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Graphene Intercalation with Iron and Cobalt: a Brief Review

E.Yu. Lobanova[1,2,*]

[1] Institute of Advanced Data Transfer Systems, ITMO University, Kronverkskiy pr., 49, lit. A, St. Petersburg, 197101, Russia
[2] Plasma Physics, Atomic Physics and Astrophysics Division, Ioffe Institute, Politekhnicheskaya st., 26, St. Petersburg, 194021, Russia

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Abstract

The attractiveness of graphene, a two-dimensional crystal consisting of carbon atoms arranged in a hexagonal lattice, for various technological applications stems from its outstanding physical, mechanical and optical properties. The intercalation of magnetic metal atoms under graphene is a flexible tool for creating new functional materials for electronics and spintronics. In this review, we consider the works devoted to the intercalation of graphene by iron and cobalt atoms, where graphene on a metal (graphene sythesized by chemical vapor deposition method) and dielectric (graphene grown on silicon carbide) substrate is used as the initial structure.

Keywords: Graphene; Intercalation; Spintronics

1. INTRODUCTION

The intercalation of graphene with atoms or molecules of other substances is one of the promising ways to control the electronic and magnetic properties of graphene/substrate structures. The potential of the intercalation approach as a tool for modifying the properties of graphene has been demonstrated by now in a number of works. Thus, it has been shown that the intercalation of graphene with alkali metal atoms makes it possible to effectively control the level of electron doping of graphene [1], which is essential in microelectronics applications. At the same time, the intercalation of graphene with hydrogen atoms [2] or noble metals [3,4] leads to a decrease in the interaction between graphene and the substrate and the restoration of the electronic properties of freestanding graphene. A number of groups have studied the intercalation of graphene by atoms of ferromagnetic metals and demonstrated the possibility of fabricating structures with perpendicular magnetic anisotropy (PMA) in a wide range of thicknesses of magnetic films under graphene [5–8], which paves the way towards high-speed, low-energy consumption nanodevices. Materials with large PMA are of great interest in light of developing spin transfer torque magnetic random access memory devices.

Since such materials are of great interest for the development of spintronics, interfaces based on graphene and magnetic metals remain the subject of active research. In present review we consider works on the intercalation of graphene by transition metal atoms (Fe and Co). Section 2 describes the general features of the electronic structure of graphene and its changes due to the contact with a substrate. Sections 3 and 4 review recent works devoted to study intercalation of CVD graphene (graphene synthesized by chemical vapor deposition method) on a metal substrate and graphene grown on a dielectric substrate (SiC), respectively.

2. ELECTRONIC STRUCTURE OF GRAPHENE ON A SUBSTRATE

Graphene is a monoatomic layer of sp^2-hybridized carbon. Its unit cell consists of two atoms forming two sublattices (Fig. 1a). The lattice constant of graphene is equal to 2.46 Å, the distance between the two nearest carbon atoms is 1.42 Å. The reciprocal lattice of graphene also has a hexagonal structure. The first Brillouin zone of graphene has a hexagonal shape (Fig. 1b).

The outstanding physical and chemical properties of graphene stem from its electronic structure, which was first calculated in 1947 using the tight-binding approximation [9]. Fig. 2 shows the band structure of graphene calculated along the highly symmetric directions of the Brillouin zone (ΓMKΓ). The four valence orbitals of each

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[*] Corresponding author: E.Yu. Lobanova, e-mail: elobanova@itmo.ru

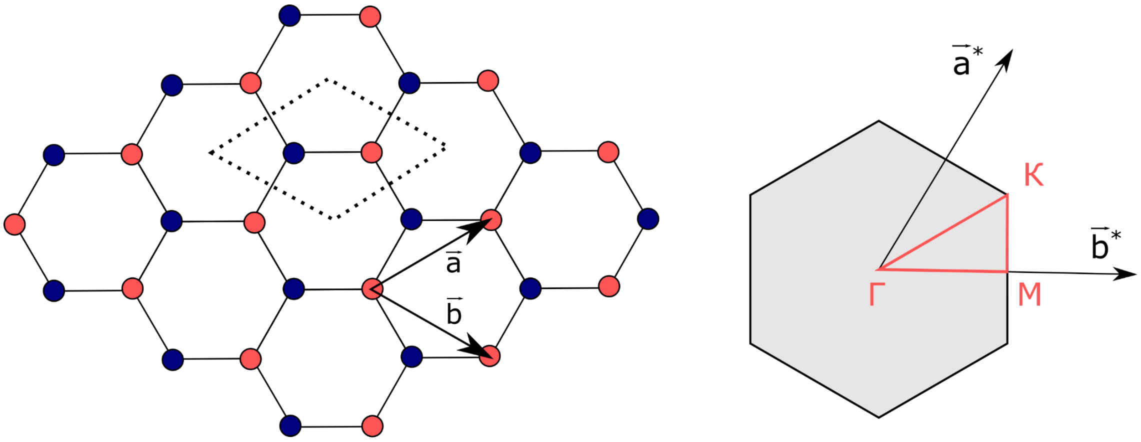

Fig. 1. Graphene lattice in direct and reciprocal space.

graphene carbon atom form three σ-bonds and one π-bond. The main feature of the electronic structure of graphene is the presence of a linear dispersion of π-states near the K point. The conical surface $E(k)$ near the K point is called the Dirac cone. The bonding π-orbital of carbon is completely filled, and the antibonding π*-orbital is empty. The filled and unfilled cones touch each other at the K point at the Fermi level. In this case, degeneracy of the conduction and valence bands is observed. Therefore, graphene is classified as a gapless semiconductor.

The linear dispersion near the points of contact between the valence band and the conduction band is not observed in all cases, since graphene is usually placed on a substrate. The interaction with the substrate leads to modifications of the electronic structure of graphene, which are determined by the properties of the substrate material, as well as by the graphene synthesis method. To control the characteristics of graphene, it is necessary to understand how the interaction between graphene and its substrate takes place. In light of graphene intercalation with transition metals, modifications of the electronic structure of graphene on a metal substrate are of great interest.

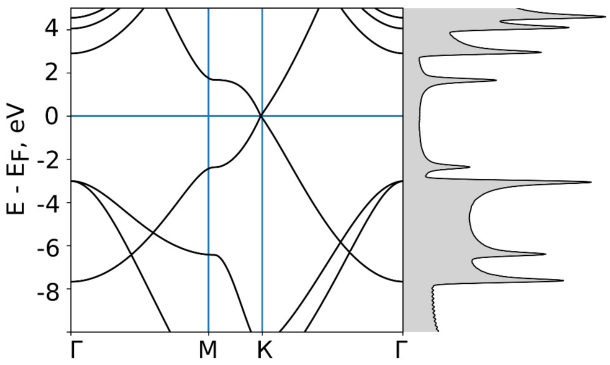

Fig. 2. The band structure of graphene plotted along the highly symmetric directions of the first Brillouin zone (left) and the corresponding density of electronic states (right).

A general approach to understanding the electronic structure of graphene on a metal substrate is proposed in work [10]. When graphene is adsorbed on *sp*-metals, the *sp*-electrons of the metal fill the Dirac cone, which leads to its shift to the region of high binding energies and *n*-doping of graphene. The magnitude of this shift, as well as the equilibrium distance between graphene and the substrate, depends on the difference between the work functions of the metal and graphene. In this case, the linear dispersion of π-states of carbon remains undisturbed.

A different situation is realized when graphene is placed on metals with an unfilled *d*-shell. During the rearrangement of the electronic structure of graphene, two processes occur. Firstly, the Dirac cone is displaced due to its filling with *sp*-electrons of the substrate. As a result, the π-states of carbon begin to overlap with the *d*-states of the metal on the energy scale. As a result, hybrid states occur near the Fermi level and the linear dispersion of π-states of carbon vanishes.

When graphene interacts with a metal with a closed *d*-shell, its electronic structure rearranges according to the same scenario: the initial doping of graphene is due to the *sp*-electrons of the metal; however, the filled *d*-shell is located below the Dirac point, so the formation of hybrid orbitals does not affect the Dirac cone.

Iron and cobalt have unfilled *d*-shells and, hence, hybrid states are formed on contact between graphene and intercalated ferromagnetic film.

3. INTERCALATION OF CVD GRAPHENE

During CVD synthesis, hydrocarbon molecules, such as methane (CH_4), acetylene (C_2H_2), hexane (C_6H_{14}), etc., decompose on the surface catalyst into free molecules of carbon and hydrogen at high temperature (650–1200 °C). Then, diffusion of carbon atoms occurs along the surface of the catalyst (usually a metal), followed by the formation of graphene when the limit of carbon solubility in the substrate is reached. CVD is widely used to synthesize graphene on metal substrates. Graphene can be successfully synthesized on Ni, Co, Cu, Ir, Ru, Rh, and Au [11,12].

Depending on the crystal structure of the substrate various reconstructions can be realized during the graphene growth. For example, during the synthesis of graphene on close-packed Ni(111) and Co(0001) faces with lattice constants close to the lattice constant of graphene, a flat *p*(1 x 1) [13] interface is formed. In the case of a significant mismatch between the lattice constants of graphene and the substrate, graphene corrugation and moiré formation occur (for example, during the synthesis of graphene on an Ir(111) substrate [14]).

To date, graphene on a Ni(111) substrate has been studied in sufficient detail [3,5,10,13,15–18]. In the course of experimental and theoretical studies of this system, it was shown that the presence of a metal substrate has a significant effect on the electronic structure of graphene. The distance between graphene and substrate (2.10 Å) is small compared to the interlayer distance in graphite (3.34 Å), which causes modification of the electronic structure of graphene due to the hybridization of *d*-states of nickel and p_z-states of carbon [17].

Let us consider the works devoted to the intercalation of magnetic atoms under graphene obtained by the CVD method. Particular attention was paid to graphene grown on nickel [4,19,20], iron [21,22] and cobalt [8,23,24] substrates. During these studies, it was found that graphene in such structures is strongly bonded with the metal layer. Thus, the interaction of carbon atoms with metal atoms affects the electronic and magnetic properties of graphene and the metal surface in contact with it [5]. For example, graphene-coated cobalt films show an unusually smooth thickness-dependent spin reorientation transition in the intercalated cobalt layer: with increasing thickness, the magnetization vector in the metal film rotates from out-of-plane to in-plane position by less than 10° per monolayer of cobalt [8].

Another remarkable feature of graphene-coated films is their inertness. This was demonstrated by exposing intercalated iron films to oxygen, which did not affect either the composition of the films or their electronic structure [19].

The effect of iron intercalation on the electronic structure and magnetic properties of the graphene/Ni(111) interface was studied in [20,25,26]. The atomic structure and electronic structure of intercalated iron layers were studied in Ref. [19] using low energy electron diffraction, X-ray photoelectron spectroscopy, and first-principles calculations. It has been demonstrated that iron films with a thickness of one and two monolayers have the same face-centered cubic (fcc) structure as the Ni(111) substrate, and the carbon atoms are located over the iron atoms in the same places as in the case of the nickel substrate. The distance between graphene and iron layer is equal to 2.08 Å. The electronic states of graphene and iron are strongly hybridized. It is also shown that the intercalation of one monolayer of iron atoms under graphene increases the magnetic moment of carbon atoms and dramatically changes the magnetic response of the graphene layer [27].

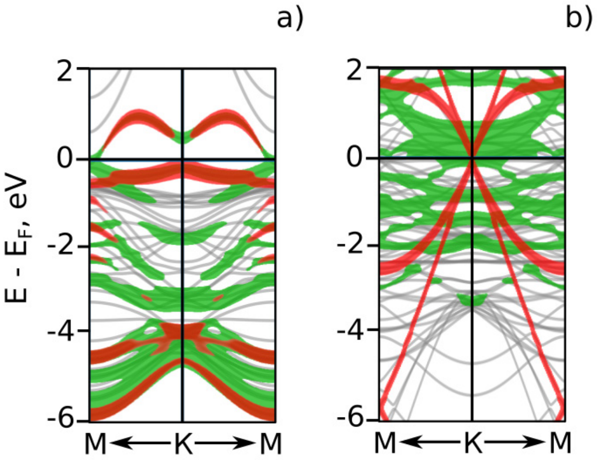

Fig. 3. Fragment of electronic structure calculations for the graphene/Fe/Ni(111) system.

As it was discussed before, due to the peculiarities of the interaction of graphene with metal, the linear dispersion in this system is absent. One of the ways to restore the electronic structure of graphene is its further intercalation with silicon atoms. In Ref. [26], a method for the synthesis of graphene-protected iron silicides was proposed. The proposed approach consists of the formation of graphene on Ni(111) followed by a two-stage intercalation of the system with iron and silicon. It is shown that the intercalation of graphene/Ni(111) by iron occurs at 400 °C in the range up to 14 monolayers. Graphene is strongly bound to iron atoms and stabilizes the fcc structure of the iron film. In this case, prior to the change of magnetization orientation, a perpendicular magnetic anisotropy of the film was observed up to 5 monolayers of iron. The subsequent intercalation of the graphene/Fe/Ni(111) system with silicon led to the formation of a Fe-Si solid solution coated with Fe_3Si surface ferromagnetic silicide with the $(\sqrt{3}\times\sqrt{3})R30°$ structure which is accompanied by an increase in distance between graphene and its substrate (up to 3.1 Å). Angular-resolved photoelectron spectra showed that upon silicon intercalation, graphene restores a linear dispersion of π-states and passes into a quasi-freestanding state. Fragments of the band structure calculations illustrating these changes are shown in Fig. 3. Similar results were observed for the case of cobalt- and silicon-intercalated graphene on Ni(111) [28].

The results of the studies of the intercalation synthesis of iron and iron silicides films under graphene are of great interest from the fundamental and applied points of view.

4. INTERCALATION OF GRAPHENE ON SILICON CARBIDE

Thermal decomposition of silicon carbide makes it possible to obtain high-quality large-area graphene [29] on a dielectric substrate. The process of growing epitaxial graphene on SiC is conceptually simple: at temperatures of 1150 °C and above, silicon carbide sublimation occurs. In this case, silicon atoms, as a more volatile element, leave the surface and near-surface layers, while carbon atoms can form strong bonds remaining on the surface. Consequently, graphene or graphite is formed on the surface, depending on the synthesis conditions. A feature of this synthesis method is the presence of a buffer layer of carbon atoms between graphene and the substrate. The buffer layer is a layer of carbon atoms covalently bonded to the silicon atoms of the substrate. It has a graphene-like crystal structure. The distance between the buffer layer atoms and silicon atoms varies from 1.98 Å to 2.25 Å. At the same time, the distance between graphene and the buffer layer is comparable to the interplanar distance in graphite and is equal to 3.15 Å. Due to the mismatch between the lattice constants of silicon carbide and graphene, a p(6√3×6√3)R30° superlattice arises, corresponding to the superposition of 169 graphene cells on 108 substrate cells. This superlattice appears both in low energy electron diffraction patterns (Fig. 4) and in images taken with a scanning tunneling microscope [30].

The electronic structure of graphene in this case also turns out to be changed in comparison with the case of free graphene without a substrate. The Dirac cone is located 0.45 eV below the Fermi energy (Fig. 5). The observed doping of *n*-type epitaxial graphene on silicon carbide is due to the presence of a buffer layer of carbon atoms [31], whose π-states are several electronvolts below the Fermi level, which indicates a strong bond between these atoms and the substrate [32]. Scattering of electrons by atoms of the buffer layer worsens the transport properties of graphene compared to the case of free-standing graphene [33,34]. The latter is the main disadvantage of graphene on a SiC(0001) substrate.

As noted earlier, the buffer layer of carbon atoms located between graphene and silicon carbide negatively affects the transport properties of graphene. In search of ways to prevent this effect, various methods have been proposed in order to separate the buffer layer from the substrate, including rapid exposure to low [35] or high temperatures [36], combining sublimation of silicon carbide with a CVD process [37], and intercalation of the graphene/SiC system with various substances (H [2,38], Li [39], O [40], F [41], Ge [42], Cu [43], Au [44] and others). These studies have shown that the intercalation of the graphene/SiC(0001) system with various substances can serve as an effective tool for reducing the interaction of the buffer layer with the substrate.

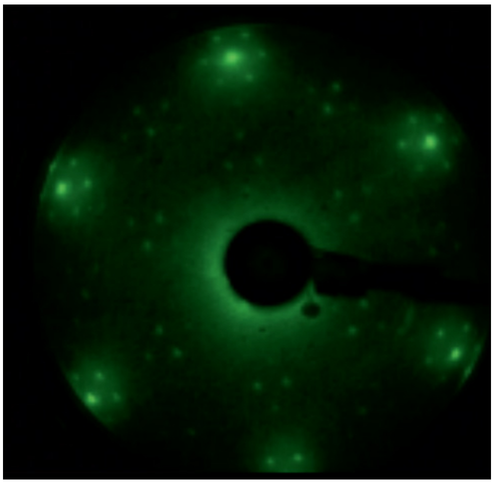

Fig. 4. Low energy electron diffraction pattern for the graphene/SiC(0001) system

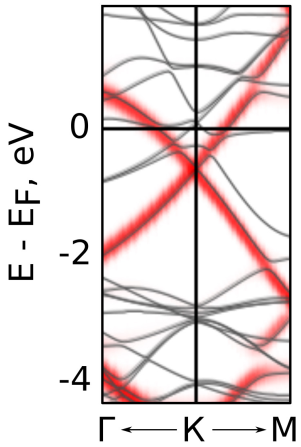

Fig. 5. Fragment of calculating the band structure of the graphene/SiC(0001) system.

In addition to monolayers of individual elements, the intercalation synthesis of various compounds under graphene on silicon carbide is possible. For example, Ref. [45] demonstrates the synthesis of ytterbium oxide by ytterbium intercalation and subsequent annealing of the sample in oxygen. In Ref. [46], ultrathin layers of gallium nitride were synthesized by gallium intercalation from gallium trimethyl followed by exposure of the samples to NH_3.

Let us consider works devoted to the formation of a graphene/ferromagnet interface using graphene on silicon carbide as the initial system. The intercalation of graphene on silicon carbide by iron atoms was studied in Ref. [47]. In this work, the intercalation of iron atoms under the buffer layer was demonstrated during sample annealing at a temperature of 600 °C. The penetration of iron atoms under the buffer layer is confirmed by experimental data and theoretical calculations. The main conclusions are drawn out of photoelectron spectroscopy data. Of main interest is the photoelectron C1*s* peak, which can be decomposed into four components [48]. The most intense component (mode G) corresponds to graphene carbon atoms. The SiC component refers to the carbon atoms in silicon carbide. Finally, the S1 and S2 modes can be associated with two types of carbon atoms in the buffer layer: the S1 component refers to carbon atoms that are bonded to the top layer of silicon carbide, and the S2 mode corresponds to carbon atoms not bonded to this layer. Attenuation of all modes except G, after iron deposition and subsequent heating of the sample, indicates the intercalation of iron and the breaking of bonds between the buffer layer and the substrate.

Additional evidence for the intercalation of iron atoms under graphene is the absence of oxidation of the resulting interface after exposure to oxygen. The buffer layer is separated from the substrate, and bilayer graphene is formed on the surface. This should lead to the appearance of characteristic parabolic dispersion curves in the vicinity of the K point. However, the spectra of angular-resolved photoelectron spectroscopy show that after intercalation of iron, the dispersion of π-states of carbon only becomes diffuse. In addition, iron is a metal with an unfilled 3*d* shell, and its interaction with the buffer layer should occur as described in the previous section.

The intercalation of the graphene/SiC(0001) system with iron was also studied in Ref. [49]. One monolayer of iron was deposited onto the initial sample followed by annealing first at 227 °C and then at 477 °C. Modifications of C1*s* spectra generally demonstrated similar behavior with the data of Ref. [47]. In this case, after annealing at 477 °C, the disappearance of iron from the photoelectron spectra was observed, which is attributed to the diffusion of iron atoms deep into the substrate. However, additional modes appeared in the Si2*p* spectra, indicating the chemical bonding of intercalated iron atoms with silicon. On the other hand, angle-resolved photoemission spectroscopy data show bifurcated dispersion dependences near the K point, which may indicate the appearance of bilayer graphene on the surface.

In Ref. [50] the effect of an intercalated FeSi layer on the electronic properties of epitaxial graphene on a SiC(0001) substrate is studied using ab initio calculations. It has been found that the intercalation synthesis of iron silicide FeSi can successfully eliminate *n*-doping of grown graphene on a SiC substrate. It is shown that although the buffer layer still exists in the case of the structure after FeSi intercalation, the intercalated FeSi layer saturates all dangling bonds of silicon atoms of the substrate and prevents the binding of the electronic states of iron 3*d*-electrons to graphene. The layer of silicon atoms formed by the intercalation synthesis of FeSi screens the charge transfer from the substrate to graphene, and graphene becomes charge neutral. In addition, the results of surface energy calculations showed that the structure with embedded FeSi is the most stable with respect to structures with intercalation of elemental hydrogen and iron in a wide range of temperatures and pressures. Therefore, the creation of a FeSi layer under graphene is considered as another potential intercalation method for obtaining charge-neutral graphene on silicon carbide.

In the work [51] the formation of cobalt silicides CoSi and Co_2Si under graphene was observed, as well as the formation of quasi-freestanding graphene on the surface of the system after cobalt intercalation. It should be noted that the conditions for the synthesis of the graphene/SiC system were chosen in such a way that only zero graphene layer (buffer layer) was synthesized on the substrate.

In Ref. [52] self-limited formation of cobalt silicide was observed during the intercalation of the graphene/SiC(0001) system with cobalt. The subsequent intercalation of cobalt leads to the formation of a smooth cobalt film between the silicide and graphene. In addition, magnetic circular dichroism data shows that the magnetization direction is in-plane for all film thicknesses. Also, intercalated cobalt was found to collect at the edges of the steps, forming self-assembled magnetic nanowires.

In Ref. [53] cobalt intercalation of the graphene/SiC(0001) system was studied using scanning tunneling microscopy and ab initio density functional theory calculations. It is shown that, during deposition, cobalt atoms are assembled into clusters on epitaxial graphene. After annealing the sample at 850 °C, intercalation of adsorbed cobalt atoms occurs under both monolayer and bilayer epitaxial graphene on SiC, which is observed in scanning tunneling microscopy (STM) images with atomic resolution. Further studies based on ab initio calculations and modeling of STM images show that, as a result of the interaction between intercalated cobalt atoms and graphene layers, the most energetically favorable intercalation sites for cobalt atoms under monolayer and bilayer graphene differ. In addition, the results show energy barriers of 0.60 eV and 0.41 eV for the penetration of cobalt through monovacancy defects in single-layer and double-layer graphene.

5. CONCLUSIONS

The present review is focused on the works devoted to the intercalation of graphene grown using CVD process and thermal decomposition of silicon carbide with cobalt and iron atoms. The main mechanism responsible for the interaction between graphene and intercalated metal is common for these two cases and lies in hybridization between p_z-states of graphene and *d*-states of metal. The main differences between CVD graphene and graphene on silicon carbide are 1) the nature of the substrate: nickel is a ferromagnetic metal, and silicon carbide is an insulator, and 2) the presence of a buffer layer of carbon atoms in the case of graphene on silicon carbide. It should be noted that silicide formation was observed during the interaction of the intercalated metal with silicon of the substrate for the case of graphene on silicon carbide.

To date, it has been shown that the intercalation approach makes it possible to successfully obtain graphene-based composite materials. The synthesis and study of the electronic structure and properties of graphene-based magnetic nanosystems is important in light of creation of new hybrid materials with unique properties for various technological applications.

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Интеркаляция графена атомами железа и кобальта: краткий обзор

Е.Ю. Лобанова

[1] Институт перспективных систем передачи данных Университета ИТМО, Кронверкский пр., 49, Санкт-Петербург, 197101, Россия
[2] Отделение физики плазмы, атомной физики и астрофизики, Физико-технический институт им. А.Ф. Иоффе РАН, Политехническая 26, Санкт-Петербург, 194021, Россия

Аннотация. Привлекательность графена, двумерного кристалла из атомов углерода, выстроенных в гексагональную структуру, для различных приложений связана с его выдающимися физическими, механическими и оптическими свойствами. Интеркаляция атомов магнитных металлов под графен – это гибкий инструмент создания новых материалов для электроники и спинтроники. В настоящем обзоре мы рассматриваем работы, посвященные интеркаляции графена атомами железа и кобальта, где в качестве исходной структуры используется графен на металлической (CVD графен) и диэлектрической (графен, полученный на карбиде кремния) подложке.

Ключевые слова: графен; интеркаляция; спинтроника