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Surface reconstructions and stability of X-shaped carbon nanotube junction

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A complete surface reconstruction takes place after a local connection between two crossed tubes is established, leading to the creation of an extended X-shaped junction constituted by topological defects with smooth negative curvature. Molecular-dynamics simulations show that the surface reconstructions occur through (1) generalized Stone-Wales transformation and (2) the movement of *sp* and sp^3 atoms and their transformation to sp^2 atoms by bond rearrangement. Based on both the principle of energy minimization and a generalized Euler's rule, it is demonstrated that the most stable structure for X junctions contains only 12 heptagons. The annealing temperature influences the topological structure and stability of junctions. © *2006 American Institute of Physics*.
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INTRODUCTION

Single-walled carbon nanotubes (SWCNTs) can be connected to form T, Y, or X junctions, which offer a new path toward extended molecular electronic circuit for their potential use in nanoscale transistor or amplifier applications.[1–8] These multiterminal junctions can be constructed by the introduction of topological defects in the form of pentagons and heptagons.[5–8] This is essential for maintaining sp^2 configuration for all carbon atoms in order to maximize stability. Crossed SWCNTs are usually nanowelded to generate X junction under electron- or ion-beam irradiation, where the irradiation-induced vacancies play a crucial role in the merging processes.[9–12] However, these high-energy process may not be desirable for nanoscale device applications because of uncontrollable bonding disorder in the joints. Our previous work found that the ideal X junctions may be formed by heating two crossed tubes without preexisting structural defects, and that the resulting X junctions only contain topological defects such as pentagons and heptagons.[13] In the present report, we focus on the topological reconstruction process during junction formation and propagating and study the stability of X junctions with various types of topological defects.

METHOD

Molecular dynamics (MD) is performed to investigate the surface reconstructions during the welding process of crossed (7, 0) and (4, 4) SWCNTs. The initial configuration of simulation is started with two perpendicularly crossed SWCNTs overlaid at a wall-to-wall distance of 4 Å. Periodic boundary conditions are imposed along both nanotube axes. The length of nanotube is 42.61 Å for (7, 0) tubes and 49.2 Å for (4, 4) tubes. The heating procedure is carried out according to Langevin molecular dynamics[14] with the interatomic forces described by the reactive empirical bond order (REBO) potential.[15] This potential can be used to describe the breaking and formation of chemical bonds during the heating-welding process. A time step of 0.5 fs is used for high computational accuracy. The obtained atomic configurations of junctions at elevated temperature are completely relaxed through annealing at 1000 K for 1.5 ns, followed by a final quenching to 0 K for energy calculation. This empirical method has been used in the analysis of energetics of nanoscale graphitic tubules and found in good agreement with the first-principles local-density functional results.[16] The high temperature greatly accelerates the simulations and allows for bond rotation, forming, breaking, and structural transformation to occur at the MD time scale, without melting, formation of vacancies and interstitials or structural collapse.

RESULTS AND DISCUSSIONS

We performed MD calculations to investigate the coalescence process of two crossed tubes into an X-shaped junction. Figure 1 presents junction configurations during welding process of two crossed (7, 0) tubes at 3450 K [Figs. 1(a)–1(d)] and of two crossed (4, 4) tubes at 3200 K [Figs.

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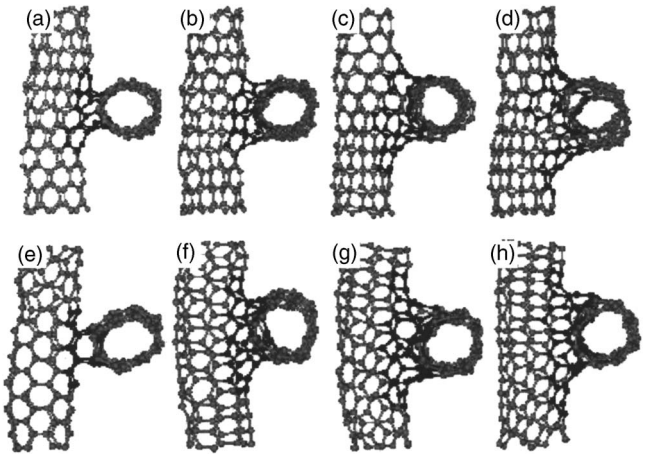

FIG. 1. Sequences of crossed SWCNTs coalescence into extended X-shape junctions, (a)–(d) for crossed (7, 0) tubes at 3450 K and (e)–(h) for (4, 4) at 3200 K. The final configurations of the two junctions include eight heptagons and two octagons (d) and fourteen heptagons and two pentagons (h), respectively.

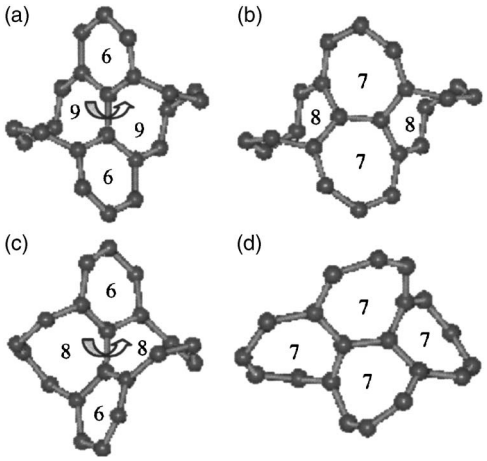

FIG. 2. The generalized Stone-Wales transformation by rotating a C–C bond around its center as block arrows indicated, resulting in the transformations from high polygons to low polygons.

1(e)–1(h)]. The topological defects, *sp* and sp^3 atoms are highlighted in black. From the figures, it is found that the connecting region is propagated along the four branches of X junction, that the intertube distance is reduced, that dynamical reconstruction happens with unstable high polygons (such as enneagons and octagons) transformed into low polygons (heptagons and pentagons), and that the final X junctions include only topological defects with all atoms maintaining sp^2 hybridization, leading to an extended X junctions with smooth negative curvature.

In the present study, we identify the detailed pathway for two crossed nanotubes to be gradually connected to form a stable junction. In fact, the surface reconstruction is the topological reconstruction. Here, two microscopic mechanisms are proposed to explain the coalescence process at the atomic scale: one is the generalized Stone-Wales (GSW) transformation[17] (i.e., by rotating a C–C bond around its center), and the other is the movement of *sp* and sp^3 atoms and their transformation to sp^2 atoms by bond rearrangement.

Nonhexagonal rings such as squares, pentagons, heptagons, octagons, nonagons, and decagons are observed at certain stages of the surface reconstruction. In our MD simulations, the unstable high polygons are found to disappear by GSW mechanism, thus leading to X junctions with topological defects mainly in the form of heptagons, shown in Figure 2. Here we take the X junction constituted by four enneagons in crossed (4, 4) tubes [Fig. 1(a)] as an example. The structure 6/9/9/6 [Fig. 2(a)] is transformed to two heptagons and two octagons [8/7/7/8 shown in Fig. 2(b)] by a GSW bond rotation (denoted by block arrow). A moment later, the two octagons in Fig. 2(b) react with another two hexagons [6/8/8/6 shown in Fig. 2(c)] to form four heptagons by another GSW bond rotation [Fig. 2(d)]. Eventually, only heptagons are present in the final configuration of the X junction. The GSW bond rotation with low activation barriers has been reported as a general mechanism for fast coalescence of SWCNTs (Ref. 18) and the interconversion between fullerene isomers.[19,20] Furthermore, the cluster of heptagons in Fig. 2(d) has the tendency to dissolve into individual heptagons separated by hexagons to eliminate the excessive angular strain,[21] resulting in the movement of the topological defects along the braches of the X junctions. This movement may make the junction more stable with a smooth negative curvature.

Our previous work showed that the initial connection between two crossed tubes was established by forming intertube sp^3-type bonds, followed by breaking intratube sp^3-type bonds.[13] sp^3 atoms are present in joints frequently. How does the hybridized disorder disappear? MD simulations give a peculiar microscopic mechanism, in which *sp* and sp^3 atoms play an important role in bond rearrangement. Figure 3(a)–3(c) show a sp^3 atom *A* and a *sp* atom *B* in a joint. The structure with a sp^3 atom [Fig. 3(b)] is metastable. One of the C–C bonds around the sp^3 atom *A* breaks to low the total energy, causing the creation of a *sp* atom A' [Fig. 3(d)]. When A' happens to attach to another carbon atom A'', A'' becomes sp^3 hybridized, Fig. 3(f). The whole process results in the movement of a sp^3 atom from *A* to A''. This kind of surface reconstruction has been reported in nanotubes responding to a uniform atom loss.[22] Similarly, the *sp* atom *B* can attach to another carbon atom to form a covalent bond, creating a metastable sp^3 atom B', Fig. 3(e). Then another carbon atom B'' becomes *sp* hybridized when the covalent C–C bond breaks [Fig. 3(g)], resulting the movement of a *sp*

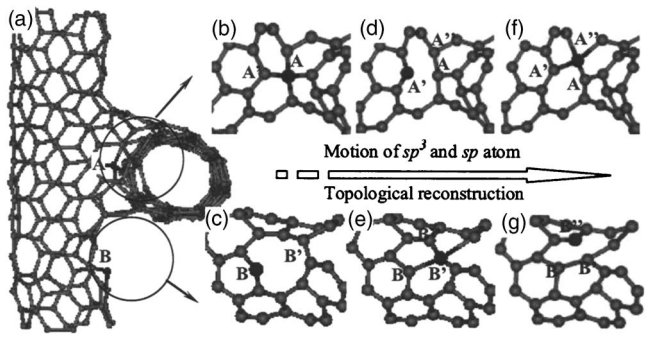

FIG. 3. The motion of *sp* and sp^3 atoms by bond rearrangements, together with the reconstruction of topological defects. *sp* and sp^3 atoms are highlighted in black.

atom from B to B'' through two rearrangements of bonds. Therefore, sp and sp^3 atoms can be transformed with each other during the welding process, leading to the movement of sp and sp^3 atoms. It is noteworthy that the movements of sp and/or sp^3 result in the topological reconstruction. When two sp^3 atoms happen to meet each other, breaking of the center bond between the two causes both atoms changing back to sp^2 hybridized.[13] A bond can be formed between two sp atoms so that both of them become sp^2 hybridized when they happen to come close with each other. The movement of sp and sp^3 atoms and their transformation to sp^2 atoms through bond rearrangement are responsible for all the atoms of the junction to maintain their sp^2 configuration to stabilize the structure.

We have simulated the coalescence processes between seven pairs of zigzag tubes $[(n,0),5\leqslant n\geqslant 12]$ and five pairs of armchair tubes $[(m,m),3\leqslant m\geqslant 7]$, with diameters ranging from 3.92 to 9.49 Å. The annealing temperatures for junction formation range from 1500 to 4000 K. The simulation results for all the junction formations are repeatable, and show the tendency that the stable and broad junction with low polygons could be obtained as the temperature increased. And the two microscopic mechanisms reported above are responsible for the coalescence process of all the crossed pairs of CNTs at the atomic scale.

If the temperature is high enough and the time for surface reconstruction is long enough, all X junctions should eventually contain only 12 heptagons in its connected region. This kind of configuration shows some similarities with the negative-curvature structure with infinite periodic minimal surfaces (IPMSs).[21,23,24] There are two basic reasons for this type of surface reconstructions. The first one is the principle of energy minimization. High polygons such as octagons and enneagon in the connected region transform into low polygons such as heptagons to lower the total energy of the structure.[19,20] The second reason is a topological one: the topological defects in X junctions must obey a generalized Euler's rule.[25] An n-edged polygon causes a bond surplus of $(n-6)$, such as -1 for pentagon, +1 for heptagon, +2 for octagon, +3 for enneagon, etc. According to the generalized Euler's rule, the total bond surplus at each X junction should be +12. Combining the principle of energy minimization and Euler's rule, the most stable structure for X junctions should contain only 12 heptagons. Those junctions containing topological defects other than heptagons may undergo further reconstruction if environmental conditions are suitable. It should be noted that one or more 5/7 pair defects may be present in the connected region during the heating process. This would not change the bond surplus but may increase the total energy of the junction. Two 5/7 pair defects can be annihilated when they glided together during the annealing which has been observed in the fullerene coalescence,[19] resulting in the decrease in total energy of the system.

The reduction in surface and strain energy can thus be regarded as a driving force to promote the surface reconstruction of a junction. Thermal processes and sufficient kinetic energy are crucial for both the formation of local interlinks and later surface reconstructions. The connected region propagates due to the dynamic nature of topological defects in these structures, resulting in the stabilization of the junction. However, in reality, the termination of the propagating process might be due to an energy barrier for bond rotation, breaking, and formation. In principle, coalescence of crossed tubes may be promoted at high temperatures when sufficient kinetic energy is available to overcome the energy barrier for further bond reconstructions.

TABLE I. The topological structures, annealing temperature, and formation energy of X junctions in crossed (7, 0) and (4, 4) SWCNTs, where P, H, O, and E represent pentagon, heptagon, octagon, and enneagon.

	Topological defects in connected region				Annealing temperature	Formation energy
Crossed tubes	P	H	O	E	(K)	(eV)
(7, 0)-(7, 0)	0	6	3	0	3200	−3.993
	1	7	3	0	3400	−5.846
	0	8	2	0	3450	−7.577
	0	12	0	0	3500	−8.82
(4, 4)-(4, 4)	0	0	0	4	2500	−2.746
	2	12	1	0	3200	−4.614
	2	14	0	0	3300	−5.216

Table I summarized the annealing temperatures, the topological structures, and formation energies (E_f^{XJ}) of X junctions in crossed (7, 0) and (4, 4) nanotubes. The total-energy change for junction formation is defined as $E_f^{\mathrm{XJ}}=E^{\mathrm{XJ}}-E^{\mathrm{crossed}}$, where E^{XJ} and E^{crossed} are the total energy of an X junction and the total energy of two initially crossed tubes, respectively. The table clearly shows that heating temperature influences the final configurations of X junctions, such as the number and the distribution of topological defects. When the annealing temperature increases, X junctions become wide, with more and more heptagons formed in the connected region in the expense of enneagons and octagons. Different topological defects in the joint can result in different negative curvatures in the joint region. It can be clearly seen from the table that the topological configuration of the junction influences its formation energy. Therefore, the thermal heating conditions have a great effect on the topological configuration and the formation energy of the junction. Two 5/7 pair defects are present in the (4, 4)-(4, 4) junction formed at 3200 and 3300 K, which cause the higher formation energy of (4, 4)-(4, 4) junctions than those of (7, 0)-(7, 0) junctions. It is also indicated that instability is associated with the existence of enneagons or octagons in the sp^2-bonded junctions, especially for enneagons. The high-temperature annealing process certainly helps to increase the stability of the junctions and introduce a smooth negative curvature in the connected regions. The diameter of crossed CNTs shows a functional relationship with the formation energy of the junction including only 12 heptagons.[26]

The distribution of the topological defects around connected region not only affects the stability of X junctions, it may also have important effects on electronic, optical, and mechanical properties of the junctions. For examples, the distributions of topological defects in intramolecular junctions influenced the positions of the localized states[27,28] of

the junctions, and the disorder of X junctions also affects their electronic conductivity.[10] A systematic study on this issue is required.

CONCLUSION

MD simulations in this report offer new insights into the formation process of X junction under heating. The surface/topological reconstruction happens through GSW bond rotation, the movement of sp and sp^3 atoms and disappearance of hybridized disorder by bond rearrangement during the welding process. Based on both the principle of energy minimization and the Euler's rule, a complete reconstruction should result in an extended X-shaped junction with only 12 heptagons—the most stable structure for X junctions, and the intertube distance should be reduced. High temperature can help the transformation of the junctions and influence the final distribution of topological defects in the connected regions. Such information may be helpful for optimizing the conditions necessary for manufacturing multiterminal junctions between crossed tubes as the building blocks for nanodevices.

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