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Single vacancy defects diffusion at the initial stage of graphene growth: A first-principles study

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ABSTRACT

The migration of a single vacancy (SV) defect in graphene fragment (GF) has been investigated by density functional theory (DFT). The results revealed that a single vacancy defect is easy to migrate to the GF edge. The interaction between an SV and a five-numbered ring at the edge results in two neighboring five-membered rings finally, while the interaction between an SV and a seven-membered ring defect at the edge of the GF leads to a five-numbered ring and a neighbor seven-numbered ring. Our findings shed light upon understanding of the growth process of the graphene grain boundary.

Graphene, a one-atom-thick planar sheet of sp^2-bonded carbon atoms in a honeycomb lattice, has drawn significant attention with its outstanding electrical [1], mechanical [2], and chemical properties [3,4]. The strong in-plane σ bonds form the backbone of the honeycomb, while the half-filled π bonds exhibit linear band dispersion near the K points [5]. It is now widely accepted that graphene is one of the most promising materials for future electronic devices. Ma and his coworkers demonstrate the growth of single-crystal graphene and three-dimensional flexible and conductive interconnected graphene networks in a chemical vapor deposition process [6,7]. Experimentally, typical CVD synthesis of graphene on a metal substrate starts with the nucleation of individual graphene grains randomly distributed across the metal surface [8–11]. Graphene grains (GB) continue to grow with time and eventually merge together to form a continuous polycrystalline film [12]. The atomic rearrangement at grain boundaries is typified by the formation of Stone–Wales (SW) defects consisting of pentagon–heptagon pairs [13,14]. Divacancies in graphene have various reconstructed structures, such as triple pentagon–triple heptagon (555-777) and pentagon–octagon–pentagon (5-8-5) patterns. [15,16]. Kotakoski et al. show how the transformation occurs step by step by nucleation and growth of low-energy multivacancy structures consisting of rotated hexagons and other polygons [17]. Karoui et al. report that the action of Ni atoms plays a key role in the healing of defective graphene sheet [18]. Vacancy defects were seldom observed spontaneously in experiments. It is generally believed to be created by energetic electrons bombarding the sample under SEM/TEM investigation [15,17,19]. However, structural defects may appear during growth or processing. Experimental results suggest that the disordered domains shrink leaving small clusters of defects alongside epitaxially matched graphene as the growth temperature is increased [14]. Study on the growing edges of graphene at the transient stages of epitaxial growth indicates the formation and collapse of large carbon rings together with the formation and healing of Stone–Wales like pentagon–heptagon defects [20]. In an addition, their results further prove the role of the substrate in the epitaxial growth and in the healing of defects [20].

The presence of defects have been shown to severely degrade the electronic, transport, and mechanical properties of graphene [21,22]. Single vacancy is a type of fundamental defect in graphene growth. In-depth understanding of the diffusion of SV is important for the synthesis and application of this two-dimensional material. Hence, the study focuses on an SV in GFs and its interaction with five-membered ring or seven-membered ring at GF edges. Our results showed that single vacancy defects prefer to diffuse to the boundary of graphene fragments, resulting in some five-membered rings at the edge of graphene fragments.

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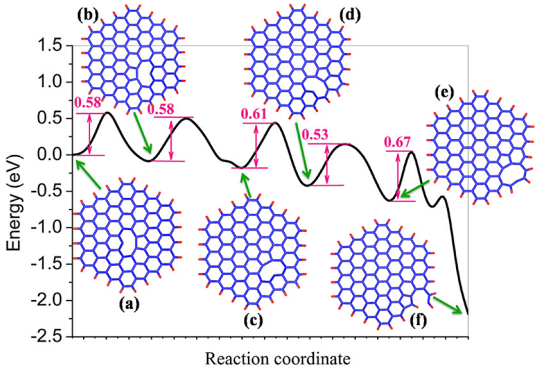

Fig. 1. Energy profile and the selected intermediate states for the process of single vacancy defect migration in $C_{95}H_{24}$.

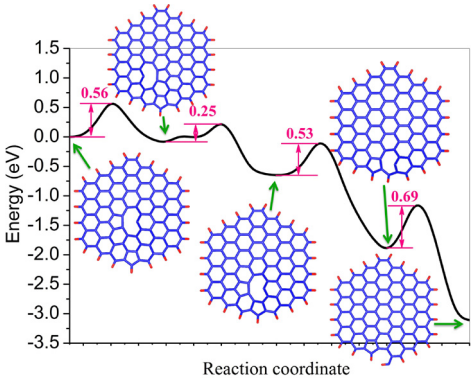

Fig. 2. Energy profile and the selected intermediate states for the process of an SV defect migration along the path from centre to the edge of graphene fragment $C_{94}H_{23}$.

The DFT calculations for structural relaxation of graphene fragments and the energy barriers for the migration of single vacancies in graphene fragments were performed using the plane-wave self-consistent field (PWSCF) code of the QUANTUM-ESPRESSO package [23]. Generalized gradient approximation (GGA) parameterized with the PBE exchange–correlation functional and Vanderbilt ultrasoft pseudopotentials was used. Reciprocal space integrations were carried out using only the Gamma point. The energy cut-offs of the plane-wave basis and electron density is 25 Ry and 250 Ry, respectively. The convergence threshold for self-consistency was set to 10^{-8} Ha, and that of the total energy tolerance to 10^{-5} Ha. The geometry optimization was performed with the force criterion on each atom being below 10^{-3} Ha/Å. The clusters were placed into a super-cell with the length of a side equal to $55 \times 55 \times 25$ Bohr to avoid spurious interactions. The convergences of the optimized geometry and the total energy have been carefully checked with respect to the above parameters. Energy barriers for the migration of single vacancies in graphene fragments were calculated using the climbing-image nudged elastic band (cNEB) method for locating the transition state [24]. The initial inter-image distance we used in our calculation is about 1.0 Bohr. The cNEB is a very useful method in finding the minimum-energy path between a given initial and final states of a reaction step. It can give a continuous path even when multiple minimum-energy paths exist [24,25].

We first studied single vacancy defect diffusion in a free-standing graphene fragment without any defect at its edge. An SV defect appears when one carbon atom is removed in the graphene fragment. The energy profile of SV diffusion in GF $C_{95}H_{24}$ and the selected intermediate structures in the migration process are displayed in Fig. 1. The energies of intermediate states (b), (c), (d), (e), and final state (f) relative to configurations (a) are −0.08 eV, −0.18 eV, −0.41 eV, 0.63 eV and −2.22 eV, respectively. The relative energies decrease in the migration process of the SV from centre to the edge of the graphene fragment. An SV defect located in the central area of the GF are shown in structures (a), (b) and (c), respectively. Total energies decrease slightly from structure (a) to (c), because the strains in the systems are released slightly as the SV moving to the edge. Energy barriers from (a) to (b), and from (b) to (c) are the same (about 0.58 eV). Near the edge of the graphene fragment, total energies decrease remarkably from structure (d) to (f), especially when the SV approaches the edge because of the entirely releasing of the strain. All the barriers are less than 0.67 eV during the migration steps. It suggests that an SV can readily move inside the graphene fragment and prefers to migrate to the periphery of the GF. Three dangling bonds are produced when one carbon atom is missing. Two of the three dangling bonds are saturated, but one dangling bond always remains owing to geometrical reasons as seen in configurations (a), (b), (c), and (d) in Fig. 1. The two-fold coordination carbon atom is out of the graphene fragment plane in configurations (a), (b), (c), and (d) which is defined as John-Teller distortion in earlier report [26]. This distortion leads to the formation of a five-membered and a nine-membered ring. The atoms around the five-membered ring are out of the graphene fragment plane in order to reduce the total energy of the system in configurations (e). But all the atoms are in the same plane when the SV migrates to the edge in configurations (f). As the SV reaches the edge, the five-membered ring remains, while the nine-membered ring collapses. In our simulation, an open six-membered ring forms after the collapse of the nine-membered ring as shown in structure (f). Earlier published results confirm that the growth of a long-range ordered graphene on metal is based on peculiar nanoscale domelike shaped carbon islands [9–11]. The reason of the formation of a domelike shape is that C atoms at the periphery of graphene islands remain bonded to the metal substrate, while the C atoms inside the graphene islands form sp^2 hybridization and become far away from the substrate. This means the sp^2 C–C bond in the graphene is much stronger than the bond between C atom and metal atoms. In our simulation, we use H atoms to saturate the C atoms at the periphery of graphene islands. So if we put the graphene fragment of structure (f) on the surface of metal substrate and use metal atom to saturate marginal C atoms, the open six-membered ring will naturally close and form a perfect six-membered ring. Based on the above data, it is clear that single vacancy defects in graphene or graphene fragment are unstable; it can readily migrate in the graphene towards the boundary and can be annihilated at the edge with the formation of a five-membered ring.

Since, the five-membered carbon rings or seven-membered carbon rings were often observed in experiments [14,15,17,27,28]. Almost all of them locate at grain boundaries. Therefore, it is naturally to believe that the diffusion of the SV is one of the reasons for the formation of the five- or seven-membered rings at the grain boundary. To further reveal the relationship between an SV defect and a five- or seven-membered ring, the diffusion of a single vacancy in GF with a five- and seven-membered ring at its edge was investigated, respectively.

Fig. 2 shows energy profile of the diffusion of an SV defect in $C_{94}H_{23}$ along the path from centre to the five-membered ring at the edge. The selected intermediate structures of the SV defect diffusion are also presented. The total energy of the GF decreases evidently as the SV defect moves from centre to the edge, especially when the SV defect reaching the edge where a five-membered ring exists. The energies of intermediate states and final state relative to the initial configurations in Fig. 2 are −0.08 eV, −0.65 eV, −1.88 eV, and −3.11, respectively. The total energy decreases by 3.11 eV, larger than the previous case without the existence of the