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# First-principles study of the impact of chemical doping and functional groups on the absorption spectra of graphene

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#### Abstract

The rational design of the electronic band structures and the associated properties (e.g. optical) of advanced materials has remained challenging for crucial applications in optoelectronics, solar desalination, advanced manufacturing technologies, etc. In this work, using first-principles calculations, we studied the prospects of tuning the absorption spectra of graphene via defect engineering, i.e. chemical doping and oxidation. Our computational analysis shows that graphene functionalization with single hydroxyl and carboxylic acid fails to open a band gap in graphene. While single epoxide functionalization successfully opens a bandgap in graphene and increases absorptivity, however, other optical properties such as reflection, transmission, and dielectric constants are significantly altered. Boron and nitrogen dopants lead to p- and n-type doping, respectively, while fluorine dopants or a single-carbon atomic vacancy cannot create a significant bandgap in graphene. By rigorously considering the spin-polarization effect, we find that titanium, zirconium, and hafnium dopants can create a bandgap in graphene via an induced flat band around the Fermi level as well as the collapse of the Dirac cone. In addition, silicon, germanium, and tin dopants are also effective in improving the optical characteristics. Our work is important for future experimental work on graphene for laser and optical processing applications.

Supplementary material for this article is available online

Keywords: graphene, optical properties, spin-polarization, functionalization, doping

(Some figures may appear in colour only in the online journal)

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#### 1. Introduction

Graphene is an intriguing two-dimensional (2D) material with intrinsically high electron mobility (200 000 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>) [1], high in-plane thermal conductivity (>1000 W m<sup>-1</sup> K<sup>-1</sup> at  $\sim 300$  K) [2], high specific surface area (2630 m<sup>2</sup> g<sup>-1</sup>) [3], and high in-plane Young's modulus ( $\sim 1$  TPa) [4]. Despite these extraordinary properties, the rational engineering of graphene in its chemical composition and nanostructure can induce additional exotic properties, thus further expanding its applications, for instance, solar-thermal vapor generation [5, 6], thermal interface material [7], thermal signal processing [8, 9], electrochemical storage [10], etc. In particular, the zerobandgap nature of pristine graphene is a major inherent constraint for its electrical, optical, and other relevant applications [11, 12]. In this regard, many initiatives were taken to establish a tunable electronic band structure, particularly, bandgap, in graphene [11-16]. Specific strategies include functionalization with hydroxyl, epoxy, and other functional groups [17, 18], formation of bilayer structure [13], and electron confinement [19, 20]. Notably, doping in pristine graphene with suitable materials [21] or reducing 2D graphene into 1D nanoribbons [22] are two most effective ways of breaking the symmetry of graphene, and these methods have been proved to be pragmatic in obtaining the desired bandgap in graphene [23].

Even as a gapless semiconductor, pristine graphene has high optical conductivity and transmittance [16]. This has piqued interest among the scientific community in fine tuning the optical properties of graphene for optoelectronic applications. A semiconducting bandgap in graphene, in particular, has a large influence on the optical absorption spectrum, which could be useful in laser and/or optical processing of graphene for a variety of applications. Although the doping method has been shown to be effective in opening a bandgap in graphene, the impact of magnetic ions as dopants in graphene via switching on the spin-polarization in the graphene structure is not yet well understood.

In this work, first-principles calculations were conducted to study the prospects of tuning the absorption spectra of graphene via defect engineering, i.e. chemical doping and oxidation. Previous reports have shown that first-principles calculations [24, 25] have been proven to be an efficient method for comprehending the doping strategy in graphenelike materials with similar structural complexity [26]. We investigated the optical properties of graphene as subjected to spin polarization by 3d magnetic atoms. The optical spectra of graphene would assist us in identifying the optimal wavelength of light for effective laser and/or optical processing and enable future experimental work. Moreover, it is essential to tune its absorption spectrum into the desired wavelength regime to maximize graphene's potential for optoelectronic applications. Prior to applying spin-polarization, we investigated the possibility of opening the direct bandgap in graphene using well-characterized dopants such as boron, nitrogen, and fluorine as well as other methods such as atomic vacancy, and functionalization with single epoxide, hydroxyl, and carboxylic functional groups. The effect of spinpolarization was studied by doping all elements in the 3d series of the periodic table (Sc–Zn). The goal of doping all elements in the 3d series is to have a better understanding of the induced weak-to-strong magnetism in the graphene structure. Additionally, we studied the optical characteristics of graphene structures doped with carbon family elements (Si, Ge, and Sn), as these dopants have been shown to be effective at opening a direct bandgap in graphene. Overall, this study is aimed at better understanding the optical absorption spectrum and other relevant optical spectra of the pristine and modified graphene layer.

#### 2. Computational methods

In this work, the pristine and modified (doped or functionalized) hexagonal (4  $\times$  4) graphene layers containing 32 carbon atoms are used for first-principles calculations. The inplane lattice constants are set to be a = b = 9.871 Å and the vacuum is set to a distance of 30 Å along the c-axis to prevent any spurious interaction between successive graphene layers. Our methodology is based on the density functional theory (DFT), as implemented in the Vienna ab initio simulation program (VASP) [27, 28]. The electron-ionic core interactions are modeled using the projector-augmented wave technique [28, 29]. The electron exchange-correlation effects are determined using the Perdew, Burke, and Ernzerhof potentials based on the generalized gradient approximation [30]. The structural relaxation of the pristine  $(4 \times 4)$  graphene layer is performed using a conjugate gradient algorithm [31] with an electronic convergence of 10<sup>-8</sup> eV and a Hellmann–Feynman force convergence of 0.01 eV Å<sup>-1</sup>. A Gaussian smearing width of 0.05 eV is employed, and the spin-polarization is switched on whenever magnetic ions are doped in the  $(4 \times 4)$ graphene layer. Throughout the computations, the energy cutoff for plane waves is set to be 600 eV.

The plotting of band structures as well as the estimation of direct and indirect bandgaps were post-processed using the Sumo python toolkit [32] for plotting and analysis of DFT calculations. The linear-optical characteristics of pristine, doped and/or functionalized hexagonal  $(4 \times 4)$ graphene layers are computed using the independent particle approximation as implemented in the VASP code. The results are post-processed using the VASPKIT tool [33]. To guarantee the quality of the calculated optical spectra, the number of empty bands used in calculating optical properties is increased to three times as many as the default value of the VASP code. The complex dielectric functions with frequency dependence are calculated by accounting for the direct transitions between the valence and conduction bands. Specifically, equation (1) is used to obtain the linear optical spectrum,

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$$
 (1)

where  $\varepsilon_1(\omega)$  and  $\varepsilon_2(\omega)$  are the real and imaginary components of the dielectric function, respectively, and  $\omega$  is the photon frequency. Within the one-electron framework, equation (2) yields the imaginary part of the dielectric function [34],

$$\varepsilon_{2}(\omega) = \frac{4\pi^{2}e^{2}}{\Omega} \lim_{q \to 0} \frac{1}{q^{2}} \times \sum_{c,v,k} 2\omega_{k}\delta(E_{c} - E_{v} - \omega) \left| \langle c | \boldsymbol{e}.\boldsymbol{q} | v \rangle \right|^{2}$$
(2)

where  $\langle c | e,q | v \rangle$  denotes the integrated optical transitions from valence (v) to the conduction states (c), e denotes the polarization direction of the photon, and q denotes the electron momentum operator. The integration over k is accomplished by summing over specific k-points with an appropriate weighting factor  $w_k$ . Equation (3) yields the real part of the dielectric function from the Kramers–Kronig relation,

$$\varepsilon_{1}(\omega) = 1 + \frac{2}{\pi} P \int_{0}^{\infty} \frac{\varepsilon_{2}(\omega')\omega'}{\omega'^{2} - \omega^{2} + i\eta} d\omega'$$
(3)

where *P* indicates the principle value and  $\eta$  represents the complex shift parameter.

The conventional equations used for calculating the refractive index  $n(\omega)$ , extinction coefficient  $\kappa(\omega)$ , absorption coefficient  $\alpha(\omega)$ , energy-loss function  $L(\omega)$ , and reflectivity  $R(\omega)$ for 3D semiconductors are not properly defined for 2D semiconductors. To determine the dielectric function in 2D semiconductors, the thickness of the vacuum needs be considered since 2D materials are usually studied within a periodic stack of layers. In our work, a wide interlayer distance to prevent any spurious interactions are added between the periodic images of the 2D layers in the conventional DFT methods [35, 36]. Therefore, the optical conductivity  $\sigma 2D(\omega)$  is used to estimate the optical properties of 2D layers to overcome the thickness issues. The 3D optical conductivity equation (4) based on the Maxwell formalism can be written as equation (4) [37],

$$\sigma_{3\mathrm{D}}(\omega) = i [1 - \varepsilon(\omega)] \varepsilon_0(\omega) \tag{4}$$

where  $\varepsilon(\omega)$  denotes the frequency-dependent complex dielectric function as shown in equation (1),  $\varepsilon_0$  represents the permittivity of vacuum, and  $\omega$  corresponds to the frequency of the incident wave. The in-plane 2D optical conductivity in equation (5) can be directly related to the respective  $\sigma_{3D}(\omega)$  part [34, 35],

$$\sigma_{\rm 2D}\left(\omega\right) = L\sigma_{\rm 3D}\left(\omega\right) \tag{5}$$

where *L* is the slab thickness of the 2D material. The normalized reflectance  $R(\omega)$ , transmittance  $T(\omega)$  and absorbance  $A(\omega)$ are given as equations (6)–(8), and the polarized light does not have a significant effect on equations (6)–(8) when a normal incidence on free 2D semiconductor layer is concerned [37, 38].

$$R = \left| \frac{\tilde{\sigma}/2}{1 + \tilde{\sigma}/2} \right|^2 \tag{6}$$

$$T = \frac{1}{|1 + \tilde{\sigma}/2|^2}$$
(7)

$$A = \frac{Re\tilde{\sigma}}{\left|1 + \tilde{\sigma}/2\right|^2}.$$
(8)

In equations (6)–(8),  $\tilde{\sigma}(\omega) = \sigma_{2D}(\omega) / \varepsilon_0 c$  denotes the normalized conductivity (*c* represents the speed of light). These equations are valid for semiconductors/insulators (presence of bandgap) while only the inter-band transitions are accounted with a limitation of A + T + R = 1. The reflectance of 2D semiconducting layers is often quite low, and the absorbance may be obtained from the approximation of the real part of  $\tilde{\sigma}(\omega)$  i.e.  $A(\omega) = Re\sigma_{2D}(\omega) / \varepsilon_0 c$ .

#### 3. Results and discussion

The modeled pristine  $4 \times 4$  primitive unit cells of graphene is illustrated in figure 1. The band structure of the pristine graphene shows a typical gap-less semiconducting nature, consistent with early findings [39, 40]. Furthermore, a variety of strategies for opening a bandgap in graphene, including doping, functionalization, and vacancy formation, were investigated. As shown in figure 2, when the graphene layer is doped with boron (figure 2(a)), nitrogen (figure 2(b)) and fluorine (figure 2(c)) or introduced with a single-atom vacancy (figure 2(d)) or functionalized with single epoxy (figure 2(e)), hydroxyl (figure 2(f)), and carboxylic (figure 2(g)) functional groups, only the graphene structure functionalized with the epoxide linkage exhibits the direct bandgap (0.579 eV), whereas all other graphene structures exhibit metallic behaviors. Previous studies [41] have revealed that boron and nitrogen doping could induce p- and n-type doping in the graphene structure, which agrees with our results. In order to open a direct bandgap in graphene and obtain a 2D semiconducting optical absorption spectrum, we focused on the epoxide functionalized graphene layer.

The absorption spectra of the pristine and epoxide functionalized graphene layers are calculated, as shown in figure 3. As observed, the epoxide functionalized graphene layers exhibit an optical anisotropy. The functionalization with an epoxide linkage increases the percentage of absorption drastically, with a higher absorption in the YY direction as compared to that in the XX direction (figure 3(a)). The absorption maximum occurs at various wavelengths ranging from 200-400 nm (UV region) to 500-700 nm (visible region). However, the epoxide functionalized graphene layers reflect a substantial portion of the light, as illustrated in figure 3(b). In figure 3(c), the epoxide functionalized graphene exhibits a lower rate of light transmission as compared to the pristine graphene. The static dielectric constant is found to be in very high value, reaching 34.39 and 66.44 in the XX and YY directions, respectively, as calculated from the real part of the dielectric function (figure 3(d)). These findings are much higher than the estimated static dielectric constant of pristine graphene, which is 7.84. However, when considering the visible region of the electromagnetic spectrum, the dielectric constant values of both the pristine and epoxide functionalized graphene show positive values at 400-500 and 600-800 nm (figure 3(d)). At 625 nm, the dielectric constant achieves its maximum value for epoxide functionalized graphene. The negative region represents that light



**Figure 1.** Modeled pristine  $(4 \times 4)$  graphene and calculated band structure of pristine  $(4 \times 4)$  graphene layer.

cannot transmit efficiently at this wavelength. Owing to the fact that the epoxide functionalized graphene displays optical anisotropy, the *YY* direction exhibits greater absorption and reflection, and a higher dielectric constant as compared to the *XX* direction. The electronic transitions from the valence to conduction band are represented by the imaginary part of the dielectric function, which is strongly related to the band structure energy as shown in figure 3(e). Two prominent peaks are observed at 400 and 600 nm for epoxide functionalized graphene.

Furthermore, the effects of spin polarization in graphene caused by doping 3d atoms into the graphene layer are investigated. We probe all the ten elements in the 3d series in the periodic table, from Sc to Zn, and the calculated electronic band structures of one 3d-atom doped graphene layers are provided in the supplementary information (figure S1 (available online at stacks.iop.org/SST/37/025013/mmedia)), except for Ti. The calculated band structures of one V, Cr, Mn, and Fe atom doped graphene layers reveal a significant spinsplitting between the up and down spins, indicating that strong magnetization is ineffective in opening a bandgap in graphene. This metallic characteristic is also observed when graphene is doped with one Co, Ni, Cu, and Zn atom. However, in these circumstances, the spin-splitting phenomena is absent. The doping of Co to Zn atoms results in p-type doping, which is analogous to boron doping, and the p-type bandgap increases gradually when the graphene layer is doped with Co to Zn atoms. Interestingly, among the 3d atoms, we observe that doping of one Ti atom in the graphene layer opens a bandgap by means of an induced flat band near the Fermi level along with a collapse of the Dirac cone, as shown in figure 4(a). The Ti-doped graphene layer exhibits a direct bandgap of 0.749 eV as well as an indirect bandgap of 0.727 eV. Moreover, the band structures of graphene doped by one Zr and Hf atom from  $d^2s^2$  group of the periodic table are calculated. Zr and Hf doped graphene layers also show both direct and indirect bandgaps, as well as induced flat bands, in their electronic band structures (figures 4(b) and (c)). Zr doped graphene has a direct bandgap of 0.707 eV and an indirect bandgap of 0.633 eV, while Hf doped graphene exhibits a direct bandgap of 0.690 eV and an indirect bandgap of 0.651 eV. The direct bandgap shrinks in the following order: Ti > Zr > Hf doped graphene.

The optical properties of graphene layers doped with one Ti, Zr, and Hf atom are calculated (figure 5). In contrast to the epoxide functionalized graphene, no optical anisotropy exists in these three cases. Figure 5(a) illustrates the absorption percentage. At a wavelength around 260 nm (UV region), the percentage of absorption is nearly the same for all the structures. However, the pristine graphene layer exhibits a greater absorption percentage in the UV (290-400 nm) and visible (600-700 nm) regions. The pristine graphene layer exhibits zero absorption in the visible region of 400-550 nm, while the Ti, Zr, and Hf doped graphene layers exhibit absorption peaks in this range. In the visible region of 450-600 nm, the Ti-doped graphene layer exhibits a higher absorption percentage than the Zr and Hf-doped layers, whereas the latter two doped layers exhibit a higher absorption percentage in the visible region of 600-700 nm. Another intriguing result is that, while the pristine graphene exhibits a higher absorption percentage, it also exhibits a markedly increased percentage of reflection (figure 5(b)). This implies that the amount of light absorbed by a pristine graphene layer is negligible. On the other hand, the reflection percentages of the Ti, Zr, and Hf-doped graphene layers are much lower than that of the pristine graphene layer. The transmittance percentage in



**Figure 2.** Calculated band structures of doped and functionalized  $(4 \times 4)$  graphene layer (a) boron-doped, (b) nitrogen-doped, (c) fluorine-doped, (d) single-carbon atom vacancy, (e) epoxide functionalized, (f) hydroxide functionalized and (g) carboxylic acid functionalized graphene.



**Figure 3.** Calculated optical properties (a) absorption, (b) reflection, (c) transmission, (d) real and (e) imaginary parts of the epoxide functionalized  $(4 \times 4)$  graphene layer.

figure 5(c) exemplifies an opposite pattern as reflection, where the doped graphene layers show higher transmittance than the pristine one. Moreover, the static dielectric constants of graphene owing to the impact of weak spin polarization caused by one Ti, Zr, and Hf atom doping is investigated. It is apparent that doping Ti, Zr, and Hf atoms significantly reduces the static dielectric constant. Ti-doped graphene layer has a static dielectric constant of 3.8632, which is lower than Zr- (3.9757) and Hf-doped (3.9853) layers. These values are reduced to almost half of that of a pristine graphene layer. Owing to the low value



**Figure 4.** Calculated spin-polarized band structures of (a) one Ti atom doped, (b) one Zr atom doped and (c) one Hf atom doped  $(4 \times 4)$  graphene layers (no spin-splitting occurs).

of the static dielectric constant, Ti, Zr, or Hf doped graphene layers can be used in low-k dielectric-based devices, and such materials are of utmost importance in the application areas of nanoelectronics, optoelectronics, radio frequency devices, microelectromechanical and nanoelectromechanical devices, sensors, and detectors. By examining UV and visible regions of the electromagnetic spectra, we noticed that the dielectric constants (real part of the dielectric function in figure 5(d)) are all positive, demonstrating that light can effectively transmit through the Ti, Zr, and Hf doped graphene layers in the UV and visible region. In figure 5(e), the imaginary part of the dielectric function has several peaks ranging from 300 to 800 nm for Ti, Zr, and Hf doped graphene layers, indicating that more electronic transitions are possible than in the pristine graphene layer.

To further investigate the effect of spin polarization induced by increasing the number of dopant (Ti, Zr and Hf) atoms, the spin-polarized band structures of the graphene layer doped with two Ti, Zr, and Hf atoms are calculated, respectively (figure 6). It is noticed that the bandgap decreases as the number of dopant atoms increases. The indirect bandgap associated with a single Ti atom doping vanishes, while only the direct bandgap derived from doping of two Ti atoms is observed. The direct bandgap is predicted to be 0.677 eV, smaller than the bandgap of a single Ti-doped graphene layer. Although the bandgaps decrease in the presence of two Zr and Hf atoms, the indirect bandgaps still exist in both circumstances. The direct and indirect bandgaps of graphene layer doped with two Zr atoms are 0.742 and 0.655 eV, respectively, while those of graphene layers doped with two Hf atoms are both 0.676 eV.

The calculated optical properties of the graphene layers doped with two (Ti, Zr and Hf) atoms are shown in figure 7. As observed, the two-atom doped graphene layers exhibit optical anisotropy, which is different from the single-atom doped ones in figure 5. The absorption and reflection percentages (figures 7(a)–(f)) are lower while the transmission percentage (figures 7(g)–(i)) is higher than the case when the graphene layer is doped with one atom. The two-atom doping, in particular, significantly reduces absorption in the UV region (300–400 nm). This observation applies equally to the reflection in the UV region. This might be related to the formation of optical anisotropy in the graphene layer as doping concentration increases. As a result, the two atoms doping is



**Figure 5.** Calculated optical properties (a) absorption, (b) reflection, (c) transmission, (d) real and (e) imaginary parts of 1 (Ti, Zr and Hf) atom doped  $(4 \times 4)$  graphene layer.

preferred whenever high transmission of light is required, but it is not suited for obtaining high absorption and reflection of light. Moreover, the static dielectric constant (figures 7(j)–(l)) is anisotropic along the XX and YY directions and is estimated to be as follows: Ti (XX = 3.8662 and YY = 4.0392), Zr (XX = 3.8970 and YY = 4.0833), and Hf (XX = 3.7605and YY = 3.9156). The imaginary part of the dielectric function (figures 7(m)–(o)) of graphene layers doped with two Ti, Zr and Hf atoms show peaks with shifted wavelengths relative to those doped with one atom due to optical anisotropy.

Finally, the graphene layers doped by carbon-family atoms (Si, Ge, and Sn) are investigated. The band structures of one Si, Ge, and Sn atom doped graphene layers are shown in figure 8. The opening of direct bandgap is observed due to the carbon-family atom doping, which is consistent with prior



**Figure 6.** Calculated spin-polarized band structures of the  $(4 \times 4)$  graphene layer (no spin-splitting occurs) doped with two (a) Ti, (b) Zr and (c) Hf atoms.

research [16, 42]. The Si, Ge, and Sn-doped graphene layers have direct bandgaps of 0.216, 0.203, and 0.252 eV, respectively. Such doping does not collapse the Dirac cone. Additionally, no flat band is formed, which is different from the cases of Ti, Zr, and Hf doped graphene. The direct bandgap is caused by the Dirac cone being pushed into the valence and conduction band regions. There is no indirect bandgap present in the structures.

The optical properties of single-atom Si, Ge and Sn-doped graphene layers are calculated as shown in figure 9. Similar to the cases of single-atom Ti, Zr and Hf-doped graphene layers, the doping of one atom of Si, Ge and Sn does not result in optical anisotropy. As observed in figure 9(a), Si, Ge and Sn doped graphene layers exhibit the reduced absorption percentage in the UV region, and the substantially increased absorption percentage in the visible region. In particular, the doping of Sn atom increases absorption at 600–700 nm with a slight redshift. Although the pristine graphene layer has no absorption at 400–550 nm, the doping of Si, Ge and Sn compensates for this shortcoming of pristine graphene by exhibiting absorption peaks in this range. Regarding the reflection

percentage (figure 9(b)), the doping of Si, Ge and Sn atoms greatly reduces the amount of light being reflected. While all three dopants greatly reduce the reflection percentage in the UV region, the reflected light in the visible region for Sn doped graphene is the highest. To minimize the reflection in this region, Si would be the ideal dopant choice. The transmittance percentage illustrated in figure 9(c) shows that the doping of Si, Ge and Sn atoms greatly enhance the transmission of light. The static dielectric constants of pristine graphene (7.8376) did not change much when doped with Si (7.4056), Ge (7.6713) and Sn (7.5349) atoms. Even the dielectric constants in the UV and visible regions follow the same pattern as graphene, with a slight shift in the wavelength and reduced intensity (figure 9(d)). However, the advantage of doping Si, Ge and Sn atoms in graphene enhances the light to pass over the material in the UV region when compared to the pristine graphene as shown in figure 9(d). The imaginary part of the dielectric function is shown in figure 9(e), where there are more peaks observed on doping Si, Ge and Sn atoms, implying that more electronic transitions occur than in the pristine graphene layer. Sn atom



**Figure 7.** Calculated optical properties (a)–(c) absorption, (d)–(f) reflection, (g)–(i) transmission, (j)–(l) real and (m)–(o) imaginary parts of the  $(4 \times 4)$  graphene layer doped with two (Ti, Zr and Hf) atoms.



Figure 8. Calculated band structure of the  $(4 \times 4)$  graphene layer doped with one (a) Si, (b) Ge, and (c) Sn atom.

doped graphene layer exhibits higher intensity peaks than the pristine, Si and Ge atom doped graphene layer in the visible region.

To study the effect of dopant concentration in terms of atom number, graphene layers doped by two atoms of Si, Ge and Sn are investigated. The calculated electronic band structure is shown in figure 10. It is noticed that the direct bandgap increases as the number of dopant atoms increases. There is no indirect bandgap in these structures, the same as in the cases of one-atom doping. The direct bandgaps of graphene layers doped with two Si, Ge, and Sn atoms are calculated to be 0.389, 0.367, and 0.432 eV, respectively. In these cases, the Dirac cone positions in the valence and conduction band regions are pushed away from the Fermi level. Moreover, the optical characteristics of graphene layers doped with two Si, Ge, and Sn atoms are calculated and shown in figure 11. When doped with two atoms, the optical anisotropy is observed. The absorption, reflection, and transmission percentages in figures 11(a)-(i) show a shift in the wavelength as a consequence of the increased doping concentration. The absorption and reflection percentages (figures 11(a)-(f)) of the graphene layer doped with two Sn atoms is lower than those of doped with two Si and Ge atoms, which is another noteworthy aspect. However, the transmission percentage (figures 11(g)-(i)) is found to be higher for the graphene layer doped with two Sn atoms than the other two dopant cases. One more significant aspect that should be mentioned is that, as the dopant concentration increased to two atoms, the graphene structure becomes more transparent to light (observed from real part of dielectric function), allowing it to flow across the UV and visible spectra (figures 11(j)–(1)). This is not the case for the one Si, Ge, and Sn atom-doped graphene layer that was found. The imaginary part of the dielectric function shows a wavelength shift of peaks for the two atoms (Si, Ge and Sn) doped graphene layer in relative to the pristine graphene layer as noticeable in figures 11(m)–(o).



**Figure 9.** Calculated optical properties (a) absorption, (b) reflection, (c) transmission, (d) real and (e) imaginary parts of one (Si, Ge and Sn) atom doped  $(4 \times 4)$  graphene layer.



Figure 10. Calculated band structure of the  $(4 \times 4)$  graphene layer doped with two (a) Si, (b) Ge and (c) Sn atoms.



**Figure 11.** Calculated optical properties (a)–(c) absorption, (d)–(f) reflection, (g)–(i) transmission, (j)–(l) real and (m)–(o) imaginary parts of the  $(4 \times 4)$  graphene layer doped with two (Si, Ge and Sn) atoms.

#### 4. Conclusion

In this work, first-principles calculations were conducted to investigate the prospects of tuning the absorption spectra of graphene via defect engineering. In specific, the modified graphene structures via strategies of single functionalization, single atom vacancy creation, doping with boron, nitrogen, fluorine, spin-polarized magnetic and carbon-family group atoms were studied. The electronic band structure is carefully examined for the presence of bandgap in modified graphene structures, and the optical properties including absorption, reflection, transmission, real and imaginary parts of the frequency-dependent dielectric function were calculated. Our calculations indicate that functionalization with epoxide linkage can drastically increase the optical absorption. However, fluorine doping and single atom-vacancy creation are ineffective in creating a bandgap in graphene and therefore a semiconducting optical absorption is not observed. Boron and nitrogen doping induce p- and n-type doping, respectively. Introducing a significantly weak spin-polarization into the graphene structure by doping Ti, Zr and Hf atoms opens bandgaps but decreases the optical absorption as compared to pristine graphene. However, the reflection rate becomes minimal and the transmission is greatly enhanced by doping with Ti, Zr and Hf atoms. Additionally, we observed significant spin splitting between the up and down spins with V, Cr, Mn and Fe atoms with metallic behavior, indicating that strong magnetization is ineffective in opening the bandgap in graphene. The doping of two Ti, Zr and Hf atoms is preferred whenever higher transmission of light is required, but it is not suitable for obtaining high absorption and reflection of light. Besides, doping carbon-family atoms (Si, Ge, and Sn) also opens a direct bandgap and exhibits reduced optical absorption and reflection while increased the transmission. However, the doping of two Si, Ge and Sn atoms in the graphene layer shows a shift in the wavelength of absorption. An optical anisotropy is observed for single epoxide functionalized and two atoms (Ti, Zr, Hf, Si, Ge and Sn) doped graphene layer. We envision that the results and knowledge gained in this research will benefit future applications of graphene structures and enable nanomanufacturing innovations towards defect engineering of graphene, particularly laser and optical processing.

### Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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