(0001) simulation.](image_url)

Now let us consider the localization of iron atoms in the graphene/Fe/SiC system. First, calculations were performed for the cases of adsorption of iron atoms on the surface of graphene and two variants of iron intercalation: between graphene and the buffer layer and between the buffer layer and the substrate. Comparison of the total energies of these systems is presented in the table 1. It is seen that the most energetically favorable position of Fe atoms corresponds to their location between the buffer layer and the top layer of the substrate. Then, to establish the exact localization sites of iron atoms, calculations were also carried out for various places of introducing single Fe atom into the space between the buffer layer and the substrate. Possible iron intercalation sites are shown in figure 2, a. For all sites geometry optimization was performed prior to self-consistent calculations. Comparison of the total energies of different localization sites showed that the most favorable is the location of the iron atom in the _fcc_ position in accordance to the SiC lattice (shown in figure 2, a, number 4).
Figure 2. Supercells for the graphene/Fe/SiC(0001) simulations: a – possible sites of Fe; b – supercell for the case of 1 monolayer of iron under graphene.

The supercell used for calculations of the electronic structure of the system with 1 monolayer of iron intercalated under graphene is shown in Fig. 2b. It was obtained by filling all of the most favorable Fe positions. The geometry of this supercell was also optimized. The distance between the buffer layer and the layer of iron atoms turned out to be equal to 1.89 Å, while the distance between the buffer layer and graphene is 3.27 Å. At the same time, unlike the case of graphene on silicon carbide, the buffer layer became flat. Thus, bilayer graphene is formed on the surface.

Table 1. Total energies of structure after adding a Fe atom to the supercell of initial graphene/SiC(0001) system.

| Localization of Fe | Total energy, Ry |
|--------------------|------------------|
| on top of graphene | -433.251         |
| between graphene and the buffer layer | -433.328 |
| between the buffer layer and the substrate in position: | |
| 1                  | -434.178         |
| 2                  | -434.185         |
| 3                  | -434.186         |
| 4                  | -434.330         |
| 5                  | -434.216         |
| 6                  | -434.265         |
| 7                  | -434.232         |

4. Electronic structure

After the geometry optimization had been done a self-consistent calculations were performed for all systems. For the convenience of the electronic structure interpretation k-resolved partial densities of states were extracted from the output data. Information of $p_z$ states of carbon atoms is especially important since these states are responsible for the Dirac cone formation. The results of the electronic structure calculation for the initial graphene/SiC system are shown on figure 3, a. The contributions of the $p_z$ states of graphene (left frame) and the buffer layer (right frame) are highlighted. It is seen that electronic states of graphene atoms are similar to the case of free-standing graphene. The Dirac cone is
slightly n-doped. At the same time the electronic states of the buffer layer are strongly modified due to the interaction with the substrate. Since any magnetic atoms are absent, the electronic structure is independent on spin direction.

Figure 3. (a) Electronic structure of graphene/SiC(0001) system. Contributions of carbon atoms $p_z$ states are shown for a graphene (left side) and the buffer layer (right side). (b), (c) Electronic structure of the graphene/Fe/SiC system for the different spin projections for graphene and the buffer layer, respectfully.
Now consider the electronic structure of the system after intercalation of iron. The electronic structure plots with highlighted $p_z$ states of graphene and the buffer layer for the graphene/Fe/SiC (0001) system are shown in figure 3 b and c, respectfully, for two spin subsystems. The contributions of the $p_z$ states of carbon atoms remain unchanged compared with the case of the initial system, which indicates that the properties of graphene are preserved during iron intercalation. At the same time, the dispersion curves corresponding to the contributions of atoms of the buffer layer undergo significant changes. They become dependent on the spin due to the introduction of magnetic iron atoms. Due to the small distance between the buffer layer and the iron layer, the $p_z$ carbon orbitals are overlapped with the d-orbitals of iron in energy and in direct and reciprocal space, and, therefore, hybridization of these states occurs. This leads, on the one hand, to the appearance of states of a buffer layer at the Fermi level in the vicinity of point K, on the other hand, to the removal of the degeneracy of these states along the spin. In this case, carbon states at the Fermi level arise only for spin projection "upward", which is caused by hybridization with iron states dependent on the spin direction. For both spin projections at point K, a state arises at a binding energy of $-3$ eV, which is also due to hybridization and is in excellent agreement with previous calculations for graphene on iron [7].

5. Conclusion
In summary, in the present work intercalation of iron under the graphene grown on SiC is studied in the frame of density functional theory. Localization sites of iron atoms are established. It is shown that the buffer layer after the introduction of iron becomes flat and from that point of view formation of bilayer graphene on the top of the substrate occurs. On the other hand, self-consisted calculation of electronic structure has shown that due to hybridization electronic states of the buffer layer are strongly influenced by the interaction with the substrate and, hence, the electronic structure of the graphene/buffer layer system is different from the case of freestanding bilayer graphene. In the same time it was previously shown that formation of iron silicide under graphene grown on Ni substrate leads to a reduction of interaction between graphene and its substrate and transfer of graphene into a quasi-freestanding state [8]. That is why there is a theoretical possibility to synthesize iron silicide instead of thin iron film under graphene grown on silicon carbide and obtain truly bilayer graphene on the top of the structure.

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