Modifications of optical properties in doped germanene nanosheet

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Abstract: Optical properties, like complex dielectric constant, absorption coefficient, refractive index and reflectivity have been analysed via density functional theory (DFT) of As and Ga doped free standing (FS) germanium (Ge) nanosheet. Position dependent (same or different sub-lattice positions) doping mechanism of foreign elements along with concentration variation up to 6.25%, in pristine germanene layer has been adopted for the whole work. Interesting modifications in optical anisotropy than pristine layer have been observed as a consequence of doping. Such modifications, like enhancement or reduction of peak intensity or shifting of peak positions may be useful to design smart germanene based opto-electronics devices in upcoming future.

Keywords: germanene; density functional theory; optical properties.


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1 Introduction

Two-dimensional (2D) materials are defined by the single layered substances with few nanometer or less thickness, in which electrons are free to move in 2D plane but their motion is however restricted in third direction. Graphene, a single layer of graphite, has attracted a lot of research attention in recent years due to its unique band structure, high electronic mobility and ultra-thin dimensionality (Mas-Balleste et al., 2011). The fascinating opto-electronic properties of graphene have prompted scientists to investigate more about 2D materials beyond graphene (Balendhran et al., 2015; Chowdhury and Jana, 2016). Germanene, germanium (Ge) analogue of graphene, a new member in this 2D family, is a very appealing novel material in modern nano-science (Acun et al., 2015). Like any other 2D materials germanene also shares some physical properties of graphene. But, in contrast, stable mono-layer germanene possesses a buckled configuration, as a consequence of mixed sp2-sp3 hybridisation (Roome and Carey, 2014). Experimentally, hexagonal germanene has been synthesised successfully in year 2014 using gold (111) and Pt. (111) as substrate (Davila et al., 2014; Li et al., 2014). For practical applications of a 2D material, basic requirement is to gather information about interaction mechanism between substrate and its free standing (FS) form. So, it is necessary to investigate about FS germanene, despite the fact that, yet it is not possible to synthesise germanene in FS form experimentally. Optical properties of germanene in terms of real and imaginary parts of 2D optical conductivity have been theoretically studied using density functional theory (DFT) (Matthes et al., 2014). It has been concluded that optical anisotropy is mainly due to interband transitions for these ultra-thin 2D materials. The imaginary part of dielectric function of germanene has also been analysed theoretically (Ozcelik et al., 2015). It has been reported that, main peaks in absorption spectra have appeared due to interband transitions and strong absorption phenomenon takes place below 0.3 eV for bare germanene. More interestingly, first principles study has also indicated the fact that intrinsic carrier mobility in germanene is higher than graphene or silicene, which is very useful in device applications (Ye et al., 2014). Graphyne is another 2D carbon allotrope in which acetylenic bonds are present in the unit cell, rather than double bond in graphene (Bhattacharya et al., 2016; Bhattacharya and Sarkar, 2016a). Electronic and optical properties of such 2D materials can be modified by different mechanisms like doping or adsorption (Bhattacharya and Sarkar, 2016b; Sarkar et al., 2015) of foreign materials, applying electric field, introducing vacancies etc., which are necessary for device applications (Chowdhury et al., 2017; Cahangirov et al., 2017). It has been observed from a theoretical calculation that, semi-metallic germanene has been transformed to n type semiconductor by adsorption of transition metal atoms (Kaloni, 2014). It is also possible to open a significant amount of bandgap (maximum ~391 meV) in case of germanene antimonene nanocomposites, which make these heterobilayer structures viable candidate for nano-electronics industry (Chen et al., 2016). Optical properties of germanene can be modified by incorporating suitable foreign elements in proper positions of pristine layer and also by varying doping concentrations. As and Ga are used for doping elements due to their natural radius matching with Ge. It has already been reported that, there is a opening of bandgap due to sub-lattice symmetry breaking which is a consequence of doping of As and Ga in Ge-nanosheet (Dhar et al., 2017). Motivated from this, different optical properties of As and Ga doped Ge-nanosheet have been explored systematically in terms of complex dielectric constant, absorption spectra, refractive index and reflectivity.
in this present work. We hope, this study may be helpful for better understanding and applications of 2D germanene based nano-technology beyond graphene in near future.

2 Computational methodology

All calculations are carried out using DFT as implemented in SIESTA package (Soler et al., 2002) with pseudo-atomic orbitals (PAO) basis set. Spin polarised generalised gradient approximation (GGA) of Perdew, Burke and Ernzerhof (PBE) functional is applied for all computations (Perdew et al., 1996). Brillouin Zone is sampled with the equivalent of a $24 \times 24 \times 1$ Monkhorst-Pack in k space. A $4 \times 4 \times 1$ super cell of germanene, containing 32 Ge atoms is used. Atoms are allowed to relax until residual forces achieve a value less than 0.05 eV/Å. Optimised values of Ge-Ge bond length, buckling and bond angle are 2.44 Å, 0.69 Å and 112° respectively for bare germanene. These values are obviously modified for optimised doped structures. S1 and S2 are single As and Ga doped structures respectively with 3.125% doping concentration. S3 and S4 are double As and Ga doped structures at equivalent sites, whereas, S5 and S6 are As and Ga doped structures at non-equivalent sites with 6.25% doping concentration. S7 and S8 are AsGa co-doped structures, where foreign elements are incorporated at same and different sub-lattice positions respectively. Different optimised doped structures are shown in Figures 1 and 2. Optimisation graph of two arbitrarily choosen configurations S4 and S8 are depicted in Figure 3. Complex dielectric function $\varepsilon(\omega)$ is defined as $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$, $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ are real and imaginary parts of $\varepsilon(\omega)$ respectively and $\omega$ frequency of electro-magnetic (EM) wave in energy unit. Applying first order time dependent perturbation theory in the dipole approximation $\varepsilon_2(\omega)$ is interpreted in long wavelength limit ($k \rightarrow 0$) as,

$$
\varepsilon_2(\omega) = \frac{2e^2}{\Omega} \sum_{K,CB,VB} \left| \langle \psi_{CB}^R | \mu_r \psi_{VB}^C \rangle \right|^2 \delta \left( E_{CB}^C - E_{VB}^B - \omega \right)
$$

(1)

Here $\Omega$ is volume of unit cell, $\varepsilon_0$ is permittivity in vacuum, $CB$ and $VB$ are conduction and valence band respectively. $\mu$ and $r$ represent polarisation and position vectors of electric field of EM wave respectively. $\varepsilon_1(\omega)$ depends on $\varepsilon_2(\omega)$ and they are connected via Kramers-Kronig (KK) relation. Different optical properties (Jana et al., 2013; Das et al., 2015) have been analysed both for parallel and perpendicular polarisations.

Figure 1 Structures S1, S2, S3 and S4 respectively from left to right (see online version for colours)

Note: Ge, As and Ga atoms are indicated by black, yellow and green colours respectively.
3 Results and discussion

3.1 Optical properties

3.1.1 Dielectric functions

To study different optical properties, real ($\varepsilon_1(\omega)$) and imaginary ($\varepsilon_2(\omega)$) parts of dielectric constant are computed and analysed for all structures. It can be depicted from Figures 4 and 5 that, all configurations possess several number of plasma frequencies ($\omega_p$), in case of parallel polarisation. There are four $\omega_p$ for pristine structure, whereas this number reduces to two in case of structures S1, S2, S3 and S8 (Table 1). Electron energy loss spectra (EELS) take large value when $\varepsilon_1(\omega)$ is zero and $\varepsilon_2(\omega)$ approaches a low but finite value. From Figure 6, it can be elucidated that at $\omega_p = 7.25$ eV, $\varepsilon_2(\omega)$ is very low and EELS approaches a large value in case of pristine germanene. This fact is valid for all other doped configurations too (not shown in figure). So, EELS peak at 7.25 eV corresponds to the characteristic of germanene associated with plasma oscillation. But at all other $\omega_p$, value of $\varepsilon_2(\omega)$ is large and as a result EELS is very low. It is also very clear from Figures 4, 5 and Table 1 that, values of static real part of dielectric function ($\varepsilon_1(0)$) are highly site dependent. For example, in case of structure S3 (double As doped configuration at same sub-sublattice positions), $\varepsilon_1(0)$ reduces than pristine layer as number of $\omega_p$ also decrease. But for S5, where also double doping of As is induced, but at different sub-lattice positions of a hexagonal cell, $\varepsilon_1(0)$ is enhanced.
than pristine layer and number of \( \varepsilon_0 \) also remain same with virgin layer. Maximum value of \( \varepsilon_1(0) \) is obtained in case of S6, where number of valence electrons are reduced than pristine layer due to doping. For co-doping of AsGa this value of \( \varepsilon_1(0) \) is enhanced than pristine system for structure S7, where As and Ga are doped at equivalent sites. Maximum intensity peak of \( \varepsilon_2(\omega) \) originates due to transition of electrons between VB to CB (Bhattacharya et al., 2015a, 2015b). In case of parallel polarisation, for structure S6, interband transition \( \varepsilon_1 \) 0.49 eV is responsible for maximum highted \( \varepsilon_2(\omega) \) peak at 0.48 eV (not shown in figure). This fact is valid for all structures too (Dhar et al., 2017). Variation of \( \varepsilon_2 \) of co-doped structures S7 and S8 are depicted in Figure 5, for perpendicular polarisation. It can also be noticed that, although the positions of \( \varepsilon_2 \) peak remain almost same with pristine, but there are several modifications in intensity of peaks due to doping, which may be useful to design modern electronic devices.

Figure 4  Real part of dielectric constant for As and Ga doped structures for parallel polarisation (see online version for colours)

![Figure 4](image)

Figure 5  Real and imaginary parts of dielectric constant for AsGa co-doped structures for parallel polarisation (see online version for colours)

![Figure 5](image)

3.1.2 Optical absorption

The absorption coefficient \( \alpha(\omega) = \frac{2k_0}{c \hbar} \) of As and Ga doped structures, including pristine are depicted in Figure 7, in case of perpendicular polarisation. \( c \) is velocity of light in vacuum and \( k \) is imaginary part of complex refractive index. Oscillations are
mainly restricted in the energy range 5 to 15 eV which is in ultraviolet (UV) region of electromagnetic spectrum. Prominent peak positions appear at 7 eV, 8.24 eV, 8.97 eV, 9.69 eV and 11.07 eV for pristine germanene layer. From Figure 7, it can be elucidated that, peak positions are red shifted for As doped structures and blue shifted for Ga doped structures with increase in doping concentration.

Figure 6  Correspondence between eels, real and imaginary part of dielectric constant of bare germanene for parallel polarisation (see online version for colours)

Table 1  Predicted plasma frequency and static real part of dielectric constant of different structures for parallel polarisation

<table>
<thead>
<tr>
<th>Structure</th>
<th>Plasma frequency (ωp in eV)</th>
<th>Static real part of dielectric constant (ε1(0))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine</td>
<td>0.68, 0.86, 4.40, 7.25</td>
<td>15.84</td>
</tr>
<tr>
<td>S1</td>
<td>4.41, 7.25</td>
<td>7.83</td>
</tr>
<tr>
<td>S2</td>
<td>4.37, 7.25</td>
<td>7.95</td>
</tr>
<tr>
<td>S3</td>
<td>4.43, 7.25</td>
<td>9.98</td>
</tr>
<tr>
<td>S4</td>
<td>0.66, 1.07, 4.26, 7.25</td>
<td>17.67</td>
</tr>
<tr>
<td>S5</td>
<td>0.61, 0.96, 4.37, 7.25</td>
<td>17.53</td>
</tr>
<tr>
<td>S6</td>
<td>0.55, 1.17, 4.32, 7.25</td>
<td>27.17</td>
</tr>
<tr>
<td>S7</td>
<td>0.61, 0.90, 4.33, 7.25</td>
<td>17.85</td>
</tr>
<tr>
<td>S8</td>
<td>4.36, 7.25</td>
<td>13.07</td>
</tr>
</tbody>
</table>

Figure 7  Absorption coefficient for As and Ga doped structures for perpendicular polarisation (see online version for colours)
3.1.3 Refractive index and reflectivity

Real part of complex refractive index
\[
n(\omega) = \left(\frac{\sqrt{\varepsilon_1^2 + \varepsilon_2^2 + \varepsilon_3^2}}{2}\right)^{1/2}
\]
is directly related to \(\varepsilon_1(\omega)\) and \(\varepsilon_2(\omega)\). In case of perpendicular polarisation, maximum value of \(n(\omega)\) is obtained to be 1.74 for bare Ge-nanosheet. Peak positions remain almost same, but intensity of peaks are diminished due to co-doping of AsGa (Figure 8). Values of static real part of refractive index \(n(0)\) is almost same for pristine structure and S7 but increases slightly (by \(\sim\)2% than pristine) for S8, where As and Ga co-doped at non-equivalent sites. So, it can be concluded that, value of \(n(0)\) is not affected by various doping concentrations when electric field is applied in the direction perpendicular to the plane (along Z axis) of 2D germanene sheet.

Next, reflectivity
\[
R(\omega) = \frac{(n-1)^2 + k^2}{(n-1)^2 + k^2}
\]
at normal incidence, is computed using real and imaginary parts of complex refractive index for perpendicular polarisation. It can be elucidated from Figure 8 that, value of static reflectivity \((R(0))\) is independent of doping concentrations which is consistent with the observation of \(n(0)\). Two peaks with maximum intensities, both of height 0.26, appear at positions 9.12 eV and 11.28 eV for Ge-nanosheet. In case of Ga doped structures, (Figure 8) very low, uniform value of reflectivity is obtained in the energy range 0 to 5 eV. Optical anisotropy in \(R(\omega)\) is also observed in the energy range 5 to 15 eV and after 15 eV, \(R(\omega)\) almost vanishes.

4 Conclusions

In summary, a first principles study of As and Ga doped FS Ge-nanosheet has been employed theoretically, using DFT, in this present work. It is possible to enhance or reduce different optical properties by choosing proper doping element, doping sites and concentration. The peaks in absorption spectra are red shifted compared to pristine germanene, for As doped structures with increase in concentration of As. Whereas, blue
shifting nature of such peaks are observed than pristine sheet, in case of Ga doped structures. It has been demonstrated that, in case of perpendicular polarisation, optical anisotropy is mainly observed in UV region (5-15 eV) of energy spectrum. Thus, optical properties of FS Ge-nanosheet can be tuned by incorporating adatoms in virgin structure. We expect, this investigation may assist to anticipate FS germanene to substrate interaction and may shed light for next generation 2D germanene based nano-industry.

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