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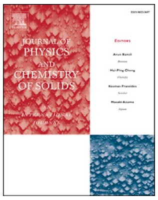

Magnetic and optical properties of carbon and silicon decorated free standing buckled germanene: A DFT approach

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ABSTRACT

Ab initio magnetic and optical properties of group IV elements (carbon (C) and silicon (Si)) decorated free standing (FS) buckled germanene systems have been employed theoretically. Our study elucidates that, decoration of these elements in proper sites with suitable concentrations form dynamically stable configurations. Band structure is modified due to decoration of these atoms in Ge-nanosheet and pristine semi-metallic germanene undergoes to semiconductors with a finite amount of bandgap. Interestingly, this bandgap value meets closely the requirement of gap for field effect transistor (FET) applications. Moreover, significant magnetic moment is induced in non-magnetic germanene for C decorated structure and ground state in anti-ferromagnetic in nature for this structure. Along with magnetic property, optical properties like dielectric functions, optical absorption, electron energy loss spectra (EELS), refractive index and reflectivity of these systems have also been investigated. Maximum number of plasma frequencies appear for Si decorated configuration considering both parallel and perpendicular polarizations. In addition, birefringence characteristics of these configurations have also been studied as it is an important parameter in various applications of optical devices, liquid crystal displays, light modulators etc.

1. Introduction

Since the very invention of graphene and its fruitful applications in designing novel nano-electronics devices [1,2], theoretical and experimental scientists have devoted their research works to realize this two-dimensional (2D) family in more advanced and extensive form. As a consequence of intense research interests, many new graphene beyond 2D materials like silicene, germanene, phosphorene, stanene etc. have got their recognition to enrich the 2D spectrum [3–6]. Their entry obviously opened a new door in various fields starting from basic sciences to vast technical applications [7,8] during last few years. Germanene is germanium (Ge) version of graphene, in which carbon (C) atoms of graphene are replaced by Ge atoms keeping the same hexagonal crystal symmetry respected by graphene [9,10]. But, in opposition to graphene, spin-orbit coupling (SOC) is quite large for stable germanene (~46.3 meV) and mixed sp^2-sp^3 hybridization is favourable rather than only sp^2 hybridization of graphene [11,12]. As a result, germanene possesses a buckled configuration rather than a planar one in its optimized conformation [13]. Nijamudheen et al. have also confirmed that, buckling plays a crucial role in structural stability of germanene and its hydrogenated form (germanane) via ab initio calculations [14]. Some previous investigations have demonstrated the fact that, although Fermi velocity of germanene is two thirds that of graphene [15] but, intrinsic carrier mobility (ICM) of germanene is almost two times higher than graphene [16]. This higher value of ICM makes this material more realistic in potential device applications. Rather, Mortazavi et al. have currently provided an interesting evidence for effective applications of germanene in Na or Li ion batteries [17]. They have estimated high charge capacities of around 369 mAh/g for Li or Na ions storage using single layer germanene. So, in present situation, germanene and its heterostructures [18,19] have attracted research interests in application of nano-devices. Hexagonal germanene was first synthesized by Davila et al., in 2014 using gold (Au) (111) substrate successfully [20,21]. They have identified germanene layer on Au substrate by critical core-level spectroscopy measurements along with advanced density functional theory (DFT) calculations. Through another recent experimental as well as first principles based calculations, Zhuang et al. have provided a clear evidence about formation of buckled germanane rather than bulk germanium on Au (111) substrate [22]. They have established by Raman spectra analysis that, there exists several distinct phonon modes in honeycomb germanene supporting their results. Being exactly hexagonal, just like graphene germanene possesses Dirac cone properties in its free

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standing (FS) form [23]. But, the difference with graphene is that, a finite bandgap ~24.3 meV at Dirac K point can be opened if SOC of germanene has been taken into consideration [24]. Otherwise, buckled germanene is also a zero bandgap semi metal like graphene without SOC. Bandgap tuning is essential in order to application of a material in semiconductor nano-industry. Most popular and easiest ways of achieving finite bandgap are, by adding some foreign impurities or creating some vacancies or making some surface functionalization (like strain engineering, hydrogenation, fluorination etc.) in pristine system. Defects can appear practically during fabrication procedure of these 2D materials experimentally [25,26]. So, theoretical investigations on defected germanene systems might have a close resemblance with future experimental works with this material. Jamdagni et al. have performed first principles based calculations of electronic properties of some vacancy induced fluorine (F), hydrogen (H) or oxygen (O) functionalized germanene systems [27]. They have reported that, it is possible to open a bandgap maximum ~230 meV for these configurations. Besides, germanene can also act as good gas sensors for N_2, NH_3, NO_2, NO and O_2, because it can absorb these gases strongly [28–30]. Dhar et al. have investigated about modifications of electronic, optical and magnetic properties of germanene by incorporation of arsenic (As) and gallium (Ga) as adatoms [31,32]. They have concluded that, semi-metallic germanene have been transformed to semiconductor or metallic nature by suitable site and concentration dependent doping of these elements. Moreover, Ali et al. have shown by modern DFT calculations that, sizeable bandgaps of 0.37, 0.47 and 0.51 eV are opened in vacancy induced germanene systems with vacancy concentrations 1%, 2% and 3.2% respectively [33]. Along with bandgap tailoring, it also possible to induce magnetism in non-magnetic germanene by adopting proper mechanisms. Finite magnetic moment (μ) in defected germanene layer can play an important key role for application of this material in spintronics. Liang et al. have predicted how surface functionalization and strain have tailored the magnetic property of germanene via DFT calculations [34]. They have demonstrated that, hydrogenated, fluorinated, and chlorinated germanene acquire magnetic moments ~0.33 μ_B, 0.28 μ_B and 0.28 μ_B respectively, where, μ_B is Bohr magneton. It has also been reported by Pang et al. that, a significant magnetic moment ~4.46 μ_B can be induced in transition metal (TM) chromium (Cr) adsorbed germanene [35]. Dhar et al. in a very recent investigation, have established that, beryllium (Be) doping in Genanosheet with 18.75% doping concentration can induce magnetic moment ~ 0.39 μ_B, whereas, introduction of vacancy in bare germanene does not however induce any magnetism in germanene layer [36]. Ozcelik et al. have estimated that, Ge adatom adsorbed germanene system forms a stable dumbbel configuration with magnetic moment ~2 μ_B per supercell [37]. In addition to these, now-a-days, scientists have also paid their attention to add some special decoration of foreign elements in pristine 2D layers in order to achieve better modifications of electronic, optical or magnetic properties [38]. Rojas et al. have analyzed about H_2 adsorption capability by potassium (K) decorated germanene layer [39]. They have found that, K decorated germanene possesses enough energy to adsorb the H_2 within the range of Van der Waals interaction.

Motivated from these previous works, we have estimated different electronic, magnetic and optical properties of carbon (C) and silicon (Si) decorated germanene configurations. C and Si are chosen in order to observe the effect of group IV elements decoration in germanene, which have less atomic number than Ge. Decoration of C and Si are introduced in germanene in equivalent and non-equivalent sites with specific 9.38% and 18.75% concentration of C or Si respectively. Effects of co-decoration of C and Si in Ge-nanosheet have also been incorporated in this present investigation. Several interesting and crucial results are observed, which are discussed in following sections. Significant amount of magnetic moment and bandgap are achieved in case of C decorated germanene. We expect, this study may help to design germanene based advanced novel semiconductor devices in near future.

2. Numerical methodology

Necessary numerical computations of this present work have been executed in DFT framework by using double-zeta plus polarization (DZP) basis set, with the spin polarized generalized gradient approximation (GGA) of Perdew, Burke and Ernzerhof (PBE) functional [40] as accomplished in SIESTA software package [41–43]. A 4 × 4 × 1 supercell of germanene nanosheet containing 32 Ge atoms in X—Y plane has been invoked The vacuum space in Z direction (distance between adjacent impurity cells in periodic structure) is about 20 Å to ignore spurious interactions between the neighbouring slabs. Brillouin zone (BZ) is sampled in k space with the equivalent of a 24 × 24 × 1 Monkhorst-Pack (MP) [44] of k point grid. Convergence precision for total energy of the self-consistent field (SCF) cycle is taken as 10^{-5} eV. The atoms were allowed to relax until the residual forces were smaller than 0.08 eV/Å. The mesh cutoff is set to 300 Ry. The formation energy ($E_{d,\ f}$) of a decorated germanene system per defect has been defined by the relation,

$$E_{d,f} = \frac{1}{(n_C + n_{Si})}[\{E_d + (n_C + n_{Si})E_{Ge}\} - \{E_{Pr} + n_C E_C + n_{Si} E_{Si}\}] \tag{1}$$

where, E_d, E_{Ge}, E_{Pr}, E_C, E_{Si} are total energy of decorated system, single germanene atom, pristine germanene supercell (32 atoms), single C atom, single Si atom respectively. n_C and n_{Si} are the number of C and Si impurity atoms in the system respectively. To estimate different optical properties accurately, number of empty bands is set to 400, which is quite large to give reliable consistent results as a consequence of inclusion of high frequency effects in interband transitions. However, excitonic effects are not taken into considerations. Complex dielectric function $\varepsilon(\omega)$ is defined as, $\varepsilon(\omega) = \varepsilon_1(\omega) + \varepsilon_2(\omega)$, $\varepsilon_1(\omega)$and $\varepsilon_2(\omega)$ are real and imaginary parts of $\varepsilon(\omega)$ respectively and ω frequency of electro-magnetic (EM) wave in energy unit. Applying first order time dependent perturbation theory in the dipole approximation $\varepsilon_2(\omega)$ is calculated as [45–47],

$$\varepsilon_2(q\to 0_{\vec{u}}, \hbar\omega) = \frac{2e^2\pi}{\Omega\varepsilon_0}\sum_{k,v,c}\left|\langle\psi_k^c|\vec{u}\cdot\vec{r}|\psi_k^v\rangle\right|^2\delta(E_k^c - E_k^v - E) \tag{2}$$

in long wavelength limit (k→0). Here, Ω is volume of unit cell, ε_0 is permittivity in vacuum. u and r represent polarization and position vectors of electric field of electromagnetic (EM) wave respectively. ω is the photon frequency, ψ_k^c, ψ_k^v are the wave function of the conduction band (CB) and the valence band (VB) respectively $\varepsilon_1(\omega)$ depends on $\varepsilon_2(\omega)$and they are connected via Kramers-Kronig (KK) relation. Both type of polarizations (parallel or perpendicular) of EM field are taken into account for optical calculations. For parallel polarization, electric field is applied along X axis and for perpendicular polarization the same is applied along Z axis. The value of optical broadening used in the computations for all optical calculations is set at 0.2 eV. The complex refractive index ($\tilde{N}$) of a material is related to $\varepsilon(\omega)$ by the equation $\tilde{N} = \sqrt{\varepsilon(\omega)}$ where, $\tilde{N} = n(\omega) + ik(\omega)$. n and k are the real and imaginary part of refractive index. They are correlated to ε_1 and ε_2 as,

$$n(\omega) = \left(\frac{\sqrt{\varepsilon_1^2 + \varepsilon_2^2} + \varepsilon_1}{2}\right)^{\frac{1}{2}} \tag{3}$$

$$k(\omega) = \left(\frac{\sqrt{\varepsilon_1^2 + \varepsilon_2^2} + \varepsilon_1}{2}\right)^{\frac{1}{2}} \tag{4}$$

Now, by knowing expression of (4) absorption coefficient (α(ω)) at normal incidence is defined as,

$$\alpha(\omega) = \frac{2k\omega}{c\hbar} \tag{5}$$

where, c is the speed of light in vacuum and w is in energy unit. The

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