IOP Conf. Series: Materials Science and Engineering **394** (2018) 022020 doi:10.1088/1757-899X/394/2/022020

Molecular Dynamics Simulations of Si ion Substituted Graphene by Bombardment

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Abstract. Molecular dynamics simulations with Tersoff-Ziegler-Biersack-Littmark (Tersoff-ZBL) potential and adaptive intermolecular reactive empirical bond order (AIREBO) potential are performed to study the substitutional process of silicon ions by bombardment. The silicon ions bombardment of graphene is simulated at energies 100 eV, 100 eV, 68 eV and 67 eV, respectively. All silicon atoms are substitute for the relevant carbon atoms at these energies. And a perfect region of SiC structure in graphene sheet is observed, this approach can viewed as a new preparation of graphene-based SiC electronics in theory.

1. Introduction

Graphene-based electronics has aroused much attention due to its excellent electronic properties[1,2], as well as its predominant thermal[3,4], mechanical[5], and optical properties.[6] And it is extensively used to transistors[7,8], transparent electronic materials[9], and sensors[10,11]. For mainstream logic applications, graphene material is needed to control over the band structure and electrical properties. Defect formation is a method of tuning the electronic structure and properties. Simulations on the electron or ion bombardment of various nanostructures demonstrate that this approach presents beneficial effects[12], leading to its widespread application in the high-precision manipulation of nanomaterial structures and properties.[13] Recently, performing molecular dynamics simulation, Bellido[14] studied the effect of irradiating graphene with carbon ion at different positions and energies. The simulation revealed four processes: absorption, reflection, damage, and transmission. Zhao[15] used two types of clusters to determine the influence of such clusters on graphene after bombardment, and demonstrated that by choosing a suitable cluster species and controlling its energies, nanopores of desired sizes and qualities can be fabricated in a graphene sheet. Another method of modifying the band structure of material effectively achieved through functionalization. Santos[16] studied the magnetism of the recently detected substitutional Ni (Ni_{sub}) impurities, and reported that Ni_{sub} defects are nonmagnetic in flat graphene and develop a nonzero-spin moment only in metallic nanotubes. Gan[17] have observed substitutional Au and Pt atoms in graphene monolayer and pointed out that the high stability for such substitutional defects was due to the strong covalent carbon-metal bonding. Using density functional theory (DFT), for example, Zhou[18] studied the structural and electronic properties of Si-substituted graphene and

found substitution-induced band gap changes. Silicon carbide (SiC) is a promising material for operation in harsh environments because its large drift velocity, breakdown voltage, and thermal conductivity.[19] Using molecular dynamics simulations, the multiple carbon atoms in graphene sheet are bombarded by multiple silicon ions with certain energy level. The process of silicon atoms substitute for relevant carbon atoms is analyzed. And these cases of substitution in graphene, offering a potential for preparation of new SiC material—graphene-based silicon carbide—with exceptional properties, such as low density, tunable band gap, and possible transport properties. In this paper, the graphene sheet is bombarded by different positions of four silicon ions. We report a series of processes of Si atoms substitute for carbon atoms in graphene sheet, by molecular dynamics simulations based on hybrid Tersoff-ZBL potential and adaptive intermolecular reactive empirical bond order (AIREBO) potential.

2. Simulation conditions and methods

Empirical molecular dynamics was performed to simulate the bombardment of Si ion on the monolayer graphene. The interaction between silicon atom and carbon atom were described with a hybrid Tersoff-ZBL potential[20-23] that smoothly connects the Tersoff and the ZBL potentials. The Ziegler-Biersack-Littmark (ZBL) potential, also known as the universal repulsive potential, is the most widely used analytical potential to describe collision. The Tersoff potential were recently used to study the structural, energetic, and elastic properties of carbon nanomaterials. To model the C-C interatomic interaction in the graphene, the adaptive intermolecular reactive empirical bond order (AIREBO) potential[24] is used. This potential enables the breaking and creation of covalent bonds, and has been successfully used to study the properties of carbon-based nanomaterials.[25]

The graphene target used in the simulations has dimensions of 10×10 nm^2 and consists of 3807 atoms. To conveniently analyze the bombardment results, these atoms are labeled, Si_1 denotes the silicon ion whose ID is 1. And Si_2, Si_3, and Si_4 are the silicon ion whose ID is 2, 3, and 4, respectively. C_1, C_2, and C_3 are the carbon atom whose ID is 1, 2 and 3, respectively. The graphene sheet was centered at the origin of coordinates, lying on the x-y plane; the initial positions of these Si ions are shown in table 1.

Table1. The initial positions of silicon ions.

	Si_1	Si_2	Si_3	Si_4
x	0.0	-1.23	1.23	-2.46
y	0.0	2.13	2.13	0.0
z	40.0	50.0	61.0	71.0

Two opposite ends of the graphene are fixed to simulate a suspended system. Periodic boundary conditions were applied on the x and y directions. The time step chosen was 0.05 fs in whole simulation. After minimization, a temperature ramp of 20 K to 300 K was applied with a Berendsen thermostat[26], and a damping time of 1000 fs was adopted. Then, the system was kept at 300 K with a damping time of 1000 fs until it reached equilibrium. Finally, an NVE ensemble was set for the rest of the simulations, in which ion bombardment was induced. Velocity is imposed in the −z direction to the every silicon ion. A neutral silicon atom is considered for the bombardment simulations, because if the bombardment were performed with charged atoms then the charge of the ion would have been neutralized on the surface by charge exchange. The model of bombardment is shown in Figure 1.

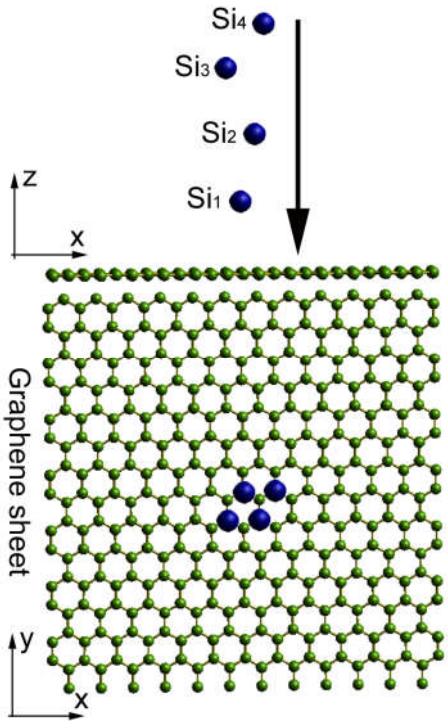

Figure 1. The model of bombardment. This figure has shown the front view and top view during bombardment. And the initial kinetic energy of Si_1, Si_2, Si_3, Si_4 is 100 eV, 100eV, 68 eV 67 eV, respectively.

3. Results and analysis

MD simulation of silicon ion-bombardment is performed at four different positions on the same simulation. The substitutional process, which carbon atom far away from the balance position and relevant silicon atom occupied the place, is observed by special visualization tools in our simulation.

This process of bombardment has experience a series of steps. Figure 2 shows the snapshots of structural evolution with time in graphene sheet. Initial kinetic energy of 100 eV, 100eV, 68 eV, 67eV are imposed on Si_1 ion, Si_2 ion, Si_3 ion, Si_4 ion to impact the graphene sheet, respectively. At 0 fs, all silicon ions were placed at its initial position, and all the carbon atoms of graphene sheet were located in balance positions. The graphene sheet maintained a perfect benzene-ring structure (Figure 2(a)). Then these energetic silicon ions move along the z-axis toward the graphene sheet to impact the carbon atoms of graphene sheet. During the bombardment, the procedure of energy transfer and the repulsive interaction between the incident ion and carbon atom in the graphene sheet play an important role in collision at the NVE ensemble. When the time is 170 fs, the C_{1944} atom is knocked by Si_{3808} ion with the energy of 100 eV, because the Si_{3808} ion has enough energy to overcome the electrostatic repulsion of graphene sheet. The C_1-C_5, C_1-C_6 and C_1-C_7 bonds are broke by energetic Si_1, and the C_1 atom moves away from the graphene due to it possess sufficient energy to conquer the attractive force of neighboring carbon atoms. After this, the Si_1 atom replaces the position of C_1 atom, the interaction between the incident Si_1 ion and neighboring atoms promotes bond formation. The phenomena of Si_1 atom substitute for C_1 atom is present with the Si_1-C_5 bond, Si_1-C_6 bond and Si_1-C_7 bond formation (Figure 2(b)). At 205 fs, the C_2 atom is collided by Si_2 ion with the energy of 100 eV, and it escape away from the lattice position after the C_2-C_5, C_2-C_8 and C_2-C_9 bond breakage. Then Si_2 atom occupies the place of C_2 atom, however, just two bonds (Si_2-C_8 bond and Si_2-C_9 bond) are formed and a distorted 10-membered-ring of Si-C is present (Figure 2(c)). This phenomena is due to the large relative distance between Si_2 atom and C_2 atom (1.989 Å) than Si-C bond length (1.889 Å)[27], and the graphene lattice is disturbed by bombardment. At 300 fs, the C_3 atom is replaced by Si_3 atom with the

initial energy of 68 eV, and severely distortion of graphene lattice is observed in this condition (Figure 2(d)). As a result of severely distortion, the Si_3-C_9 bond and Si_3-C_{10} bond are not formed. And the distance from Si_3 atom to C_9 atom is 1.917 Å, the distance from Si_3 atom to C_{10} atom is 2.378 Å. A distorted 12-membered-ring with interstitial Si atom is observed. At 375 fs, Si_4 with initial energy of 67 eV takes over the position of C_4 atom (Figure 2(e)). The energetic Si_4 ion breaking three bonds (C_4-C_5 bond, C_4-C_{11} bond and C_4-C_{12} bond), and then the C_4 atom moves from the lattice position. The Si_4-C_{11} bond and Si_4-C_{12} bond as well as lattice distortion are observed in this moment. A distorted 12-membered-ring with interstitial Si atom and a distorted 10-membered-ring are present. When the time from 500 fs to 1500 fs (Figure 2(f), 2(g), 2(h)), the extent of lattice distortion decreases with time due to the process of lattice thermal vibration. As a result, this process results in the Si_4-C_5 bond, Si_3-C_9 bond and Si_3-C_{10} bond formation. Finally, a prefect substitution is observed in Figure 2(h).

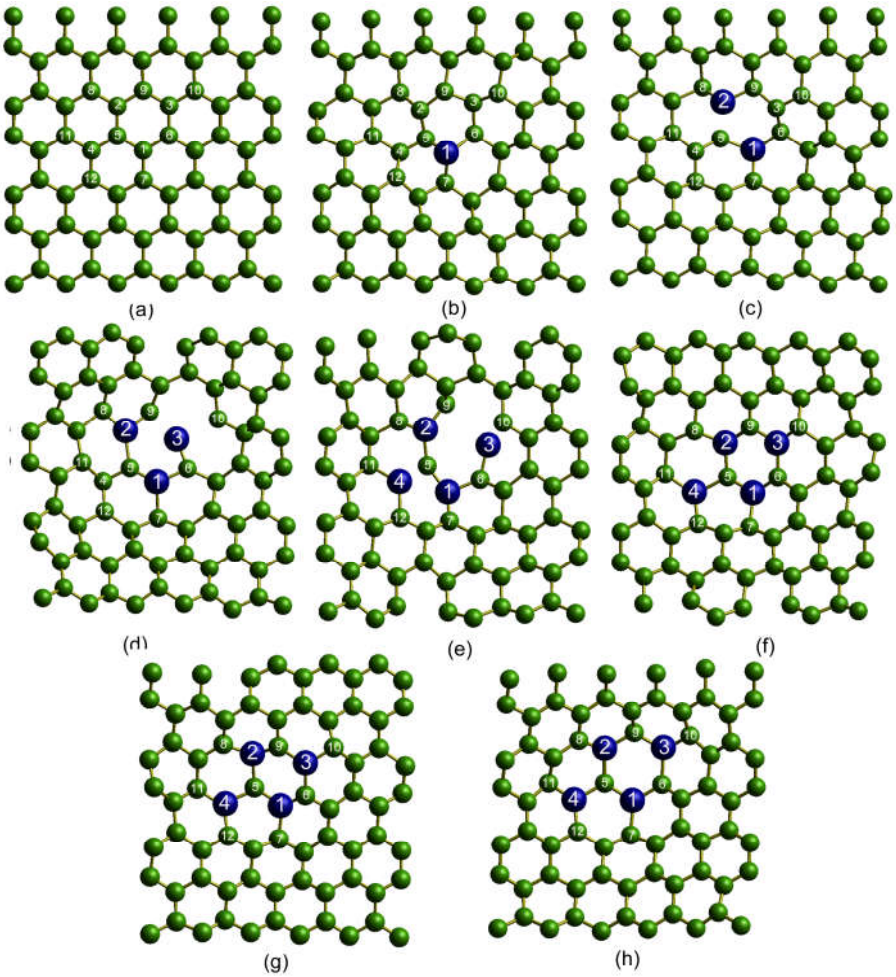

Figure 2. The structural evolution of graphene during bombardment with four energies silicon ions: (a) 0 fs; (b) 170 fs; (c) 205 fs; (d) 300 fs; (e) 375 fs; (f) 500 fs; (g) 100 0fs; (h) 1500 fs.

4. Conclusion

MD simulations were performed to investigate the substitutional process of Si ions. The silicon ions bombardment of graphene is simulated at energies 100 eV, 100 eV, 68 eV and 67 eV, respectively. All silicon atoms are substitute for the relevant carbon atoms at these energies. Finally, a perfect region of SiC structure which different from traditional SiC structure is observed in this condition. And this model can be viewed as a preparation method of new SiC structure material from graphene.

Acknowledgments
This work is supported by the Natural Science Foundation of Guizhou Province of China (Grant NO. [2015] 2001), the innovation team of Anshun University (Grant NO. 2015PT02), the school project of Anshun University (Grant NO. [2015]AQ07).

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