Effects of Defects and Doping on an Al Atom Adsorbed on Graphene: A First-Principles Investigation

Xiaoshuang Dai 1,2, Tao Shen 1,2,*, Jiaojiao Chen 1,2 and Hongchen Liu 3

1 Heilongjiang Provincial Key Laboratory of Quantum Manipulation & Control, Harbin University of Science and Technology, Harbin 150080, China; 13103809866@163.com (X.D.); chen_summers@163.com (J.C.)
2 Key Laboratory of Engineering Dielectrics and Its Application, Ministry of Education, Harbin University of Science and Technology, Harbin, 150080, China
3 School of Electrical Engineering and Automation, Harbin Institute of Technology, Harbin 150001, China; fenmiao@hit.edu.cn
* Correspondence: taoshenchina@163.com; Tel.: +86-451-86390867; Fax: +86-451-86390867

Received: 25 December 2019; Accepted: 30 January 2020; Published: 3 February 2020

Abstract: In order to enhance the interaction between an Al atom and graphene in graphene-reinforced aluminum-based composites, the method of first-principles calculation was used to investigate the adsorption behavior of Al atoms on graphene. Our calculations indicate that defective and doped graphene are energetically favored for Al atom adsorption compared with pristine graphene. The adsorption effects show that both defects and doping can improve the stability of the Al–graphene system. Furthermore, it was also found that defects and doping lead to a red-shift of the highest optical absorption peaks. The results of the investigation provide a theoretical basis for the future application of graphene-reinforced aluminum-based composites in optical and optoelectronic devices.

Keywords: graphene; adsorption; electronic properties; optical properties; first-principles

1. Introduction

Composite material is a type of material with strong vitality emerging in response to the needs of modern scientific development [1]. It is composed of two or more materials with different properties that are combined through various technological means. In addition, Al-based composites have high specific strength and specific stiffness, good high-temperature performance, better fatigue and wear resistance, good damping performance, and a low thermal expansion coefficient [2–4]. Therefore, Al-based composites have become one of the most essential materials in metal matrix composites [5]. It is widely used in electronic and optical instruments. However, although the traditional reinforced materials such as silicon carbide, alumina, and boron carbide have high strength and other properties, their plasticity is significantly reduced [6]. The performance of ordinary Al-based composites has been unable to meet the requirements of modern industrial technology. Graphene, a new two-dimensional material, has much higher physical and mechanical properties than traditional materials [7]. As an ideal reinforced material, it has been proved that graphene can greatly improve the properties of composites [8]. The Al–graphene composite material has high specific strength, excellent ductility, and good mechanical properties, and its properties are significantly improved compared to the traditional Al matrix composite material.

In recent years, some scholars have investigated metal–graphene composites and made corresponding progress. Experimentally, Chen et al. [9] prepared Mg–graphene composite materials by using liquid ultrasonic, as well as solid stirring, technology, and tested the microhardness of related composite materials. Jagannadham et al. [10] prepared Cu–graphene composite film by the
electrochemical method. In addition, the thermal conductivity of the composite film was calculated, and it was determined that the interface’s thermal resistance was not the limiting factor to improve the thermal conductivity of Cu–graphene composite film. Zhao et al. [11] obtained a small amount of Al–graphene matrix composite by the mechanical stirring method, and the hardness was found to be significantly improved compared with pure Al. Politano et al. [12] explored a silver/graphene oxide/gold sandwich structure, in which the graphene oxide film was inserted between magnetron sputtered gold and silver thin films. The results contributed to improving our understanding of graphene oxide’s interaction with magnetron sputtered metal thin films. The optical properties of a CVD-grown monolayer graphene, transferred from a copper substrate onto SiO2/Si, were studied by Castriota et al. [13] in a broad energy range (0.38–6.2 eV) using Variable Angle Spectroscopic Ellipsometry (VASE). At present, the experimental research on Al–graphene composites is mainly in the field of tissue characterization and performance research, while the research on the interfacial binding mechanism of the composites is restricted by graphene’s characteristics and equipment factors. The first-principles calculation is not limited by materials and instruments in the field of composite material interface bonding, bonding type, interface electronic structure, or other fields, making up for the shortcomings of the experiment. Zhou et al. [14] studied the adsorption of Ag on defective and Ce-doped graphene by first-principles calculation. They obtained data on the adsorption energy and charge transfer, which are usually difficult to obtain via experiments. Liu et al. [15] investigated the adsorption of Cu on vacancy-defected and Au-doped graphene using first-principles calculation. Rad et al. [16] studied the electronic structure and properties of pristine, as well as Al-doped, graphene sheets towards the adsorption of some halomethane compounds (trichloromethane, dichloromethane, and difluoromethane) using DFT calculations. These calculated results indicate the suitability of Al-doped graphene as a good adsorbent/sensor for halomethane compounds. Moreover, Fan et al. [17] adopted the first-principles calculations based on density functional theory to investigate the adsorption energy, bond length, and Mulliken charge of monovacancy and deformation on an Al atom adsorbed on graphene. The calculations indicate that both vacancy and deformation enhance the adsorption energy of an Al atom adsorbed on a graphene system, but vacancy is more effective.

However, the present work aims to understand the adsorption behavior and electronic properties not studied in previous reports on graphene-reinforced aluminum-based composites. As far as we know, the electronic and optical properties of vacancy-defected, B-doped, and N-doped aluminum-based composites have not been elaborately investigated. In this work, using first-principles calculations, the adsorption behavior of Al atoms on VG, B-doped graphene, and N-doped graphene are investigated. Moreover, the electronic and optical properties of Al-based composites are also discussed. Our theoretical results show that Al-based composites have broad application prospects.

2. Calculations and Computational Details

2.1. Computational Details

In the study, the first-principle calculations were performed using the Cambridge Sequential Total Energy Package (CASTEP) Code [18]. The electron exchange–correlation interactions were expressed by the generalized gradient approximation (GGA) [19,20] in the form of the Perdew–Burke–Ernzerhof (PBE) function [21]. The BFGS algorithm [22] was used in the geometric optimization process. The interaction between electrons and ions was approximated by the ultra-soft pseudopotential. After a series of convergence tests, the convergence accuracy was achieved when the energy was set to 310 eV and the Monkhorst–Pack k-point mesh [23] was performed with dimensions of 5 × 5 × 1. The convergence tolerances for the geometric optimization were set as follows: the convergence energy was 2.0 × 10−5 eV·atom−1; the maximum force was 0.05 eV·Å−1; the maximum stress on each cell was 0.1 GPa; the maximum displacement on each atom was 0.002 Å; and the self-consistent field (SCF) was set to 2.0 × 10−6 eV·atom−1.
2.2. Computational Model

The ideal graphene structure is a planar hexagonal lattice, which can be viewed as a layer of exfoliated graphite molecules. Every carbon atom is hybridized in the form of sp"2. The carbon atoms are connected by strong σ bonds, which guarantee the stability of the structure and excellent mechanical properties [24]. In addition, the remaining electrons in the p-orbital form the π bond, which is perpendicular to the carbon plane.

At first, the original graphite model was imported. Then, a layer of carbon atoms was removed to create graphene on the basis of symmetry cancellation. The vacuum was set to 20 Å in the z direction in order to avoid the interaction between the layers of graphene [25]. The models of VG, N-doped graphene, and B-doped graphene are shown in Figure 1. The doping concentration was 3.125%. The vacancy defect graphene (VG) model was established by removing the selected C atoms in the pristine graphene. The model of B-doped graphene was established by replacing the C atom in pristine graphene with a B atom. In the same way, the model of N-doped graphene was established by replacing the C atom in pristine graphene with a N atom. A single Al atom was placed above the graphene to establish the model for Al adsorption on VG or doped graphene. The adsorption energy of an Al atom on graphene ($E_{ad}$) is calculated by the following expression:

$$E_{ad} = E_{Al} + E_{graphene} - E_{Al–graphene}$$

where $E_{Al–graphene}$, $E_{Al}$, and $E_{graphene}$ are the energies of the graphene–Al system, an isolated Al atom, and graphene, respectively. According to the definition, the larger the adsorption energy, the more stable the structure.

![Physical models of graphene: (a) Vacancy defect graphene (VG); (b) B-doped graphene; (c) N-doped graphene.](image)

**Figure 1.** Physical models of graphene: (a) Vacancy defect graphene (VG); (b) B-doped graphene; (c) N-doped graphene.

3. Results and Discussion

3.1. Adsorption Energy and Charge Transfer

The adsorption results of an Al atom adsorbed on graphene are shown in Table 1. Due to the effect of the vacancy, the adsorption energy between the Al atom and VG increases from 1.412 to 5.763 eV. This result of pristine graphene with the adsorbed Al atom is similar to previous literature [17]. The adsorption height between the Al atom and VG decreases from 2.228 to 1.989 Å. These data indicate that the VG composite aluminum matrix material is more stable than that of pristine graphene. Compared with charge transfer between the Al atom and pristine graphene (0.16 e), there exists a larger charge transfer from Al to VG (0.21 e). The adsorption results will vary with the doping atoms. The adsorption height decreases and the adsorption energy increases. In short, both are more stable than pristine graphene. For B-doped graphene, the charge of the Al atom increased by 0.29 e. For N-doped graphene, the charge of the Al atom increased by 0.1 e. Figure 2 shows the front view and the top view of VG with the adsorbed Al atom, and the B-doped graphene with the adsorbed Al atom. The adsorption is set to the top site in graphene. Due to the presence of vacancy or doping atoms, the symmetrical...
structure of graphene is destroyed, and local deformation occurs. In addition, changes in electrical properties have emerged.

**Table 1.** The adsorption height (D), adsorption energy \((E_{ad})\), and charge transfer \((Q)\) of the Al atom absorbed on graphene.

| Structure          | D/Å     | \(E_{ad}/\text{eV}\) | Q/e  |
|--------------------|---------|----------------------|------|
| pristine graphene  | 2.228   | 1.412                | 0.16 |
| VG                 | 1.989   | 5.763                | 0.21 |
| B-doped graphene   | 2.145   | 2.024                | 0.45 |
| N-doped graphene   | 2.216   | 1.805                | 0.26 |

**Figure 2.** The front view and the top view of graphene with adsorbed Al atom: (a) the top view of VG with adsorbed Al atom; (b) the front view of VG with adsorbed Al atom; (c) the top view of B-doped graphene with adsorbed Al atom; (d) the front view of B-doped graphene with adsorbed Al atom.

3.2. Electronic Properties

In order to study the microscopic mechanism of graphene-reinforced aluminum-based composites, band structures were calculated for pristine graphene, VG, B-doped graphene, and N-doped graphene with an absorbed Al atom, which are shown in Figure 3. It is well-known that the band gap of pristine graphene is zero and the Dirac point is located at the Fermi energy level [26–28]. The adsorption of the Al atom on pristine graphene leads to small changes in the band structure, while for the adsorption of the Al atom on VG, the existence of dangling bonds would cause the Dirac point to disappear, which would lead to an electron deficiency and a decline in the Fermi level. The results can be further confirmed by reference [29]. Furthermore, p-type doping is formed, which facilitates electron transfer between Al and graphene. Moreover, new bands are also introduced between the top of the valence band and the bottom of the conduction band. For the Ag atom on VG [14], there are also new bands introduced. The results of the two studies are similar. For the adsorption of the Al atom on B-doped graphene, the Fermi level experienced an obvious decrease, indicating the formation of p-type doping. However, for the adsorption of the Al atom on N-doped graphene, the Fermi level experienced an obvious increase, indicating the formation of n-type doping. The changes in this case are probably due to the electron transfer between Al and doped graphene. In addition, it still depends on the contribution of each atom to the density of states.
Figure 3. Band structure: (a) Pristine graphene with adsorbed Al atom; (b) VG with adsorbed Al atom; (c) B-doped graphene with adsorbed Al atom; (d) N-doped graphene with adsorbed Al atom.

Figure 4 shows the density of states (DOS) results of pristine graphene with the adsorbed Al atom (a), VG with the adsorbed Al atom (b), B-doped graphene with the adsorbed Al atom (c), and N-doped graphene with the adsorbed Al atom (d). From Figure 4a, it can be seen that the p-orbital of the adsorbed Al atom would not interact effectively with the p-orbital of the C atom. The result shows that it is physical adsorption, confirming consistency with the adsorption results in Table 1. For VG with the adsorbed Al atom, both the p-orbital and s-orbital of the Al atom interact well with the p-orbital of the C atom. The result verifies a stable chemical adsorption between VG and the Al atom. For B-doped graphene with the adsorbed Al atom, the p-orbital of the Al atom displays coupling with the p-orbitals of the C atom and the B atom near the Fermi level, indicating that the adsorption structure is stable in B-doped graphene. For N-doped graphene with the adsorbed Al atom, the p-orbital of the Al atom interacts with the p-orbital of the N atom, which shows a chemical adsorption between N-doped graphene and the Al atom.
3.3. Optical Properties

Generally speaking, the optical properties of composite materials are closely related to their electronic structures. The investigation of the optical properties of composite materials has important application significance. Figure 5 shows the change in the optical absorption of graphene with the adsorbed Al atom. For the sake of ease of expression in Figure 5, PG-Al represents pristine graphene with the adsorbed Al atom, VG-Al represents VG with the adsorbed Al atom and the B-doped graphene with the adsorbed Al atom; however, the n-type doping was formed for VG with the adsorbed Al atom and the B-doped graphene with the adsorbed Al atom; and NG-Al represents N-doped graphene with the adsorbed Al atom. In the case of the highest absorption peak, it is worth noting that, compared to pristine graphene with the adsorbed Al atom, the maximum absorption peaks of the other graphene-reinforced aluminum-based composites all show different degrees of red-shift. B-doped graphene with the adsorbed Al atom has the highest absorption peak among these composites. The results obtained have reference value for the field of optoelectronic devices.

Figure 4. Density of states: (a) pristine graphene with adsorbed Al atom; (b) VG with adsorbed Al atom; (c) B-doped graphene with adsorbed Al atom; (d) N-doped graphene with adsorbed Al atom.

Figure 5. Optical absorption of pristine graphene with adsorbed Al atom, VG with adsorbed Al atom, B-doped graphene with adsorbed Al atom, and N-doped graphene with adsorbed Al atom.

4. Conclusions

The adsorption of the Al atom on pristine, VG, B-doped, and N-doped graphene has been investigated by first-principles calculations. Our calculations indicate that VG and doped graphene with the adsorbed Al atom can significantly improve the final adsorption height, adsorption energy, and charge transfer between graphene and the Al atom. The p-type doping was formed for VG with the adsorbed Al atom and the B-doped graphene with the adsorbed Al atom; however, the n-type doping
was formed for N-doped graphene with the adsorbed Al atom. Importantly, the adsorption results and DOS show that there exists a stable chemical adsorption after defects or doping. Moreover, we also found that defects and doping lead to a red-shift of the highest optical absorption peaks. The results of the investigation provide a theoretical basis for the future application of graphene-reinforced aluminum-based composites in optical and optoelectronic devices.

**Author Contributions:** Conceptualization, X.D. and T.S.; methodology, X.D. and T.S.; software, T.S. and H.L.; validation, X.D. and T.S.; formal analysis, X.D. and T.S.; investigation, X.D. and J.C.; resources, T.S. and H.L.; data curation, X.D.; writing—original draft preparation, X.D.; writing—review and editing, J.C.; visualization, T.S.; supervision, T.S.; project administration, T.S.; funding acquisition, T.S. All authors have read and agreed to the published version of the manuscript.

**Funding:** The authors acknowledge the financial support from the National Natural Science Foundation of China (Grant No. 51677044), the Natural Science Foundation of Heilongjiang (Grant No. E2018047) and the Outstanding Youth Innovation Foundation of Harbin (Grant No. 2017RAYXJ022).

**Conflicts of Interest:** The authors declare no conflict of interest.

**References**

1. Stankovich, S.; Dikin, D.A.; Dommett, G.H.; Kohlhaas, K.M.; Zimney, E.J.; Stach, E.A.; Piner, R.D.; Nguyen, S.T.; Ruoff, R.S. Graphene-based composite materials. *Nature* **2006**, *442*, 282. [CrossRef] [PubMed]
2. Bartolucci, S.F.; Paras, J.; Rafiee, M.A.; Rafiee, J.; Lee, S.; Kapoor, D.; Koratkar, N. Graphene–aluminum nanocomposites. *Mat. Sci. Eng. A* **2011**, *528*, 7933–7937. [CrossRef]
3. Wang, J.; Li, Z.; Fan, G.; Pan, H.; Chen, Z.; Zhang, D. Reinforcement with graphene nanosheets in aluminum matrix composites. *Scripta Mater.* **2012**, *66*, 594–597. [CrossRef]
4. Tjong, S.C. Recent progress in the development and properties of novel metal matrix nanocomposites reinforced with carbon nanotubes and graphene nanosheets. *Mater. Sci. Eng. R Rep.* **2013**, *74*, 281–350. [CrossRef]
5. Seyed, P.N.; Asgharzadeh, H. Aluminum Matrix Composites Reinforced with Graphene: A Review on Production, Microstructure, and Properties. *Crit. Rev. Solid State Mater. Sci.* **2019**. [CrossRef]
6. Singh, J.; Chauhan, A. Overview of wear performance of aluminum matrix composites reinforced with ceramic materials under the influence of controllable variables. *Ceram. Int.* **2016**, *42*, 56–81. [CrossRef]
7. Novoselov, K.S.; Geim, A.K.; Morozov, S.V.; Jiang, D.; Zhang, Y.; Dubonos, S.V.; Grigorieva, I.V.; Firsov, A.A. Electric field effect in atomically thin carbon films. *Science* **2004**, *306*, 666–669. [CrossRef]
8. Meng, J.; Shi, X.; Wang, M.; Zhang, S.; Kong, X. Microstructure and wear resistance of graphene-reinforced aluminum matrix composites. *Mater. Res. Express* **2018**, *6*, 026517. [CrossRef]
9. Chen, L.Y.; Konishi, H.; Fehrenbacher, A.; Ma, C.; Xu, J.Q.; Choi, H.; Xu, H.F.; Pefferkorn, F.E.; Li, X.C. Novel nanoprocessing route for bulk graphene nanoplatelets reinforced metal matrix nanocomposites. *Scripta Mater.* **2012**, *67*, 29–32. [CrossRef]
10. Jagannadham, K. Electrical Conductivity of Copper-graphene Composite Films Synthesized by Electrochemical Deposition with Exfoliated Graphene Platelets. *J. Vac. Sci. Technol. B* **2012**, *30*, 6887–6890. [CrossRef]
11. Zhao, Z.Y.; Guan, R.G.; Guan, X.H.; Feng, Z.X.; Chen, H.; Chen, Y. Microstructures and properties of graphene-Cu/Al composite prepared by a novel process through clad forming and improving wettability with copper. *Adv. Eng. Mater.* **2015**, *17*, 663–668. [CrossRef]
12. Politoano, G.G.; Cazzanelli, E.; Versace, C.; Castriotta, M.; Desiderio, G.; Davoli, M.; Vena, C.; Bartolini, R. Micro-Raman investigation of Ag/graphene oxide/Au sandwich structure. *Mater. Res. Express* **2019**, *6*, 075605. [CrossRef]
13. Castriotta, M.; Politoano, G.G.; Vena, C.; De Santo, M.P.; Desiderio, G.; Davoli, M.; Vena, C.; Cazzanelli, E.; Versace, C. Variable angle spectroscopic ellipsometry investigation of CVD-grown monolayer graphene. *Appl. Surf. Sci.* **2019**, *467*, 213–220. [CrossRef]
14. Fan, Z.; Hu, M.; Liu, J.; Luo, X.; Zhang, K.; Tang, Z. First-Principles Investigation of Adsorption of Ag on Defected and Ce-doped Graphene. *Materials* **2019**, *12*, 649. [CrossRef] [PubMed]
15. Liu, Y.; An, L.; Gong, L. First-principles study of Cu adsorption on vacancy-defected/Au-doped graphene. *Mod. Phys. Lett. B* **2018**, *32*, 1850139. [CrossRef]
16. Rad, A.S. Al-doped graphene as a new nanostructure adsorbent for some halomethane compounds: DFT calculations. *Surf. Sci.*, **2016**, *645*, 6–12. [CrossRef]

17. Dazhi, F.; Guilu, L.; Shuang, Z. Effects of vacancy and deformation on an Al atom adsorbed on graphene. *Chin. J. Phys.* **2018**, *56*, 689–695. [CrossRef]

18. Clark, S.J.; Segall, M.D.; Pickard, C.J.; Hasnip, P.J.; Payne, M.C. First principles methods using castep. *Z. Kristallogr.* **2005**, *220*, 567–570. [CrossRef]

19. Perdew, J.P.; Chevary, J.A.; Vosko, S.H.; Jackson, K.A.; Pederson, M.R.; Singh, D.J.; Fiolhais, C. Erratum: Atoms, molecules, solids, and surfaces: Applications of the generalized gradient approximation for exchange and correlation. *Phys. Rev. B* **1993**, *48*, 4978. [CrossRef]

20. Perdew, J.P.; Burke, K.; Wang, Y. Generalized gradient approximation for the exchange-correlation hole of a many-electron system. *Phys. Rev. B* **1996**, *54*, 16533–16539. [CrossRef]

21. Perdew, J.P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868. [CrossRef] [PubMed]

22. Dai, Y.H. Convergence properties of the BFGS algorithm. *SIAM J. Optim.* **2002**, *13*, 693–701. [CrossRef]

23. Lin, K.H.; Sun, C.; Ju, S.P.; Smith, S.C. Density functional theory study on adsorption of Pt nanoparticle on graphene. *Int. J. Hydrogen Energ.* **2013**, *38*, 6283–6287. [CrossRef]

24. Zhou, X.; Zhao, C.; Wu, G.; Chen, J.; Li, Y. DFT study on the electronic structure and optical properties of N, Al, and N-Al doped graphene. *Appl. Surf. Sci.* **2018**, *459*, 354–362. [CrossRef]

25. Wan, W.; Wang, H. First-Principles Investigation of Adsorption and Diffusion of Ions on Pristine, Defective and B-doped Graphene. *Materials* **2015**, *8*, 6163–6178. [CrossRef]

26. Dai, X.; Shen, T.; Liu, H. DFT study on electronic and optical properties of graphene modified by phosphorus. *Mater. Res. Express* **2019**, *6*, 085635. [CrossRef]

27. Surya, V.J.; Iyakutti, K.; Mizusek, H.; Kawazoe, Y. Tuning electronic structure of graphene: A first-principles study. *IEEE Trans. Nanotechnol.* **2012**, *11*, 534–541. [CrossRef]

28. NE, M.L.O.; Boujnah, M.; Benyoussef, A.; El Kenz, A. Comparative study of electronic and optical properties of graphene and germanene: DFT study. *Optik* **2018**, *158*, 693–698.

29. Yu, W.J.; Liao, L.; Chae, S.H.; Lee, Y.H.; Duan, X. Toward tunable band gap and tunable dirac point in bilayer graphene with molecular doping. *Nano Lett.* **2011**, *11*, 4759–4763. [CrossRef]