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FIRST PRINCIPLES STUDY ON Si ATOM DOPED AND ADSORBED MONOVACANCY GRAPHENE SUPERCELLS

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Ab initio calculations of the vacancy formation energy and magnetic moments formed in defective graphene supercells have been carried out. It was found that Si-doped or Si-adsorbed graphene supercells consisting of 32, 50 and 64 carbon atoms with vacancies exhibit ferromagnetic spin ordering. Approximations are given for the density of states (DOS) of Si-doped graphene consisting of 64 atoms with a vacancy. The DOS of supercells and local magnetic moments formed in the vicinity of vacancy carbon atoms are calculated. The calculated energy characteristics and magnetic moments of Si containing defect graphene supercells comply with the literature data.

Keywords: *graphene supercells, Si adsorbed and doped on monovacancy graphene, density of state, Atomistix ToolKit software package, local spin density approximation*

Introduction

Graphene has significant electronic, thermal and mechanical properties that make it attractive for technical applications [1]. Graphene is like a two-dimensional (2D) crystalline material and it has an electronic structure with an almost zero band gap. The physical properties of graphene can be controlled by adsorption, which are the processes of adding impurities to the intrinsic atoms of the graphene lattice. For instance, Si-doped graphene, called siligraphene, exhibits high optical properties and high thermal stability [2,3].

It turned out that the introduction of various defects into the graphene structure increases the stability of the graphene sheet, which is confirmed by calculations of the properties and energy of lattice formation. It is shown that the replacement of single, di, and three carbon atoms on the surface of a 2D graphene sheet with gold strongly affect the electronic properties of graphene. The tendency of a decreduction in the energy of formation of a graphene lattice in the number of defects leads to an increase in the stability of graphene. [4].

However, despite the properties mentioned above, graphene lacks a band gap, which is typical for semiconductor materials. In addition, graphene has a nonmagnetic nature, which limits its practical application [5,6]. These met-

hods include the mutual interaction between graphene layer and its substrate, doping with surface adatoms, substitutional doping, vacancy creation, and edges and strain manipulation.

There are published datason the study of the adsorption of various adatoms on pure graphene, for example, [7,8]. In [9], the electronic properties were determined and vacancies in graphite were studied from first principles calculations. The structure of the ground state of graphite is associated with a formation energy of 7.4 eV and arises as a result of a combination of symmetric relaxation and distortion of degenerate structures associated with symmetry. The formation, behavior, and healing of defects are usually determined by the energy characteristics of atomic-scale structural changes. Review article [10] is devoted to atomic-scale reactions during thermally activated and radiation-induced processes in graphene. The energies of formation of vacancies, adatoms, and topological defects in graphene are discussed. For the energy of formation, in particular, of vacancies, values are given from 7.35 to 8.58 eV.

The silicon-based microelectronics are developed diverse methods for determining the characteristics and behavior control of doping and defects. Taking into account these methods, modern computational methods, for example, density functional theory (DFT) calculations al-

so make it possible to modify the properties of graphene [11-13]. Effective methods of material surface treatment in microelectronics include implantation, millisecond annealing, photostimulation, and surface engineering. However, such methods for processing and controlling defect for micro- and nanoelectronics applications that are not based on other materials, in particular on graphene, have not been developed.

In particular, surface treatment technology can be extended to graphene, opening up new possibilities for doping and defect control. To investigate these effects, we had chosen as doping element and / or adsorbate silicon, controlling the surface of graphene. In other words, doped (or adsorbed) Si was used to control and modification surface state of the graphene. Computational studies of the behavior of vacancies and adsorbed Si in graphene make it possible to determine their effects on surface electronic states. And this, in turn, opens up the possibilities of using the material. The state of the surface, in particular, can significantly affects the behavior of defects and properties, which influences the self-diffusion profiles in the electronic material.

In this research, we present ab initio DFT calculations of the electronic distortions of 2D graphene when creating a carbon vacancy. The results of calculations of the properties of graphene also doped or adsorbed by Si atoms are considered; the results of calculations of the energy of formation are also presented. These investigations are performed by DFT based on the first principle calculations using local spin density approximation (LSDA) method by employing the ATK program package.

Computational methods

The electronic and magnetic properties of Si doped graphene supercells with a monovacancy were studied theoretically. The graphene properties were calculated using the DFT method implemented using the Atomistix ToolKit. In addition, the band structure and density of states were investigated for the graphene supercell model. The energies of formation of various graphene supercells containing 32, 50 and 64

carbon atoms had been calculated. The magnetic properties of Si-adsorbed graphene on the surface were also researched.

First-principles calculations of graphene properties were carried out on the basis of the spin-polarized density functional theory. The local spin density approximation in the Perdew–Burke–Ernzerhof (PBE) parameterization was employed for the exchange–correlation functional. The kinetic cut-off energy was 150 Ry. The primitive cell of Graphene was relaxed and optimized with force and stress tolerances of $0.01\text{eV}/\text{\AA}$ and $0.01\text{eV}/\text{\AA}^3$, respectively. A $2 \times 2 \times 2$ k point was used for geometry optimization and total energy calculations.

Results and discussion

Point defects, that is, atomic vacancies that arise when a carbon atom is removed from a graphene cell, are a simple type of defects. The formation of a vacancy is accompanied by a partial change in the properties of the samples. In particular, the formation of a monovacancy in graphene is justified by the rearrangement of the nearest C-C bonds and the formation of nonagon and pentagons. Double vacancies (created by merging two monovacancies or removing two adjacent carbon atoms) unlike polygons. The vacancy formation energy (the energy required to remove a carbon atom from the cell) is high ($E_f > 7\text{ eV}$, [13]), which leads to the formation of topological defects. Considering the above, we will consider the properties of graphene with the participation of a monovacancy.

Electronic structure and magnetic properties

The total magnetic moments were investigated for Si doped and adsorbed on different graphene supercells with a carbon vacancy (table 1). The values of the magnetic moment was derived from Mulliken population analysis [13] for graphene consisting of 32, 50 and 64 carbon atoms. In addition, values of the magnetic moments was calculated for Si adsorbed graphene consisting of 32, 50 carbon atoms with vacancy.

The different values of magnetic moment doped (or adsorbed) graphene depend on the graphene structure with vacancy. The graphene has a two-dimensional hexagonal crystal lattice with two identical atoms (denoted by the letters A and B) in the unit cell. Then the atomic structure of graphene can be represented as composed of two equivalents triangular sublattices of atoms A and B. The distance between the nearest graphene atoms is 0.14 nm, the lattice constant is $d \approx 0.25$ nm (Fig. 1). Upon doping or adsorption, these structural parameters in graphene with a vacancy change. According formed local magnetic moments near graphene vacancies also change.

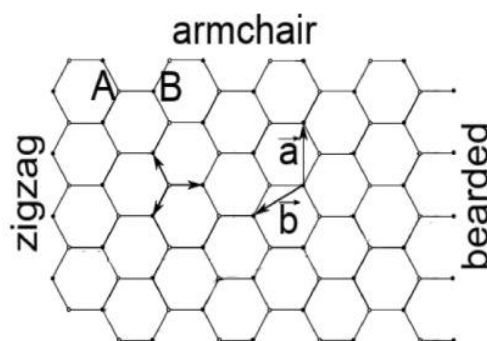


Fig. 1. Straight crystal lattice of graphene

In Fig. 1 a and b denote the translation vectors of the graphene crystal lattice $a = d(1, 0)$, $b = d(1/2, \sqrt{3}/2)$. If we take into account the projective band structure of graphene, it turns out that the size of the 1D Brillouin zone does not coincide with the size of the projection of the “bulk” 2D Brillouin zone onto the boundary. The nearest-neighbor approximation is insufficient for a satisfactory description of edge states (ES) in graphene. Fig. 1 shows two types of edge: 1) a zigzag and 2) an armchair. Thus, the edge states in graphene leads to new physical effects. In particular, within the framework of the tight-binding model taking into account the spin-orbit interaction, the obtained spectrum for a graphene band with a zigzag edge differs from a band with an armchair edge. In other words, the ES in the structure leads to the fact that the spin-polarized ES at the edge of graphene (zigzag or armchair) apart from each other.

Increasing magnetic moment in graphene containing vacancy depends on rise lateral side of the supercell. According to calculation in the vacancy case Si doped 8×4 supercell of graphene acquires the highest value of magnetic moment.

Table 1

The value of magnetic moment for in Si atom doped and adsorbed on graphene supercells with vacancy

Graphene with monovacancy	total magnetic moments	magnetic moments around monovacancy
Si doped 4×4 graphene	$0.932 \mu_B$	$0.343 \mu_B (C_{11}) \vee 0.343 \mu_B (C_{20})$
Si doped 5×5 graphene	$1.011 \mu_B$	$0.489 \mu_B (C_{22}) \vee 0.489 \mu_B (C_{33})$
Si doped 8×4 graphene	$4.171 \mu_B$	$0.497 \mu_B (C_8), 0.515 \mu_B (C_{23}), 0.497 \mu_B (C_{31}), 0.497 \mu_B (C_{47})$
Si adsorbed on 4×4 graphene	$1.998 \mu_B$	$0.818 \mu_B (C_{19}) \vee 0.629 \mu_B (Si_{31})$
Si adsorbed on 5×5 graphene	$-0.997 \mu_B$	$0.807 \mu_B (C_{27})$

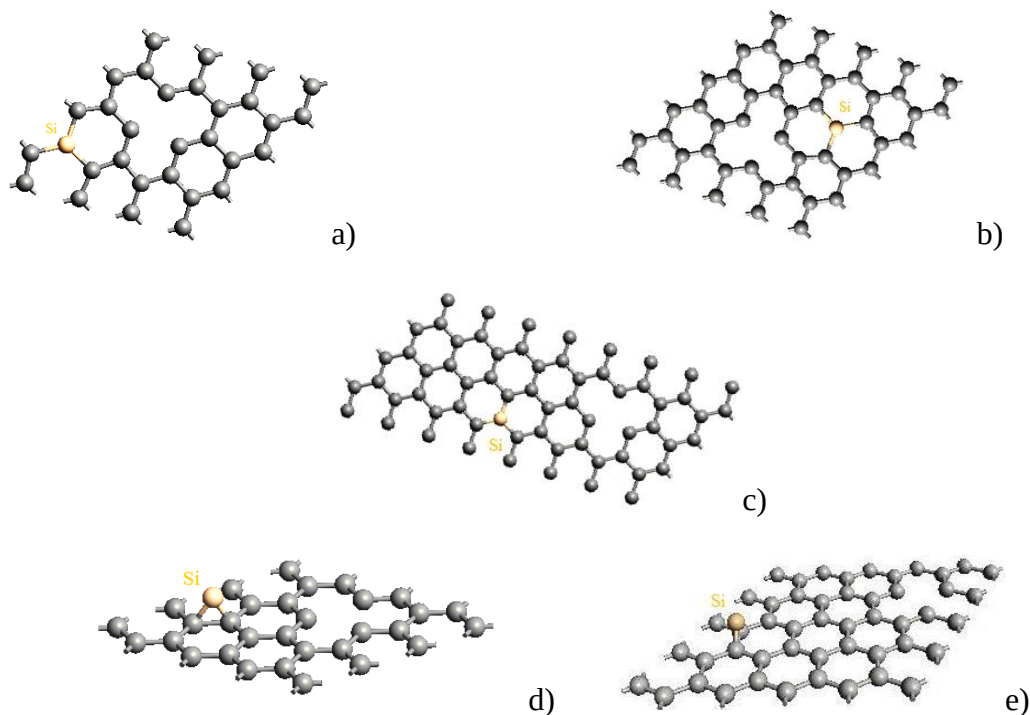


Fig. 2. Atomic structure of Si doped a) 32, b) 50, c) 64 and Si adsorption on d) 32 and e) 50-atoms graphene cell with vacancy

Comparison results of our calculations of M (μB) silicon containing graphene supercells (Table 1) with a monovacancy, and published data [13] showed that the values of the total magnetic moments are in agreement with each other. It was found that Si-doped (or adsorbed) graphene supercells with vacancies exhibit ferromagnetic spin ordering. In Fig. 2 indicates schematic of the atomic structure for Si doping and adsorption graphene structure with a single carbon vacancy. Fig. 3 illustrates the DOS for spin up and spin down s-, p-, d-electrons of the dopant Si in the 64 atoms supercell with vacancy. The results of calculations of the density of states (DOS) of Si-doped graphene with a vacancy and local magnetic moments formed in the vicinity of vacancy carbon atoms agree with the literature data, in particular, with data [13].

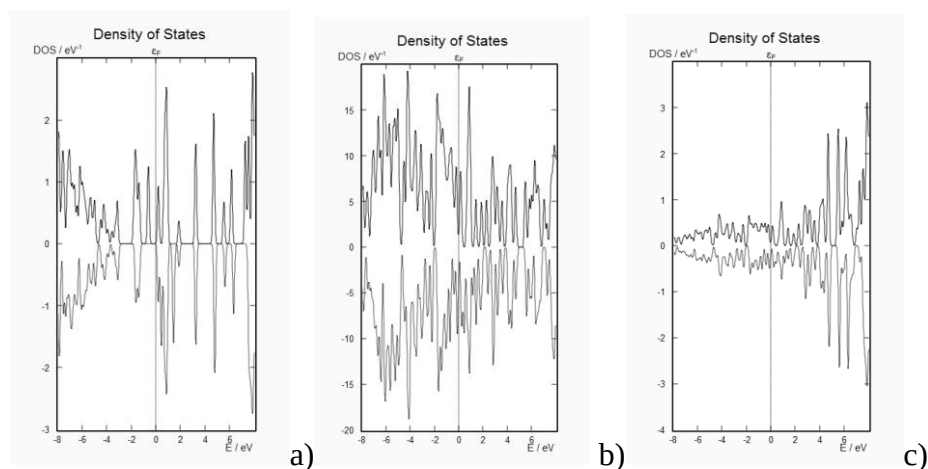


Fig. 3. DOS of Si doped graphene consisting 64 atoms with vacancy

Formation energy

The formation energy for graphene structure containing vacancy is defined as [13]:

$$E_f = E_{gr+vac} - \frac{N-n}{N} E_{gr},$$

whereas for doping structure with vacancy, the formation energy was calculated as:

$$E_f = E_{gr+vac} - \frac{N-n}{N} E_{gr} - \mu(Si),$$

where E_{gr+vac} is the total energy of a graphene with vacancy, E_{gr} is the total energy of pure graphene, $\mu(Si)$ is the chemical potential of silicium, N is total number of atoms in graphene supercell and n is number of vacant carbon atoms.

Table 2

Formation energies for different graphene supercells

Graphene supercells	Formation energy	
	Our work	Literary data
4×4 graphene with monovacancy	8.52eV	7.30eV [13] 7.83eV [14]
5×5 graphene with monovacancy	8.45eV	7.83eV [14]
Si doped 4×4 graphene monovacancy	4.26eV	
Si doped 5×5 graphene monovacancy	4.19eV	

We performed our calculations of the vacancy formation energy for 32- and 50-atom graphene supercells, as well as taking into account the effects of doping and vacancies. The vacancy formation energy for different graphene supercells is given in table 2. Inspection of the results introduced in this table reveals that for Si doped on graphene with vacancy acquires less formation energy than the monovacancy in graphene. In other words, in silicon-doped defect graphene, the vacancy formation energy is almost two times less than in undoped graphene with a vacancy.

According to the obtained results Si-doped and adsorbed graphene supercell consisting of 32, 50 and 64 carbon atoms with vacancies differ from each other.

- The total magnetic moment Si doped graphene with vacancy: 4×4 graphene 0.932 μ_B , 5×5 graphene 1.011 μ_B , 8×4 graphene 4.171 μ_B , Si adsorbed on 4×4 graphene 1.998 μ_B , Si adsorbed on 5×5 graphene -0.997 μ_B .

- accrued magnetic moments are: Si doped 4×4 graphene 0.343 μ_B (C_{11}, C_{20}), Si doped 5×5 graphene 0.489 μ_B (C_{22}, C_{33}), Si doped 8×4

graphene 0.497 μ_B (C_8, C_{31}, C_{47}), 0.515 μ_B (C_{23}), Si adsorbed on 4×4 graphene 0.818 μ_B (C_{19}), 0.629 μ_B (Si_{31}), Si adsorbed on 5×5 graphene 0.807 μ_B (C_{27})

Results

The use of spin-polarized DFT calculations of the properties of 32, 50, and 64 atomic graphene supercells with vacancy demonstrates that the properties change due to edge states in the graphene structure. In particular, the formation energy and magnetic moments for various graphene supercells differ from each other. Vacancy formation energy calculation displays that decreases from 8.45-8.52 eV to 4.19-4.26 eV in both of monovacancy and Si doped 32 and 50 atom monovacancy graphene. First principle calculation of total spin polarization show that Si doped graphene consisting of 32, 50 and 64 carbon atoms with vacancy magnetic moment raises with increasing number of carbon atoms, Si adsorbed graphene magnetic moment decreases. The magnetic moments in graphene supercells created near a vacancy due to Si doping (0.343-0.515 μ_B) and Si adsorption (0.629-

0.818 μ_B) differ from each other. In particular, the magnetic moment for Si doped graphene supercell consisting of 64 atoms with vacancy is acquired 4.171 μ_B .

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TƏMƏL PRİNSİPLƏRDƏN Sİ İLƏ LEQİRLƏNMİŞ VƏ YA ADSORBSİYA OLUNMUŞ VAKANSİYALI QRAFEN SUPERQƏFƏSLƏRİNDƏ ELEKTRON HALI SİXLİYİNİN HESABLANMASI

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Ab initio hesablamalarına əsasən, defektli qrafen superqəfəslərində defekt əmələ gəlmə enerjisi və maqnit momenti araşdırılmışdır. Struktur, maqnit və elektron xassələrinin izahı nəzəri olaraq modelləşdirilmişdir. Vakansiya olunmuş 32, 50 və 64 sayda karbon atomlu qrafen superqəfəslərinin Si atomu ilə aşqarlanma və adsorbsiya hallarının ferro-maqnit spin düzlüyü tapılmışdır. 64 atomdan ibarət olan qrafen superqəfəsi üçün hallar sıxlığının təsviri verilmişdir. Vakansiya olunmuş karbon atomu ətrafında hallar sıxlığı və lokal maqnit momenti hesablanmışdır. Si ilə leqirlənmiş vakansiyalı qrafen superqəfəslərinin hesablanmış enerji xüsusiyyətləri və maqnit momentlərinin qiyməti ədəbiyyat məlumatları ilə uyğun gəlir.

Açar sözlər: qrafen superqəfəslər, təkvakansiyalı qrafendə Si ilə leqirlənmə və adsorbsiya, hallar sıxlığı, ATK proqram paketi, Spin Lokal Sıxlıq Yaxınlaşması

ПЕРВЫЕ ПРИНЦИПЫ ИССЛЕДОВАНИЯ МОНОВАКАНСИИ ГРАФЕНА, ДОПИРОВАННЫХ ИЛИ АДСОРБИРОВАННЫХ Si АТОМОВ

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Проведены *ab initio* расчеты энергии образования вакансий и магнитных моментов, образующихся в дефектных сверхъячейках графена. Было обнаружено, что легированные или адсорбированные кремнием графеновые суперячейки, состоящие из 32, 50 и 64 атомов углерода с вакансиями, обладают ферромагнитным спиновым упорядочением. Даны приближения для плотности состояний (DOS) легированного Si графена, состоящего из 64 атомов с вакансией. Рассчитаны плотность состояний сверхъячейки и локальные магнитные моменты, формирующиеся в окрестности вакансионных атомов углерода. Рассчитанные энергетические характеристики и магнитные моменты Si-содержащих дефектных графеновых суперячеек согласуются с литературными данными.

Ключевые слова: графеновые суперячейки, адсорбированный и легированный Si на моновакансионном графене, плотность состояний, Atomistix ToolKit пакет программного обеспечения, приближение локальной спиновой плотности