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Chapter

Structural, Electronic, and Optical Properties of Mono- and Co-Doped Graphene with Ti and Ru

Lutendo Phuthu, Nnditshedzeni Eric Maluta and Rapela Regina Maphanga

Abstract

Due to its properties, graphene is considered a revolutionary material for the future, and as a two-dimensional material it has received a lot of research attention over the last two decades. For graphene to be used in different technologies such as solar cells, much more work needs to be done to understand its properties and engineer its properties by combining it with other materials such as semiconductors. This research work reports computational investigation of the electronic and optical properties of Ti and Ru mono-doped and co-doped graphene. Geometry optimizations for the electronic and optical properties were performed by first-principles calculations based on density functional theory. Various supercells of graphene were modeled and optimized, and their properties were calculated. The results show that different graphene supercells have different electronic and optical properties. The energy bandgap of pure graphene is zero, and after doping with Ti and Ru it increases to 0.550 eV, and 0.786 eV, respectively. The co-doped graphene bandgap is 0.272 eV. The calculated optical properties showed that doping graphene with Ti and Ru shifts the absorption from the visible to the near-infrared region, and these results open possibilities of using doped graphene as a semiconductor material.

Keywords: graphene, density functional theory, bandgap, doping, optical properties

1. Introduction

Graphene has sparked great interest in recent decades due to its remarkable electrical and optical capabilities, as demonstrated by a groundbreaking experiment in graphene research in 2004 [1]. Graphene is a honeycomb-shaped two-dimensional sheet crystalline structure of atomically thick sp2-hybridized carbon (each carbon fortifies covalently with three other carbon atoms) [2–5]. It serves as a building block for various carbon dimensionalities, such as zero-dimensional Buckyball, one-dimensional nanotube, and three-dimensional graphite [2]. A pristine graphene has zero bandgap, because its conduction and valence bands meet at a single location at the Dirac points [6–12]. Graphene is considerably stable due to the tight packing of carbon atoms and hybridization of sp2, but only when the graphene size is smaller
than 20 nm; otherwise, it is thermodynamically unstable [13, 14]. The classification of graphene as a metal, nonmetal, or semimetal is still up for discussion [13].

The properties of graphene depend on the number of graphene layers. A pristine graphene, for example, has a theoretical surface area of 2630 m²g⁻¹, which is more than the surface area of carbon nanotubes (100–1000 m²g⁻¹) [15, 16]. Furthermore, as compared to graphene with a few layers, a single-layer graphene has a higher surface area [14]. According to numerous studies, graphene has a high charge carrier mobility of 250,000 cm²v⁻²s⁻¹ at room temperature [5, 17, 18]. Furthermore, each layer of graphene absorbs up to 2.3% of the incident light with a reflectance of less than 0.1% [6]. As a result, it has a very high optical transparency of 97.7% as well as a high degree of flexibility [6, 19]. At room temperature, a single-layer graphene has a high thermal conductivity of 3000–5000 Wm⁻¹K⁻¹ [20]. Other properties include an electrical conductivity of 6000 S cm⁻¹ [21] and a Young’s modulus of 1.0 TPa [22].

Graphene offers potential application in areas such as high-speed electronics, data storage, liquid crystal display (LCD) smart windows, organic light emitting diode (OLED), supercapacitors, solar cells, and electrochemical sensing [19, 23]. The combination of high electrical conductivity, chemical and thermal stability, and outstanding stretchability provides significant benefits for employing graphene as a transparent conductor in organic electronic devices. It is mostly used as a hybrid with other materials to enhance the properties of other materials making them stronger, valuable, and light weight [24–28]. Studies have shown that the number of graphene layers, defects in graphene layers, various concentrations of graphene, and different sizes of graphene have impact on properties of graphene [28–32]. Graphene has been modified in various ways to broaden its application in a variety of fields. One method to modify graphene is to introduce foreign elements into it to tempt its electronic properties. Mukherjee and Kaloni investigated the effect of boron and nitrogen doping on graphene. Their calculations showed that N-doped graphene had a Dirac point shift below the Fermi level and B-doped graphene had a Dirac point shift above the Fermi level, resulting in a bandgap opening. The opening of the bandgap appears at the Fermi level for co-doped graphene [33]. Sara Varghese et al. investigated the structural, energetic, and electronic properties of graphene doped with boron and nitrogen atoms at different doping concentrations. They observed that doping increases the bandgap and decreases the energetic stability [34]. Olaniyan et al. conducted a systematic study of the stability, electronic, and optical properties of mono- and co-doped graphene with beryllium and nitrogen. Be-N was found to be more stable than Be-doped graphene. The study also shows that when graphene is doped with Be and N, it transforms from semi-metallicity to semi-conductivity [35]. Despite the substantial amount of work that has been put into the theory and experimentation of doped graphene, there are still a great many applications that have not been fulfilled. As a result, research into doped graphene systems with superior performance continues to be pushed forward.

First-principle calculations are used in this study to evaluate several graphene supercells and examine the effects of those supercells on the electrical and optical properties of graphene material. In addition, it investigates how the electrical and optical properties of graphene change when doped with titanium or ruthenium and a combination thereof.

2. Computational details

Geometry optimizations for the electronic and optical properties were performed by the first-principle calculations based on DFT implemented in the Material Studio.
CASTEP code, using the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE), norm-conserving pseudopotential, periodic boundary conditions, and space group of P6/mmm. The k point was set at 6x6x1 with a cutoff energy of 350 eV and energy tolerance of 1.0x10^{-6} eV. The force tolerance was set at 0.03 eV, the displacement tolerance 0.0001 Å, and convergence threshold of 1.0x10^{-6} eV/atoms.

3. Results and discussion

3.1 Structural properties of graphene supercells

A graphene unit cell of two carbons was constructed with a 1.42 Å C-C bond lengths, 120 bond angles, and the lattice parameters a = b = 2.46 Å and c = 6.8 Å (see Figure 1a). The unit cell was then extended to construct n x n supercells (where n is an integer number). A total of seven graphene supercells were constructed. A 4x4 supercell is shown in Figure 1b. A space group of P6/mmm was used for all supercells. The constructed supercells are listed in Table 1.

3.2 Electronic properties of graphene supercells

Table 1 shows all the possible combinations of n x n graphene supercells constructed in this work along with the number of carbons of that supercell. We use C# to denote the number of carbons of an n x n supercell, where # is an integer number representing the number of carbons. The calculated band structures are shown in Figures 2 and 3. The Fermi level was set to zero and is indicated by the red dashed lines.

The band structures of the supercells studied show Fermi levels at the Dirac points, showing a bandgap of zero, which agrees with other literature [6–12]. It is observed...
that the bandgap energy of graphene is not affected when the size of the supercells is changed.

To investigate the nature of the states that comprise the conduction and valence band edges, we calculated the contributions of all atomic orbitals in the total density of states (TDOS) and the unique atomic shells in the partial density of states (PDOS) band edges. Figures 4 and 5 show the density of states (DOSs), which describes the number of states per energy interval. The DOS agrees with the calculated band structure. At the Fermi level, the DOSs are very low, which are consistent with the calculated band structure.

Table 1.
Different graphene supercells.

<table>
<thead>
<tr>
<th>Supercell (n × n)</th>
<th>Number of carbons</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unit cell 2 (C2)</td>
<td>2 (C2)</td>
</tr>
<tr>
<td>2 × 2</td>
<td>8 (C8)</td>
</tr>
<tr>
<td>3 × 3</td>
<td>18 (C18)</td>
</tr>
<tr>
<td>4 × 4</td>
<td>32 (C32)</td>
</tr>
<tr>
<td>5 × 5</td>
<td>50 (C50)</td>
</tr>
<tr>
<td>6 × 6</td>
<td>72 (C72)</td>
</tr>
<tr>
<td>7 × 7</td>
<td>98 (C98)</td>
</tr>
</tbody>
</table>

Figure 2.
Calculated band structures of (a) C2, (b) C8, (c) C18 and (d) C32.
Figure 3. Calculated band structures of (a) C$_{50}$, (b) C$_{72}$, and (c) C$_{98}$.

Figure 4. TDOS and PDOS for the (a) C$_2$, (b) C$_8$, (c) C$_{18}$, and (d) C$_{32}$ graphene supercells.
It was found that the electron distribution in graphene is due to the contribution of the s and p atomic shells, which are responsible for the energy transfer in graphene. The results show that the s and p states are dominant in both the conduction and valence bands. However, at the Fermi level or near the Fermi level, only the p state is dominant.

3.3 Optical properties of graphene supercells

To investigate the optical response of graphene, we calculated its absorption, dielectric function, and refractive index. Figure 6 illustrates the optical absorption calculations for different supercells. It can be observed that C8, C32, and C50 supercells exhibit strong absorption in the ultraviolet-visible range that extends into the infrared. The C2 and C18 supercells absorb more light in the UV area and dissipate in the visible region around the wavelength of 600 nm. C98 enhances the absorption activity to 700 nm, while C72 enhances it to 900 nm.

Dielectric materials tend to become polarized when exposed to an external electric field. The term “dielectric function” refers to the property of a substance that determines its polarization. The dielectric function is defined as follows:

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

where $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ are the real and imaginary parts of the dielectric function.

The real part of the dielectric function is connected to the material’s polarization, whereas the imaginary part is related to the electronic absorption. Figure 7 shows the calculated dielectric function of the seven graphene supercells up to a photon energy of 10 eV. In the limit of zero photon energy, the findings showed dielectric constant $\varepsilon_0$ values of 4.97, 6.82, 4.23, 11.92, 7.44, 6.07, and 6.03 for the supercells C2, C8, C18, C32, C50, C72, and C98, respectively. The dielectric constant is proportional to the...
electric displacement, which is proportional to the polarization of the material. The imaginary part of the dielectric function shows that the low-frequency peaks are located at 1.93 to 3.62 eV.

The real part $n(\omega)$ and imaginary part $k(\omega)$ (extinction coefficient) of the refractive index are determined by the dielectric function using the Kramers-Kronig transformation and are defined as:

$$n(\omega) = \left( \frac{|\varepsilon(\omega)| + \varepsilon_1(\omega)}{2} \right)^{\frac{1}{2}}$$  

(2)

Figure 6. Calculated absorption properties of the graphene supercells.

Figure 7. Calculated dielectric function properties of the graphene supercells.
The extinction coefficient is relative to the amount of light absorbed. Figure 8 shows the calculated refractive index of graphene supercells. The refractive index $n_0$ is equal to the $\sqrt{\varepsilon_0}$ in the limit of zero photon energy. These findings reveal refractive index $n_0$ values of 2.23, 2.61, 2.06, 3.45, 2.73, 2.46, and 2.46 for supercells C2, C8, C18, C32, C50, C72, and C98, respectively. The extinction coefficient has low-frequency peaks located from 2.28 to 3.97 eV.

### 3.4 Electronic properties of doped graphene

According to the findings of research conducted on the optical properties of various graphene supercells, the 4x4 graphene supercell demonstrates a superior optical response compared to other graphene supercells. These results have contributed to the author’s decision to use the 4x4 graphene supercell and dope it with titanium and ruthenium atoms to study its electronic and optical properties. In the case of mono-doped graphene, the doping was accomplished by exchanging one of the graphene’s carbon atoms for either titanium or ruthenium as shown in Figure 9(a). On the other hand, in the case of co-doped graphene, two carbon atoms were exchanged for titanium and ruthenium, as illustrated in Figure 9(b).

Figure 10 presents an illustration of the band structure that was computed for the doped graphene 4x4 super cell. The results show that doping graphene causes an increase in the bandgap, which can be seen near the Fermi level in Figure 10. While the energy of the bandgap of Ti-doped graphene is 0.555 eV, the energy of the bandgap of Ru-doped graphene is 0.786 eV, and the energy of the bandgap of co-doped graphene is 0.272 eV. As a result of these properties, graphene can now be categorized as a material that falls into the category of semiconductor. The band
Figure 9. Structures of doped graphene: (a) mono-doped and (b) co-doped.

Figure 10. Calculated band structures of doped graphene with (a) Ti, (b) Ru, and (c) co-doped graphene.
structures shown in Figure 10a and b both exhibit an indirect bandgap, whereas the bandgap shown in Figure 10c exhibits a direct bandgap.

Figure 11 shows the contribution made by doping graphene to the atomic shells. Doping graphene with the selected elements results in the introduction of numerous minor state density peaks, which can be clearly seen in the Fermi level region, as shown in Figure 11. This can be clearly observed by comparing Figure 11 with the density of states of the 4x4 graphene supercell as shown in Figure 5(d). Ru is a transition metal having a 4d electron configuration, whereas Ti has a 3d electron configuration. The 3d contribution from Ti is highlighted by the cyan color in Figure 11a, and the 4d contribution from Ru is highlighted by the cyan color in Figure 11b. Both of these contributions are in the energy range of −6 eV to 6 eV. In the vicinity of the Fermi level, the 3d state density has a modest peak, whereas the 4d state density has obvious peaks.

3.5 Optical absorption of mono and co-doped graphene

The calculated results of the optical absorbance of the doped graphene are illustrated in Figure 12. The results demonstrate that, when graphene is doped with titanium and ruthenium, there is no change in the activity of the absorption in the ultraviolet area. When Ti and Ru are added to graphene, a blue shift occurs in the
visible area. This blue shift is found for both mono-doped and co-doped graphene. Graphene with one dopant also exhibits this blue shift. Because of the dopants that were introduced into graphene, there is a red shift that occurs in the infrared region, which is located above 800 nm.

4. Conclusion

Using density functional theory as it is embodied in Material Studio, a number of electrical and optical properties were successfully explored. The results of our research indicate that the electrical structure of different graphene supercells is the same. The band structure computations showed that the Fermi level in all graphene supercells is located at the Dirac point, which indicates that there is no bandgap energy. According to the results of the density of state calculations, the s and p orbitals predominated in the valence band as well as the conduction band. According to the findings of the absorption, certain graphene supercells have minimal activity in the visible region, but other graphene structures have high absorbance in the visible area reaching all the way to the infrared sector of the spectrum. The findings suggest that graphene has a high dielectric constant, which qualifies it as an excellent candidate for application in various electrical devices. When graphene is mono-doped or co-doped with either titanium or ruthenium, a bandgap opening occurs. These results demonstrate a change from semi-metallic to semi-conducting behavior. This paves the way for the exploration of novel applications for graphene as a semiconductor.

Acknowledgements

The authors acknowledge the Centre for High Performance Computing (CHPC) for computing.
Resources. LP thanks the National Institute for Theoretical and Computational Sciences (NITheCS) and Armaments Corporation of South Africa SOC Ltd. (ARMSCOR) for financial support.

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Graphene - A Wonder Material for Scientists and Engineers


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