Energetics and dynamics of a new type of extended line defects in graphene

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We revealed a novel extended line defect (ELD) containing tetragonal rings embedded in graphene, formed as growth fault, with its energetic and dynamic behavior studied via first-principles calculations. In our finding based upon the Molecular Dynamics simulation, transformation between locally stable ELDs in graphene at high temperatures simultaneously with contrastive electronic properties can be applied to predetermined formation process and reconstruction of ELDs.

Graphene, a single layer of graphite, is a potential candidate for several technological applications due to its outstanding structural, electronic, thermal and mechanical properties. Graphene inevitably involves defects which are introduced during growth or during irradiation with electrons or ions. Atomic level defects in graphene are known to significantly modify graphene properties and thus allow tuning for novel applications. Therefore, the design of graphene with defects offers a broad potential for useful applications. Investigations of the energetic and dynamic behavior of graphene in the process of formation and growth are important for surveying possible stable local defects. Diffusion, coalescence and reconstruction of vacancy defects and divacancy defects have been theoretically studied. It has been reported recently that an extended line defects (ELD) containing octagonal and pentagonal carbon rings (“585 ELD” as shown in Fig. 1e and 1f) embedded in a perfect graphene sheet was experimentally realized, which has attracted considerable interest in the family of ELD graphene.

In the present paper we predict a new ELD containing tetragonal carbon rings (“4 ELD”) in graphene, by performing geometry optimizations and constant temperature molecular dynamics (MD) simulations at the density functional level of theory (DFT). By investigating the energetic stability and reconstruction process of the novel ELD, several interesting ELDs containing tetragons and heptagons are also discovered. The reconstruction process confirms the importance of the 4 ELD graphene as a starting point for formation of other possible ELDs and in turn suggests the possibility of its formation by transformation from other ELDs. The transition between these ELDs with different electronic properties, such as magnetic moment and conductance, opens up the possibility of developing electronic devices with ELDs.

We used the Troullier-Martins pseudopotential with the generalized gradient approximation (GGA) (Perdew-Burke-Ernzerhof functional) for the density functional theory as implemented in the SIESTA package, with inclusion of spin polarization and an energy mesh cutoff of 250 Ry. In these calculations, a linear combination of numerical localized atomic orbitals (split-valence double-ζ basis set with polarization orbitals) is used as the basis representation of the Kohn and Sham wavefunctions. Our calculations employ periodic boundary conditions with a tetragonal periodic unit cell and a vacuum layer of 10 Å. The size along the direction of the ELD is about 4.92 Å and we use different sizes in the perpendicular direction to represent various situations of adjacent ELDs. The Brillouin zone was sampled using a 6x6x1 Monkhorst and Pack k-point mesh. The convergence in force is 0.02 eV Å⁻¹.

ELD in a 2D lattice can be considered as a relative displacement of the two halves of the lattice, with possible removal of certain atoms located on or adjacent to the defect line, as achieved via spontaneous formation during the growth of graphene. We design the 4 ELD as a counterpart of the 585 ELD in that they share a similar fault formation in which certain lines of carbon atoms are missing during the growth of a lattice, and the adjacent half-lattices are moved together in the direction perpendicular to the defect line. The 4 ELD is formed by collapsing two adjacent lines of atoms (labeled 1 and 2) into each other, as shown in Fig. 1a-b (the similar formation of the 585 ELD is shown in Fig. 1c-d).

The optimized structure of the 4 ELD shows C2 symmetry in Fig. 2a. The middle carbon atoms (such as carbon 3 as shown in Fig. 2a) of the line defect are coordinated with four carbon atoms with all valence electrons saturated and hence energetically favorable. On two sides of the core of the line defect, atoms move out of plane in opposite directions, toward a tetrahedral arrangement similar to that of diamond. However the buckled structures of the line defect do not involve significant displacements of other atoms in the unit cell. The rest of the carbon atoms remain flat, which is quite different from the structure of the Stone-Wales (SW) defect in which the out-of-plane motion at the defect core “pulls” the neighboring atoms out of plane. Such a small structural deviation from the intrinsic graphene sheet maintains most of the electronic structure of graphene such as its Dirac point and its half-metallic properties.

Compared with the 585 ELD, this type of ELD does not change the band structure of the π orbital while only inducing two new local energy levels on both sides of the Fermi energy. Furthermore, the 4 ELD graphene shows no magnetic property. In contrast, the 585 ELD graphene is ferromagnetic with small magnetic moment. These intriguing electronic and magnetic properties of the 4 ELD are suitable for various applications and can be treated as a complementary counterpart to the case of 585 ELD graphene. The bond length C1-C3 (equivalent to all bonds with C3) with the four coordinated carbon atoms is 1.58 Å, close to the C-C bond length (1.54 Å) of diamond. This further indicates that the sp² bonding transforms to sp³ bonding in the
local area of the line defect. The perpendicular spacing between the highest and lowest carbon atoms is ~1 Å. The explanation for the buckling (i.e., out-of-plane displacement) at the line defect is straightforward. The bond angle in perfect graphene is 120°. Due to the fault growth, the bond angle at the line defect is compressed to ~61°. Since motion of carbon atoms within the plane is more difficult than out-of-plane motion, the buckling arises at the line defect to efficiently release the compression. For the relaxed structure, the bond angle C1-C3-C2 (Fig. 2a) at the line defect is ~77°. The C1-C3 (Fig. 2a) bond length at the line defect also increases from the initial 1.44 Å to 1.58 Å.

Scanning tunneling microscopy (STM) is an excellent tool to experimentally identify the existence of defects in graphene. STM simulation can be of great help for this identification due to the complication of interpretation of STM images in experiments. Therefore STM images (Fig. 2a) were calculated from the ab initio charge density (RHO) of defects embedded in the 4 ELD graphene using the Tersoff-Hamann approximation. Since this 4 ELD has not yet been reported experimentally, our simulated image can be considered as a prediction.

To assess whether the proposed 4 ELD graphene is locally stable, we performed ab initio MD simulations at various high temperatures starting from 1000 K with a 500 K increment in each following simulation to 5000 K with the relaxed 4 ELD geometry (Fig. 2a) as the initial structure. Two typical defects were observed at high temperatures: 585 ELD (Fig. 2b) and 747 ELD (Fig. 2c). The same starting structure developed into 747 ELD form at 2000 K but into 585 ELD form in the temperature range 2500 K ~ 4000 K. The structure loses stability above 3000 K. Detailed atomic processes of defect transformation and reconstruction were investigated by carefully analysing the MD trajectories. Fig. 3 presents snapshots of the atomic processes at about 3000 K. First the graphene layer with line defect in Fig. 3a was heated up to about 3000 K via constant temperature MD simulations. Near 3000 K, as shown in Fig. 3b the atom 5 departs further from the plane of the graphene layer and breaks its bonds with atoms 2 and 7. Atom 2 breaks its bond with atom 6 at the same time. In Fig. 3c, atom 5 forms a bond with carbon atom 2. In Fig. 3d, atom 2 makes a bond with carbon atom 6 to form an octagonal ring. In Fig. 3e, atom 2 breaks its bond with atom 1 to form another octagonal ring, which gradually deforms (Fig. 3f-h). Finally in Fig. 3i-j, the two carbon dimers formed by atoms 1 and 4 and by atoms 2 and 5 rotate to make a bond between atoms 1 and 5. Thus two pentagonal rings are formed adjacent to the octagonal ring. The reconstructed 585 line defect is very stable and sustains its shape without any structural transformation for about 5 ps at about 3000 K.

Fig. 4 shows snapshots of the atomic processes during the simulation at 2000 K. First the graphene layer with line defect shown in Fig. 4a was heated to about 2000 K via constant temperature MD simulations. The transformation began after 1.35ps. As shown in Fig. 4b carbon atom 1 breaks its bond with carbon 2; likewise carbon 3 breaks its bond with carbon 4. In Fig. 4c, atom 2 restores its former bond with atom 1. Carbon 3 and carbon 4 remain separated and form an octagonal ring. In Fig. 4d, atom 5 breaks its bond with atom 2 while forming a bond to carbon 3 to form the two symmetrical heptagonal rings. The reconstructed 747 line defect is very stable and sustains its shape without any structural transformation for about 4 ps at about 2000 K.

To investigate the possible interaction of adjacent line defects we also performed MD simulations with a representative larger unit cell containing two line defects separated by five carbon zigzag rows as shown in Fig. 5a. This model, denoted as 4-4’ ELD (Fig. 5a), is different from the former 4 ELD model (Fig. 2a) in that the adjacent line defects are no longer equivalent by one unit displacement along the direction of the ELD. Although the interaction could also be affected by the periodic boundary condition, the simulation could provide some hints for understanding the possible interactions in the real systems. At 3000 K, as shown in Fig. 5b, the two adjacent line defects transform differently. The left line defect transforms into the 585 ELD (similar to 4 ELD at 3000K) while the right line defect reconstructs as the 747 ELD (similar to 4 ELD at 2000K). It should be noted that the 4-4’ ELD at 2000K shows diffusion of the left line defect by one C-C bond length further from the right line defect (and closer to the nearest line defect in the next unit cell to the right, 4 zigzag C rows away). This diffusion results in the disappearance of the relative displacements between the adjacent ELDs (4-4 ELD in Fig. 5c). However the lines of defects in the 4-4 ELD are not exactly equivalent since the distances between adjacent lines are 4 and 6 zigzag rows of carbon atoms. At about 4.5 ps, this 4-4 ELD undergoes 747 and 585 ELD reconstructions similar to those occurring at 3000 K. The process indicates that the left ELD has to diffuse first so that further reconstruction toward 747 ELD could be favored, due to the interaction between nonequivalent ELD lines.

To confirm the stability of the ELDs observed in the MD reconstruction process at various temperatures, we also checked the formation energy per C atom which can be calculated as follows:

$$E_C(\alpha) = \left[ E_T(\alpha) - N_\alpha E_N / N_\alpha \right]$$

where $\alpha$ labels the type of ELD (4, 747, 585, 4’, 4-4, 585-747), $E_T(\alpha)$ is the total energy of a graphene plane containing an $\alpha$-type line of defects. $N_\alpha$ stands for the total number of atoms in the unit cell. $E_N$ is the energy per C atom in perfect graphene. Consequently, $E_C(\alpha)$ is an estimation of the amount of energy required (e.g. through thermal excitation) to achieve the reconstructions. The calculations predict that the graphene layer containing the 585 defect is most stable and its formation energy is lower than that of the 747 defect by 131 meV atom⁻¹. The formation energy of the 4 ELD is much higher than that of the 585 defect by 200 meV atom⁻¹. Our calculations also show that the 4-4 ELD and the 4-4’ ELD have the same formation energy (Table 1), higher than that of 4 ELD due to a larger density of defect lines. After relaxation, the graphene layer containing the 585 ELD recovers a planar configuration, while the 747 ELD maintains a wave-like buckling of the graphene sheet. The corresponding band structures of these 4 ELD and the 747 ELD are presented in Fig. 2(d) and (e). The band structure of the 4 ELD graphene exhibits Dirac point similar to that of the intrinsic graphene but characterizes itself with two flat bands around the Fermi level indicating the existence of the local defect. While for the 747 ELD, the band structure shows metallic property with one band across the Fermi level.

Conclusions

In conclusion, we predict a new class of line defects embedded in graphene via investigation of the reconstruction of growth faults. We observe the transition process between these ELDs under thermal excitation. Our work is expected to stimulate experiments that probe the existence of extended line defects with tetrahedral rings and that explore technical applications based on the simultaneous transformation of electronic properties, including magnetism. The possibility of the defect transforming from one to
another with different magnetic properties at different temperatures also facilitates the design and fabrication of nanoscale switches, sensors and digital devices operated at varied temperatures.

**Inserting Graphics**

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**Fig.1** Structural model and schematic formation of two kinds of extended line defects in a graphene sheet. (a) and (c) are perfect graphene sheets with two graphene half-lattices shown black and grey, respectively. The arrows show the relative movement between the two halves of the graphene honeycomb lattice. In (a) the two halves of the carbon lattice move until the two lines of atoms labeled 1 and 2 overlap. Removing a set of overlapping carbon atoms results in model (b) of a neighboring fault line defect growth. Similarly, in (c) the two halves of the carbon lattice move until the two lines of atoms labeled 1 and 2 overlap. Removing a set of overlapping carbon atoms results in the model (d) of a diagonal fault line defect growth. (e) and (f) are top and side views of the relaxed reconstructed domain boundary of (d) which is a periodic structure consisting of octagonal and pentagonal carbon rings.

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**Fig.2** (a) Top and side views (at top and center) of the optimized graphene with the 4 ELD and its simulated STM image (at bottom) at constant height 1 Bohr within a unit cell indicated in the model a) with a rectangular frame. Eight carbon atoms are highlighted in yellow or black to represent out-of-plane carbon atoms on opposite sides of the plane. The grey atoms are in-plane carbon atoms. Five atoms are labeled. (b) Reconstructed 585 ELD at 3000 K. (c) Reconstructed 747 ELD at 2000 K. (d) and (e) are band structures of the optimized 4 ELD and 747 ELD.

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**Fig.3** Snapshots of atomic processes from MD simulations at 3000 K for the 585 line defect transformation in a graphene layer. (a) at time t = 0 fs, (b) t = 20 fs, (c) t = 30 fs, (d) t = 40 fs, (e) t = 50 fs, (f) t = 60 fs, (g) t = 70 fs, (h) t = 80 fs, (i) t = 90 fs, (j) t = 100 fs. The atoms involved in the transformation process are labeled with numbers.

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**Fig.4** Snapshots of atomic processes from the MD simulations for the 747 line defect transformation in a graphene layer at 2000 K. (a) at time t = 0
fs, (b) $t = 1.35$ ps, (c) $t = 1.36$ ps, (d) $t = 1.38$ ps. The atoms involved in the transformation process are labeled.

Fig. 5 (a) Top view and side views of the optimized graphene with the 4-4' ELD. (b) Reconstructed 585-747 ELDs at 3000 K. (c) Diffused 4-4' ELD at 2000 K.

Table 1 Formation energies per atom (EC) for lines of defects embedded in graphene.

<table>
<thead>
<tr>
<th>ELD</th>
<th>4</th>
<th>747</th>
<th>585</th>
<th>4-4'</th>
<th>4-4</th>
<th>585-747</th>
</tr>
</thead>
<tbody>
<tr>
<td>E_f [meVatom$^{-1}$]</td>
<td>280</td>
<td>211</td>
<td>80</td>
<td>322</td>
<td>322</td>
<td>169</td>
</tr>
</tbody>
</table>

[a] Reconstructed structure from 4 ELD at 2000 K. [b] Reconstructed structure from 4 ELD at 3000 K. [c] Reconstructed structure from 4-4' ELD at 2000 K. [d] Reconstructed structure from 4-4' ELD at 3000 K.

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