FIRST PRINCIPLES STUDY Ge -DOPED MONOLAYER GRAPHENE

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The electronic and structural properties of vacancy in graphene and doping of graphene with Ge calculated by the density functional theory (DFT) method within the Generalized Gradient Approximation (GGA). To simulate the vacancy effects have been studied 54 and 18 atom supercells to account for possible program software. Ferromagnetic spin ordering of vacancy of carbon atoms have been studied. It was shown that ferromagnetic ordering of the carbon atoms vacancies are located near the doping Ge atom. In addition DOS for 18 graphene atoms doped by Ge for s,p,d state have been calculated.

Keywords: *ab initio* calculation, DFT, ATK, graphene, Ge-doped, supercell, DOS, magnetic moment.
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INTRODUCTION

Graphene is obvioused to have important properties, in occasion of electronic conductivity, thermal stability, structural flexibility, and surface area that make it wellsuited as a building block in 3D architectures. The [1] result gives that the graphene sheets can improve the electrochemical performances of nanostructured transition metal oxides as anode materials for lithium-ion batteries. Graphene satisfies as conductive channels; graphene nanosheets facilitate charge transfer during the cycling process by forming an electrically conductive network with nanoparticles [2]. Graphene demonstrates high electronic performance [3–5] optical properties [6] thermal performance [7], larger specific surface area [8, 9] excellent elastic modules [10]. Graphene has an unusual band structure which is practically important for electronic devices. In [11] work all cases, along with lithium adsorption, the bandgap energy is increased, so that the germanium doped compound has the highest bandgap and the structure with no doped atom has the least bandgap. In [12] work have given for this material semiconducting properties and to rate its altering energy gap. Equivalent to other 2D structures, like germanene [13], silicene [14], and phosphorene [15], it is expected that graphene may be useful for the development of leading-edge technologies.

The experimental synthesis of germanium–graphene nanocomposite material [16], which can represent for lithium-ion battery applications [17], and the simulation of low energy ion implantation of germanium into a graphene target, which may be useful for single-atom catalysis [18]. Theoretical studies using ab initio calculations constitute a important and convenient method to obtain valuable information about nanomaterials [19-22]. Al-doped graphene was theoretically found to significantly increase the adsorbing energy of CO molecule, where CO binds to the top site of Al [23].

There are two types of graphene doping: electrical and chemical [24]. Have been investigated [25] the chemical doping of graphene, where doping occurs via chemical routes, namely substitutional doping with heteroatoms. In the present contribution, it is investigated the effects of the germanium doping on the properties of graphene 54 and 18 atom supercells using first principles calculations.

MODEL AND CALCULATION METHOD

The calculations have been performed using the periodic using Atomistix Tool Kit (ATK) [26] implementing the spin-polarized DFT, PAW (projector-augmented wave method) and the PBE (Perdew–Burke–Ernzerhof exchange-correlation functional) [27].

Our calculations were performed for the primitive cell of Graphene and for a number of supercells with as many atoms as 54 by implementing the density functional theory (DFT) method within the Generalized Gradient Approximation (GGA) [28] and using the Atomistix Tool Kit program software. The Perdew-Burke-Erenzhorf (PBE) exchange-correlation functional (PBE) and Double Zeta Polarized basis sets were used in our calculations. 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 eV/Å and 0.01 eV/Å^3, respectively.

Ge DOPED AND VACANCIES IN GRAPHENE

To simulate the doping and vacancy effects we have studied bulk compound and its 54 atom graphene supercell. The following shares in the total magnetic moment are derived from Mulliken population analysis in the case of atom vacancy: 1.232 μ (μB), where μB is the Bohr magneton.

Fig. 1 shows the atomic structure of the vacancy in the 54 atoms graphene supercells and displays the density of states (DOS). The presence of carbon vacancies leads to acquired magnetic moment. 26th carbon atom acquires magnetic moment in the prefferred direction μ(C)= (0.32 μB). We estableshad that acquired magnetic moments are: 3rd carbon atom (0.32 μB), 21th (0.32 μB), 26th (0.327 μB), 9th (0.101 μB), 15th (0.101 μB) in the prefferred direction, actually μ(C)= 8th (-0.035 μB), 31(-0.036 μB), 49nd (-0.036 μB), and 14th carbon atom (-0.033 μB) on the opposite direction.

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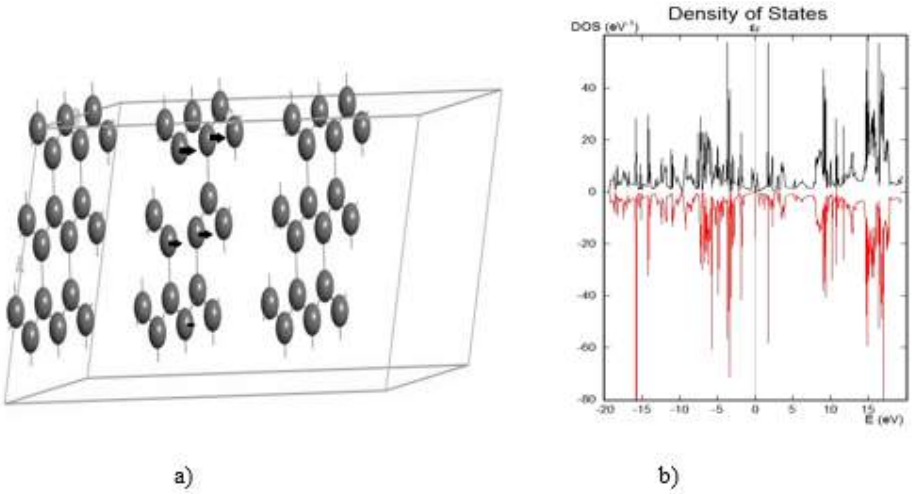

Fig. 1. The structure of defects in (a) supercell 54 atoms graphene with carbon vacancy and (b) DOS.

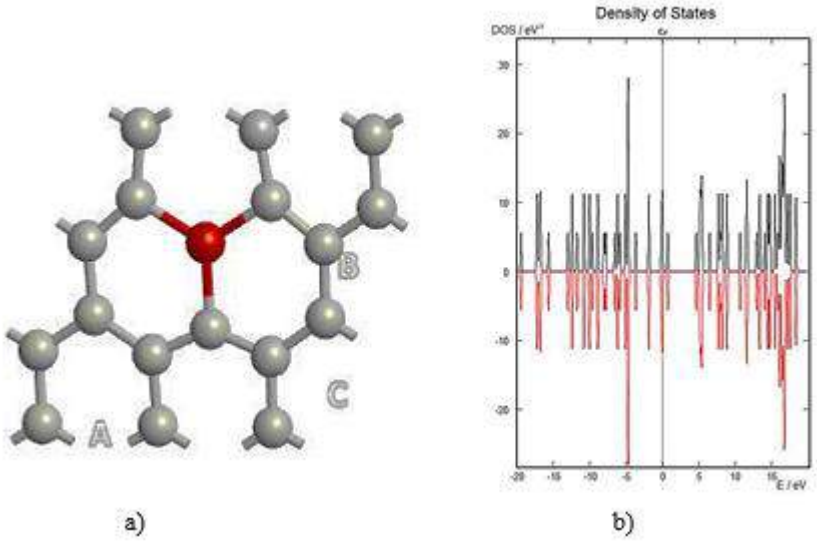

Fig. 2. (a) Atomic structure of 18 atom doped by Ge graphene and (b) density of state (DOS).

Fig. 2 displays the atomic structure of the Ge doped graphene plane and density of state (DOS).

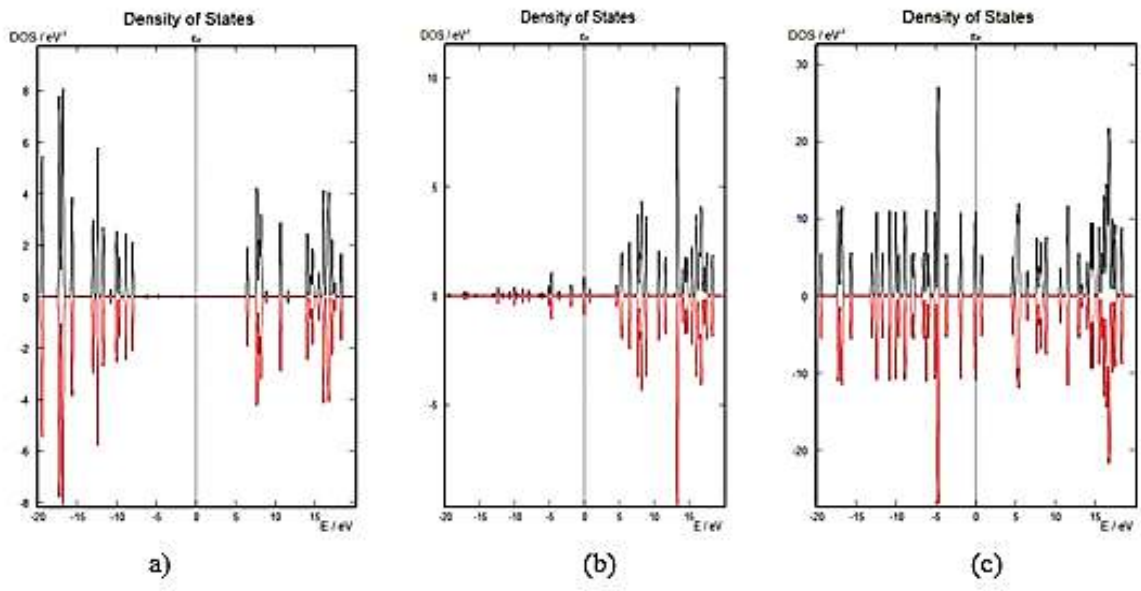

Fig. 3. The DOS for spin up and spin down d-, s-, and s p-electrons of the dopant Ge atom in the 18 atoms supercell:
a) d- state, b) s-state, c) s p –state.

Fig. 3 shows the DOS for d-, s-, and –s p electrons of dopant Ge atom in the graphene supercells. The upper curve corresponds to electrons with the direction of the spin up, and the lower with the direction of spin down.

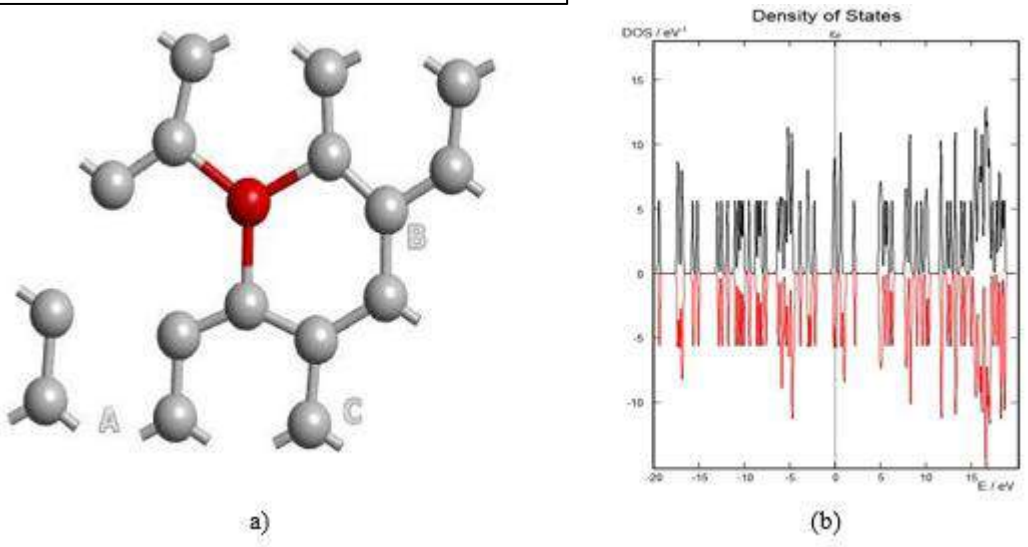

Fig. 4. (a) Atomic structure of the vacancy (Ge doped) and C vacancy in the graphene plane and (b) density of state (DOS).

Fig.4 displays the atomic structure of the Ge doped (a) graphene plane with C vacancy and (b) density of state (DOS).

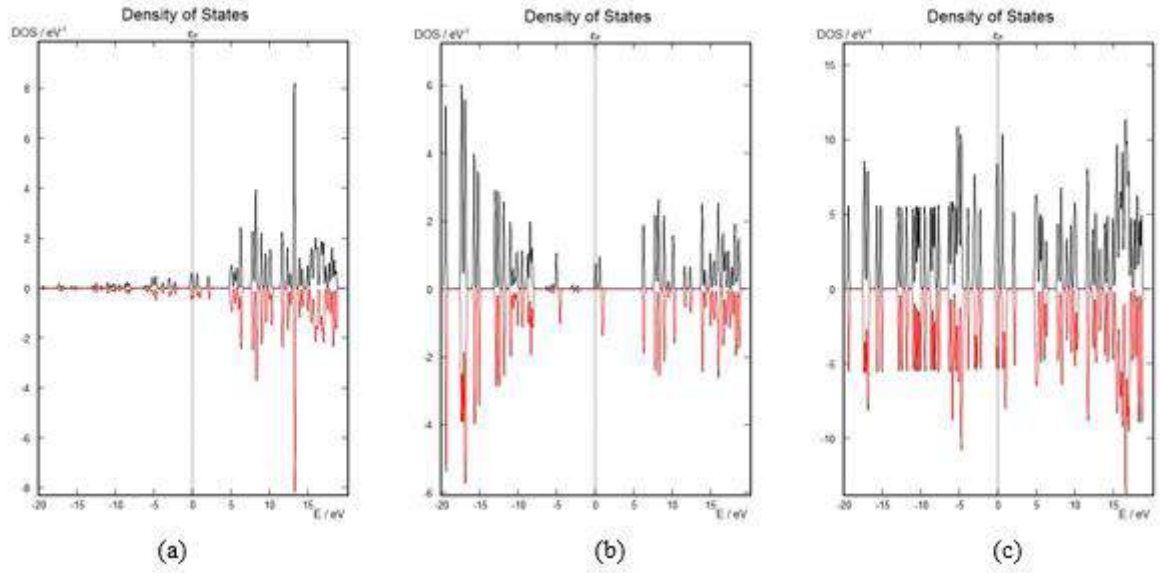

Fig. 5. The DOS for spin up and spin down d-, s-, and s p-electrons of the dopant Ge atom and C vacancy in the 18 atoms supercell : a) d-state ,b) s-state, c) s p –state

Fig. 5 shows the DOS for d-, s-, and –s p electrons of dopant Ge atom and C vacancy in the graphene. Observed for the spin-down and spin up d-states below the Fermi level.

Si was the least effective element at opening the band gap, Ge (r = 1.23 Å) is a little more effective than Si (r = 1.18 Å), probably due to its larger size, which can induce more distortion than Si in the sp^2 C (r = 0.77 Å) framework [29].

The total magnetic moment in the supercell Ge doped graphene and C vacancy: 0.998 μ (μB). In case of Ge substitution C and in presence of C-vacancy which positioned near the dopant Ge atom creates magnetic moment 0.031 μB. Near the vacancy 0.48 μ (μB) and the Ge additives 0.031 μ (μB), carbon atoms gained more magnetic moment.

CONCLUSIONS

The structural, electronic, and magnetic properties of Ge-doped graphene was studied using DFT calculations. Band structure and density of states Ge-doped, vacancy case of monolayer graphene are shown. To simulate the doping effect, we have performed our calculations for 54 atom graphene and Ge doped 18 atom-contained supercells. It has been established that doping the monolayer of graphene leads to a significant altering its electronic properties.

Mulliken population analysis shows that the presence Ge- doped and carbon vacancy state graphene supercell acquire μ (C) =(0.998 μB) magnetic moment.

The presence vacancy graphene supercell acquired magnetic moment of the carbon near the vacancy is noticeably larger μ(C) =(0.998 μB) than that of the other without vacancy state μ(C) = (0.001 μB). In the presence of Ge-doped and no vacancies in supercell, Eg =0.505eV, while Ge-doped and vacancies Eg =0.21eV.

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