Diamond & Related Materials 19 (2010) 1240–1244

Contents lists available at ScienceDirect

Diamond & Related Materials

journal homepage: www.elsevier.com/locate/diamond

Diffusion and coalescence of vacancies and interstitials in graphite: *A first-principles study*

Hongyu Zhang [a], Mingwen Zhao [a,*], Xinmei Yang [a], Huihao Xia [b], Xiangdong Liu [a], Yueyuan Xia [a]

[a] School of Physics, Shandong University, Jinan 250100, Shandong, PR China
[b] Key Laboratory of Nuclear Analysis Technique (Shanghai), Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 210800, PR China

ARTICLE INFO

Article history:
Received 12 November 2009
Received in revised form 2 May 2010
Accepted 1 June 2010
Available online 9 June 2010

Keywords:
First-principles calculations
Vacancy
Interstitial
Graphite
Diffusion
Coalescence

ABSTRACT

The study of dynamics of point defects in graphite is crucial for understanding the evolution of defect-induced ferromagnetism in $^{12}C^{+}$ irradiated graphite. In this work, we perform first-principles calculations to explore the diffusion and coalescence of vacancies and interstitials in graphite. Different kinds of point defects, such as monovacancy, divacancy, 'bridge' and 'spiro' interstitials are considered using non-interacting and interacting models. The energetics, the diffusion paths, and the migration energies of these defects and the energy barriers for the reaction between these defects are predicted. The annealing behaviors of point defects and related ferromagnetism found in $^{12}C^{+}$ irradiated graphite are discussed.

1. Introduction

Point defects in graphite, which are inevitably generated under irradiation conditions, have been studied extensively due to the technological importance of graphite as a reactor material. The simplest intrinsic defects are vacancies and interstitials (or adatoms) [1]. Thrower and Mayer derived the creation and migration energies of the vacancy and interplane interstitial from experimental data [2]. There are a number of theoretical studies on the energetics, structural and electronic properties of the vacancies [3–5] and adatoms [4,6] in graphite, but most of them modeled these defects in a non-interacting graphene sheet, especially in the study of their dynamics behaviors [5,6]. However, under ion irradiation conditions, the generated interstitials lie predominantly in the interlayer space [7], where the interactions between the point defects and the adjacent layers would inevitably affect the structure and the dynamics of the defects, in particular for the cases of interstitials [4]. Theoretically, few works have been reported regarding the diffusion and aggregation behaviors of the point defects in the interlayer space of graphite until now. These works will offer virtual information for understanding the growth mechanisms of carbon nanotubes [1,8], tailoring their physical properties [4], and engineering defect structures in carbon materials [9].

Additionally, recent experiments showed that ion implantation can trigger ferromagnetism in nonmagnetic graphite [10–13]. Both theoretical and experimental works correlated the ferromagnetism to the point defects generated under irradiation conditions [10–14]. For example, the positron annihilation spectrum of virgin and $^{12}C^{+}$-irradiated graphite indicated that carbon implantation produces monovacancies and vacancy clusters accompanied by ferromagnetism. Nevertheless, when the samples were annealed at 200 °C, the vacancies and the ferromagnetism disappeared simultaneously [13]. In order to understand the annealing behaviors and the ferromagnetism evolution in $^{12}C^{+}$-implanted graphite, theoretical study of the diffusion and aggregation of point defects is quite necessary.

In this contribution, we employed first-principles calculations within density functional theory (DFT) to study the equilibrium structures, formation energies, and migration and reaction paths of vacancy and interstitial defects in graphite. Both interacting graphite and non-interacting graphene models were considered. We aim to provide a more profound understanding of the thermal behaviors of the vacancies and interstitials in graphite which are closely correlated to magnetic carbon materials.

2. Methods and computational details

All the DFT calculations were performed using the DMOL3 package [15,16]. Generalized gradient approximation (GGA) in the form of the Perdew and Wang (PW91) [17] and the double numerical basis set with polarization function (DNP) were selected for the spin-unrestricted DFT calculations. For graphene, we used an 8×8 supercell which is repeated periodically along *x*- and *y*-directions, while a vacuum region of 13 Å was applied in the direction

* Corresponding author.
E-mail address: zmw@sdu.edu.cn (M. Zhao).

0925-9635/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.diamond.2010.06.010

perpendicular to the graphene plane to exclude the mirror interactions between adjacent images. Graphite was modeled by a $5\times5\times1$ supercell containing two graphene layers with an AB stacking sequence. The Kohn–Sham equations were solved self-consistently with a convergence of 10^{-5} hartree on the total energy. Atomic positions of reactants and products were fully relaxed without any symmetric constraints until the maximal forces were less than 0.002 hartree/Å. The linear or quadratic synchronous transit (LST/QST) transition state (TS) search algorithm [18] combined with conjugate gradient refinements was used to construct the diffusion paths. Once convergences of TS search calculations have been achieved, the vibrational spectrum of the predicted TS structure should have exactly one mode with negative vibrational frequency [19]. To determine if the transition state connects to the relevant reactant and product, we performed minimum-energy pathway (MEP) calculations using the nudged elastic band (NEB) method [20]. The formation energies (E_f) of a vacancy or an interstitial atom is defined by the formula [21]: $E_f = E_d + n\mu - E_p$, where E_d and E_p represent the total energies of defective and perfect supercells of graphene or graphite, respectively, which were calculated using the same supercell size. The chemical potential of carbon (μ) was evaluated as the total energy per atom of graphite. n is the number of carbon atoms that were removed (positive n value) or added (negative n value) to create a vacancy or an interstitial defect. Obviously, the smaller the E_f values are, the more stable the structures are [1].

As known, the interlayer interaction in perfect graphite is mainly dominated by weak dispersion forces, which may not be well reproduced in DFT. We calculated the total energy evolution as a function of interlayer spacing to test the validity of the present theoretical strategy in reproducing the stable configurations involving interlayer interactions. The equilibrium interlayer distance is about 3.4 Å, in agreement with the experimental value. Moreover, for the graphite model containing interstitials, the interactions mediated by the interstitials are much stronger than the dispersion interactions, and can be reproduced well in DFT calculations. This suggests that the theoretical strategy adopted in this work can describe efficiently the multi-layer effects on the energetics, structures, and diffusion and coalescence behaviors of point defects in graphite.

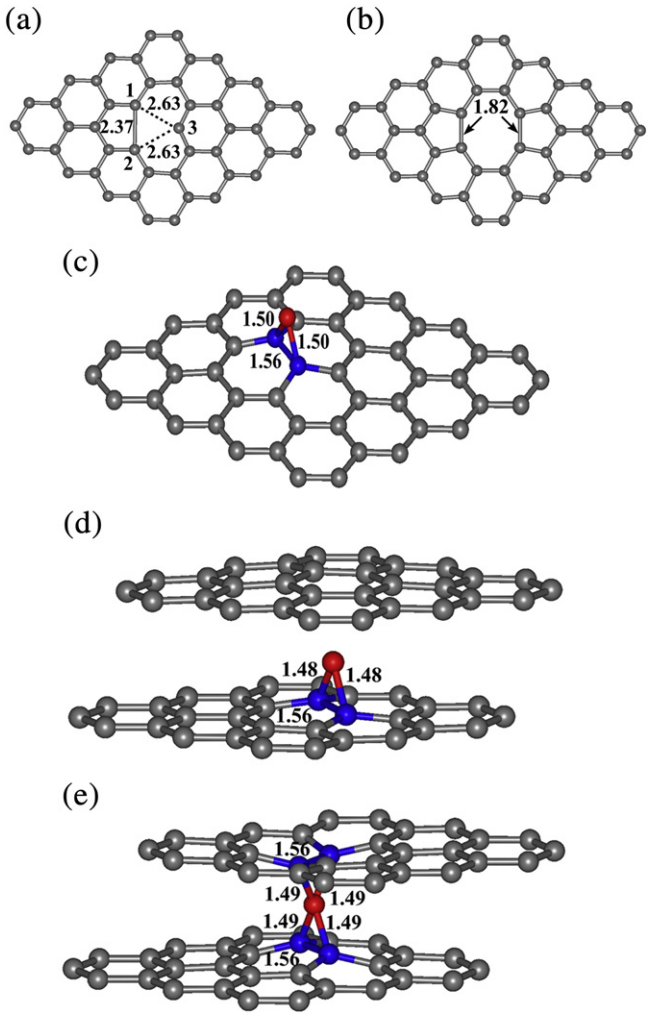

Fig. 1. Equilibrium configurations of vacancies and interstitials obtained by full optimization. (a) monovacancy and (b) divacancy on a graphene layer; (c) adatom on a graphene layer; (d) 'bridge' and (e) 'spiro' interstitial structures in graphite. Red balls represent the interstitial atoms. All distances and bond lengths are in Å.

3. Results and discussion

3.1. Vacancy defects

We first took a non-interacting graphene model to study a monovacancy defect. The monovacancy in graphene undergoes a Jahn–Teller distortion upon relaxation, where two of the atoms nearest to the monovacancy (atoms 1 and 2 in Fig. 1(a)) move closer, forming a pentagon-like structure while the third atom extrudes out of the plane by 0.29 Å, as illustrated in Fig. 1. The distance between atoms 1 and 2 is shortened to 2.37 Å in comparison with the C–C covalent bond length of 1.42 Å for graphene. Our results agree with other theoretical predictions [3,4,22] and experimental observations. Experimentally, direct imaging of monovacancies with well-defined twofold symmetry in single-layer graphene has been demonstrated at atomic resolution[23,24].The formation energy of a monovacancy was calculated to be 7.85 eV (see Table 1), consistent with the experimental value, 7.0 ± 0.5 eV [2] and other theoretical results of 7.63 eV [9] and 7.8 eV [25]. In order to evaluate the energy barrier for a monovacancy diffusing in a graphene layer, we searched for the transition state along the diffusion path, as shown in Fig. 2(a). A transition state along the migration path was identified. Starting from the transition state and moving down towards minima along both the reactant and the product directions, the reaction pathway was followed. As expected, no minima were found on the pathway other than the reactant and product. Therefore, the transition state predicted with LST/QST method does connect the reactant and product in these cases. The energy barrier is about 1.37 eV, also close to the results of previous calculations which are 1.6 eV [25] and 1.3–1.4 eV [22]. The good consistency between the results of our work and those of other theoretical and experimental works again confirms the validity of our theoretical strategy in reproducing the structures and behaviors of point defects in graphite.

Divacancy, the simplest form of multi-vacancy defects, can be characterized by removing two adjacent carbon atoms from perfect graphene. The carbon atoms in the neighborhood of vacancy site have strong tendency to move close to each other to saturate their dangling bonds [26], forming two pentagons and one octagon, which is referred to as a 5-8-5 topological defect [3,5] as shown in Fig. 1(b). The formation energy of a divacancy is 7.53 eV, lower than that of a

Table 1
Formation energies (E_f) and migration energies (E_m) for vacancies and interstitials in graphite. The numbers in parentheses are the data obtained using non-interacting model (graphene).

	Vacancy		Interstitial	
	Monovacancy	Divacancy	'Spiro'	'Bridge'
E_f (eV)	7.84 (7.85)	(7.53)	6.20	7.68 (6.64)
E_m (eV)	1.26 (1.37)	(7.49)	2.12	0.36 (0.53)