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Electronic and magnetic properties of modified silicene/graphene hybrid: Ab initio study

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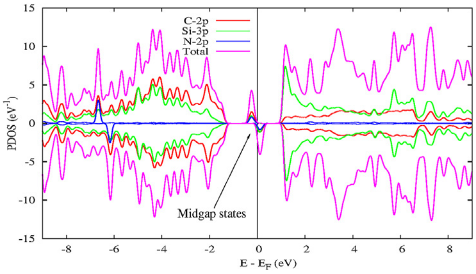
HIGHLIGHTS

- Electronic and magnetic properties of two dimensional graphene/silicene hybrid have been explored.
- There is no magnetism in the system for a single carbon atom vacancy.
- A net magnetic moment of 4.0 Bohr magneton is observed for a single silicon atom vacancy.
- Unpaired electrons introduce mid-gap states which is otherwise absent in the pure system.

GRAPHICAL ABSTRACT



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ABSTRACT

Among other two-dimensional (2D) novel materials, graphene and silicene both have drawn intense research interest among the researchers because they possess some unique intriguing properties which can change the scenario of the current electronic industry. In this work we have studied the electronic and the magnetic properties of a new kind of materials which is the hybrid of these two materials. Density functional theory (DFT) has been employed to calculate the relevant electronic and magnetic properties of this hybrid material. The pristine structure is modified by substitutional doping or by creating vacancy (Y-X, where one Y atom (Si or C) has been replaced by one X atom (B, N, Al, P or void)). The calculations have revealed that void systems are unstable while Si-B and Si-N are most stable ones. It has been noticed that some of these doped structures are magnetic in nature having induced mid-gap states in the system. In particular, Si-void structure is unstable yet it possess the highest magnetic moment of the order of 4 μ_B (μ_B being the Bohr magneton). The estimated band gaps of modified silicene/graphene hybrid from spin polarized partial density of states (PDOS) vary between 1.43–2.38 eV and 1.58–2.50 eV for spin-up and spin-down channel respectively. The implication of midgap states has been critically analysed in the light of magnetic nature. This study may be useful to build hybrid spintronic devices with controllable gap for spin up and spin down states.

1. Introduction

Two dimensional (2D) materials possess thickness of several atomic layers and are extended periodically in the other two dimensions. After the experimental discovery of graphene by Novoselov et al. [1,2], it has received considerable attention from the scientific community. Graphene has led to many new research ideas. It possesses some unique properties which has been found to have great potential for use in future nanoelectronic devices [1–6]. But the main drawback of graphene is that the band gap of

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graphene is zero. For this reason graphene is not suitable for nanoelectronic devices. So it is always desirable to have a finite band-gap. There are several ways of opening up of band-gap in graphene: (a) by B-N doping [7–10], (b) by applying strain [11], (c) by chemical functionalization [12]. Opening up of band-gap in graphene has been seen to be quite uncontrollable. This makes it incompatible for making practical devices. In this situation, researchers have focussed towards silicon (Si), the next element in the same group of C. This new 2D material having honeycomb structure is known as silicene [13]. Experimentally, silicene has been synthesized by Vogt et al. [14]. Silicene nanoribbons grown on a silver (110) substrate have been studied experimentally by Padova et al. [15]. We have studied the magnetic properties of planar silicene by using DFT [16,17] and reported that di-vacancy induced silicene exhibits large magnetic moment (~0.5 μ_B per pair of vacancies). However, it remains non-magnetic in the case of mono-vacancy. From first principles calculations, optical properties of Al and P doped buckled silicene have also been studied by us [16,18]. In that work, the signature of buckling has been noted in the optical spectra for perpendicular polarization. The magnetic and anisotropic optical properties of four differently shaped silicene nanodisks have also been explored by us. Zigzag-trigonal nanodisk has been found to possess maximum magnetic moment among all the other nanodisks. The origin of the non-zero magnetic moment has been argued in the light of zero energy states and edge atoms [16,19]. The advantage of this new 2D material is that it can easily be interfaced with the modern Si based industry. Keeping in mind the exoticness of these 2D materials, several approaches have been proposed to design novel nanostructures suitable for device applications. One of them is to combine Si and C atoms to make various nano-structures. As a bi-product of this combination Si-C nanotubes [20,21] and Si-C nanowires [22] have been proposed which have been proven to be a promising candidate for hydrogen storage. Theoretically, proposed Si-C zigzag nanoribbons have been found to be half-metal without any application of external electric field [23,24]. Experimentally Si-C nanorods have been synthesized through a reaction between carbon nanotubes and SiO [25]. Ciraci et al. [26] also have thoroughly explored 22 different honeycomb structures of group-IV elements and III-V binary compounds. In that work they have also explored the stability of Si-C nanosheet by employing DFT calculation. Drissi et al. [27] have examined the hydrogenation effect of this silicene/graphene hybrid system by using DFT. They have pointed out that full hydrogenation increases the band-gap (~1.0 eV). However, half chemical modification with hydrogen reduces the gap. Drissi et al. [28] have also calculated the electronic and optical properties of silicene/graphene hybrid by incorporating the many-body effect. From their phonon mode analysis, it has been found that the structure is stable.

The phenomena of ferromagnetic ordering observed at reasonably high temperatures in some compounds containing no atoms with open *d* or *f* shells is known as d^0 ferromagnetism [29,30] e.g. in HfO_2 [31], *ZnO* [32–34] with vacancies and so on. It should be worthy to mention here that d^0 ferromagnetism in ZnO has been explained via oxygen vacancy, defect complex on Zn, vacancy and H [33] and Zn interstitial defect states [34] and in ZnS by V_{Zn} along with S dangling bonds on the nanoparticle surface [30]. In most of the situations, ferromagnetism does not appear in the bulk when they are defect free and pure. Thus, lattice defect seems to be a genuine necessary factor for the occurrence of d^0 ferromagnetism. They may be point defects, atomic vacancies or interstitials – induced by irradiation or thermal treatments (annealing) or by lattice mismatch. Surface, grain boundaries and dislocations also can participate to generate this d^0 ferromagnetism. In other words, the defect states can give rise to an appreciable magnetic moment in connection with the molecular orbitals localized very close to the defect site [30]. The utility of d^0 ferromagnetism lies in the fact that large magnetization like Fe, Co, Ni can be achieved in a nanomaterial having an active defect. Thus, one can visualize magnetism in a non-magnetic pristine semiconducting matrices with some appropriate impurities/voids of non-magnetic sp atoms. Hence, d^0 magnetism can take an important key role in designing novel materials in spintronics at room temperature. The nanoparticle surface area in 2D systems seems to be an integral part in triggering this d^0 ferromagnetism in contrast to bulk one. Recently Ju et al. [35] have studied the d^0 ferromagnetism in hydrogenated silicene sheet by employing DFT. Here, it is to be noted that, in some alkaline-earth metal nitrides XN (X = Ca, Sr, Ba), half-metallic d^0 ferromagnetism has been predicted without any defects [36,37].

Motivated by the prospect of d^0 ferromagnetism in 2D nanomaterial and the important characteristic features of silicene/graphene hybrid, here, we have explored the electronic and magnetic properties of modified silicene/graphene hybrid where the modification has been done through doping and vacancy. This study will enable one to choose the appropriate hybrid materials having suitable band gaps and significant magnetic moments for device application.

2. Computational details

The whole calculations have been performed within the framework of DFT [38–40], using the generalized gradient approximation (GGA) according to Perdew, Burke, Ernzerhof (PBE) [41] parameterization implemented in SIESTA (Spanish Initiative for Electronic Simulations with Thousands of Atoms) [42,43] code. Well tested Troullier Martin [44], norm conserving pseudopotentials in fully separable Kleinman and Bylander form have been employed for all the elements. The double ζ plus polarized basis set is used throughout the whole range of systems. A 300 Ry mesh cutoff has been used for the reciprocal space expansion of the total charge density. Brillouin zone (BZ) has been sampled by using $10\times10\times1$ mesh of k points within Monkhorst-Pack (MP) [45] scheme. But for partial density of states (PDOS) calculation, $80\times80\times1$ mesh of k points have been used. All the structures are optimized by minimizing the forces on individual atoms below 0.02 eV/Å using the standard conjugate-gradients (CG) technique. The convergence criteria for energy of the self-consistent field (SCF) cycle is chosen to be 10^{-5} eV. Interlayer gap separation along the *z* direction between two successive silicene/graphene hybrid layers has been set at 20 Å to avoid artificial interaction among the layers.

3. Results and discussions

Both graphene and silicene have two atoms in its unit cell. In this hybrid structure, among the two atoms, one is C and the other is Si. 4×4 supercell (32 atoms) have been considered for study. Two types of modification have been done in the 4×4 supercell: (a) substitutional doping where either C or Si atoms have been replaced by other atoms, (b) void or vacancy where C or Si atoms have been removed from the system. We have also sub-divided the doping and the void case as (i) carbon replacement, where one of the C atoms has been replaced by other atom for doping or removed to create vacancy, (ii) silicon replacement, where one of the Si atoms has been replaced by other atom for doping or removed to create vacancy. As dopant atoms we have used, boron (B), nitrogen (N), aluminium (Al) and phosphorus (P) which are neighbors of C and Si in the periodic table because of their close atomic radii [46–48]. If a C atom is replaced by B, N, Al or P, we shall call the structure C-X (where X = B, N, Al or P). Similarly, when a Si atom is replaced by B, N, Al or P, we shall call the structure Si-X (where X = B, N, Al or P). On the other hand, if a C or a Si atom is completely