Carbon Nanotube "T Junctions": Nanoscale Metal-Semiconductor-Metal Contact Devices

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Stable "T junctions" of single-walled carbon nanotubes forming one of the smallest prototypes of microscopic metal-semiconductor-metal contacts are proposed. The structures have been found to be local minima of the total energy on relaxation with a generalized tight-binding molecular dynamics scheme. These quasi-2D junctions could be the building blocks of nanoscale tunnel junctions in a 2D network of nanoelectronic devices. [S0031-9007(97)04723-6]

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Since the discovery of carbon nanotubes by Iijima [1], a rich variety of carbon nanotube morphologies has been experimentally observed. The carbon nanotubes consist of rolled-up graphene sheet with various chiralities. The electronic structure of these tubes can be either metallic or semiconducting, depending on both the diameter and chirality which can be uniquely determined by the chiral vector (n, m), where n and m are integers [2–6].

The possibility of connecting nanotubes of different diameter and chirality has generated considerable interest recently [7–10]. This is because of the possibility of the junctions being the building blocks of nanoscale electronic devices. The simplest way to connect two dissimilar nanotubes is proposed to be via the introduction of a pair of heptagon and pentagon in an otherwise perfect hexagonal graphene sheet [5]. The resulting structure still contains threefold coordination for all carbon atoms.

Although their presence is hard to detect experimentally, the relative positioning of the heptagons and pentagons is said to determine the nature of the connectivity. For example, straight connection is achieved when two nanotubes with parallel (or zigzag) orientation are connected with a pair of edge-sharing pentagons and heptagons oriented parallel to the tube axis [8]. When the pentagon-heptagon pair is adjacent, the resulting structure has a small angle bend [7]. For larger acute angle bends of up to 40°, however, the pentagon and heptagon must be placed symmetrically on opposite sides of the knees (behind and in front, respectively) [11]. Geometrical analysis suggests the optimal bend angle caused by a heptagon-pentagon pair to be 30° [5]. Furthermore, by repeating the heptagon-pentagon pairs at regular intervals, bends can be brought full circle to form a torus [5].

When the junction forms part of a closed structure, Euler's theorem imposes a further constraint that every addition of a heptagon must be accompanied by a corresponding addition of a pentagon to an already existing 12 pentagons in the closed structure.

It is clear that T junctions provide a challenge to the conventional rules applicable to tube bends. This is because unlike the knee joint where one can clearly define the opposite sides of the joint as either the front or the behind, both sides are topologically equivalent. As a result, we can expect a net excess of heptagons over the pentagons at the junction. Furthermore, whereas the bend angles at a tube junction depend on the tube parameters (diameter and chirality) of both the component tubes, no such dependence exists for the T junction where the angle remains fixed at 90°.

In this Letter we explore an alternative route to the formation of T junctions that is not constrained by the usual heptagon-pentagon defect pair considerations. In particular, we examine two metal-semiconductor-metal T junctions, namely, the (5,5)-(10,0)-(5,5) [Fig. 1(a)] and (9,0)-(10,0)-(9,0) [Fig. 1(b)] junctions. We designate the former by the symbol **T1** and the latter by the symbol **T2**. The structure **T1** is composed of 314 atoms while **T2** contains 304 atoms. The numbers chosen are sufficiently large enough to avoid the effects of the dangling π bonds at the edges on the junction. The (10,0) tube is semiconducting, and the (9,0) and (5,5) tubes are semimetals. The (5,5), (10,0), and (9,0) tubes have armchair, zigzag, and zigzag configurations, respectively. In the armchair (zigzag) configuration the tubes have C-C bonds perpendicular (parallel) to their axis. As seen in Fig. 1(a), in going across the junction in **T1** from the (10,0) side to the (5,5) side, the orientation of the C-C bonds remains unchanged. Crossing the junction in **T2**, on the other hand, involves rotation of 90° for the C-C bonds. Interestingly, **T1** contains six heptagons and no pentagons at the junction [Fig. 1(a)]. **T2** contains eight heptagons and two pentagons at the junction [Fig. 1(b)]. The presence of the additional two heptagon-pentagon pairs in **T2** is associated with the change in orientation of the C-C bonds in going across the junction.

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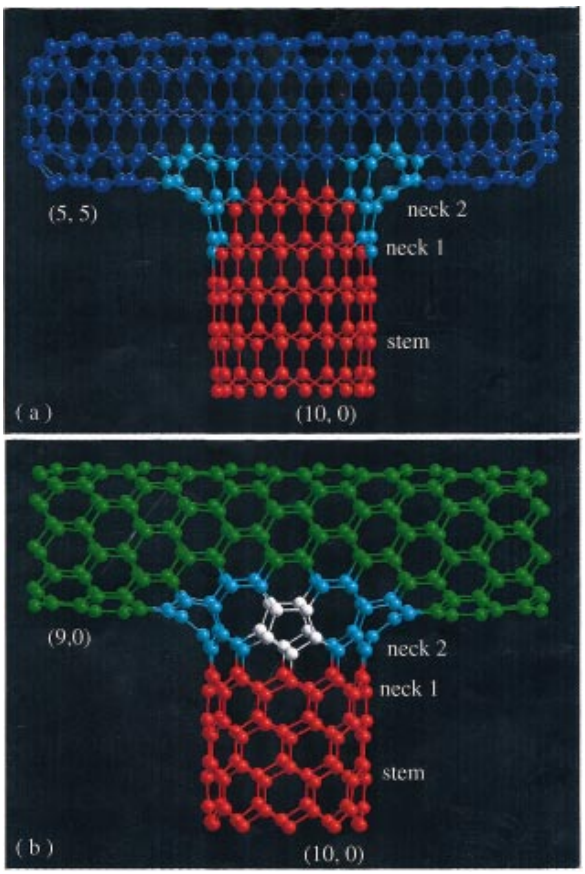

FIG. 1(color). (a) Fully relaxed (5,5)-(10,0)-(5,5) tube (**T1**). The turquoise colored balls denote the atoms forming the heptagons. The structure contains six heptagons and no pentagons. (b) Fully relaxed (9,0)-(10,0)-(9,0) tube (**T2**). The turquoise colored balls denote the atoms forming the heptagons. Pentagons are denoted by white balls. The structure contains eight heptagons and two pentagons.

Both these structures were fully optimized without any symmetry constraints using the generalized tight-binding molecular dynamics (GTBMD) scheme of Menon and Subbaswamy [6]. The GTBMD method makes explicit use of the nonorthogonality of the orbitals in treating interactions in covalent systems and has been found to be very reliable in obtaining good agreement with experimental and local density approximation (LDA) results for the structural and vibrational properties of fullerenes and nanotubes [6,12]. Additionally, GTBMD has been applied earlier to obtain equilibrium geometries for small carbon clusters [13], in good agreement with *ab initio* [14] results for the lowest energy structures of carbon clusters of size up to $N = 10$ (for which *ab initio* results are available).

The geometries shown in Figs. 1(a) and 1(b) are the GTBMD optimized structures for **T1** and **T2**, respectively. The starting configuration of **T1** has twofold coordinated atoms at the ends of the armchair portion of the tubule within strong bonding interactions of each other. The GTBMD relaxation results in the closure seen in Fig. 1(a) on relaxation with threefold coordination for all atoms at the armchair ends. No such closure results at the zigzag ends, however, as the twofold coordinated atoms are sufficiently far from each other. The turquoise colored balls in both the figures denote the atoms forming the heptagons at the junction. Pentagons in Fig. 1(b) are denoted by white balls. Table I summarizes the average bond lengths in the pentagons, heptagons, and hexagons at the junctions of **T1** and **T2**. In **T1**, the average bond length in the heptagons is found to be longer than the one for the hexagons. In **T2**, however, the average bond length in the heptagons is nearly equivalent to that in the hexagons. Also, as seen in the table, the pentagons in **T2** have larger bond length on the average when compared to heptagons or hexagons. Both the pentagons in **T2** are almost planar, with the heptagons bearing the brunt of the curvature with slight assistance from hexagons that share edges with the heptagons.

The room temperature stability of both the junctions was also tested in a classical molecular dynamics simulation employing Brenner's reactive hydrocarbon potential [15]. The junctions were found to be quite stable for the entire duration of the simulations. Additional investigations regarding their stability against externally applied strains are currently being pursued.

The Fermi levels of both (5,5) and (9,0) nanotubes lie within the gap of the (10,0) semiconducting tube. The T junctions in **T1** and **T2** form microscopic tunnel junctions, made up entirely of carbon atoms, through which electrons can cross by quantum mechanical tunneling. The tunneling current can be controlled by an application of a potential difference that raises the chemical potential of one side with respect to the other. Since the tunneling currents have been observed to obey Ohm's law, the T junctions can thus form one of the smallest microscopic Ohmic resistors. Furthermore, either n-type or p-type doping of the semiconducting portion of the T junction should yield Schottky barrier-type devices.

We investigate the local density of states (LDOS) using the tight-binding π-band approximation. Only nearest-neighbor interactions are considered with $V_{pp\pi} = 2.66$ eV [16]. Figure 2 shows the LDOS for the relaxed (5,5)-(10,0)-(5,5) structures [**T1** at various cross sections indicated in Fig. 1(a)]. LDOS for the panel labeled *stem,* for example, is for the cross section containing 20 atoms zigzagging along the circumference

TABLE I. Bond length analysis for the T junction in **T1** and **T2**. The GTBMD scheme has been used to relax both clusters. The bond lengths are averaged over the pentagons, heptagons, and hexagons.

Tube	Average bond length in pentagons (Å)	Average bond length in heptagons (Å)	Average bond length in hexagons (Å)
T1		1.427	1.419
T2	1.43	1.419	1.418

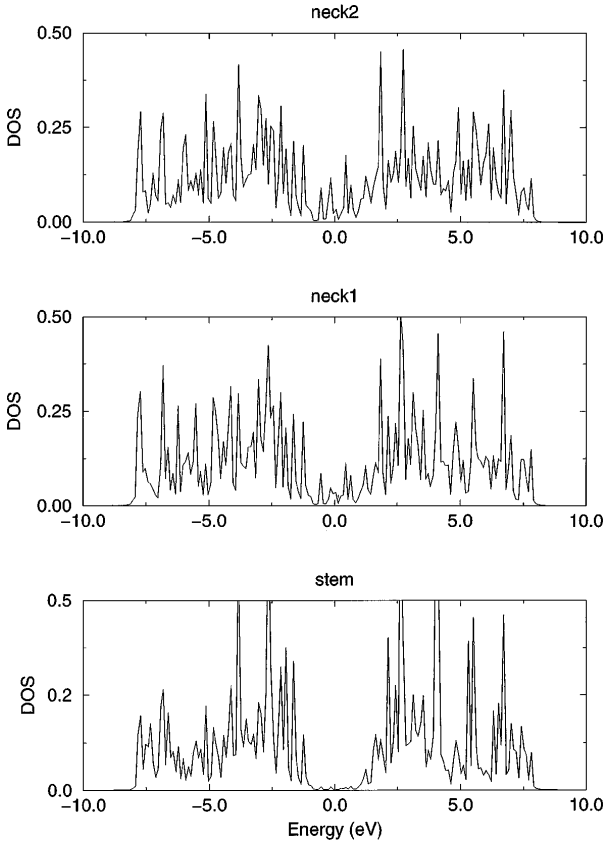

FIG. 2. LDOS for the relaxed (5,5)-(10,0)-(5,5) structures (**T1**) at various cross sections indicated in Fig. 1(a) showing the increase in the defect induced localized states in the gap as the junction is approached.

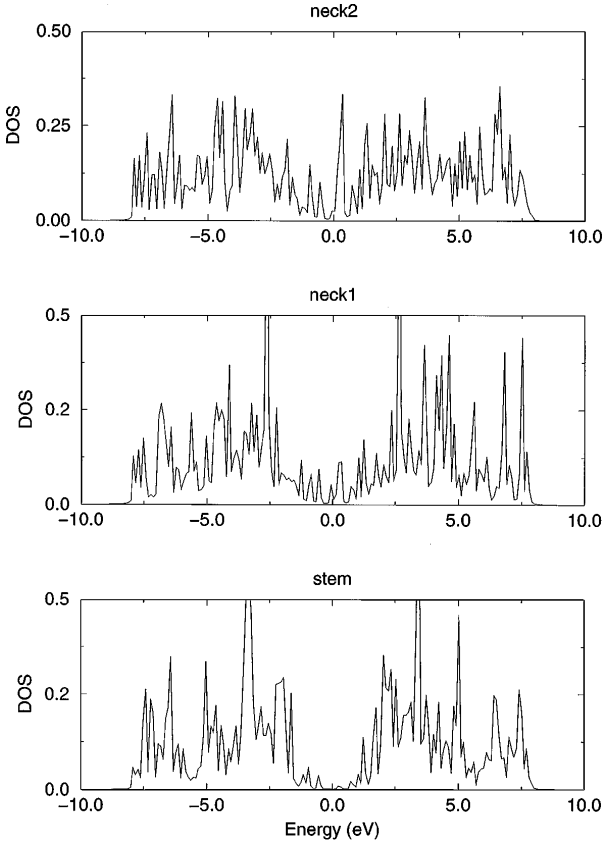

FIG. 3. LDOS for the relaxed (9,0)-(10,0)-(9,0) structure (**T2**) at various cross sections indicated in Fig. 1(b). The larger contribution in the gap is due to the presence of two extra pairs of heptagon-pentagon defects at the junction.

of the semiconducting (10,0) portion. As can be seen in Fig. 2, in going from the semiconducting side into the junction, localized states begin to appear in the gap. Detailed study indicates their origin to be the heptagonal defects present in the neck region. These defect states may pin the Fermi level of the system. Figure 3 shows the LDOS for the relaxed (9,0)-(10,0)-(9,0) structures [**T2** at various cross sections indicated in Fig. 1(b)]. The LDOS, again, is taken along the circumferential ring of zigzagging atoms in the (10,0) semiconducting portion in Fig. 1(b). The LDOS is qualitatively similar to Fig. 2 but with larger contributions in the gap. These can be attributed to the presence of two extra pairs of heptagon-pentagon defects at the junction.

The implications of these findings are intriguing. The T junctions defy the conventional arguments made in favor of an equal number of heptagon-pentagon defect pairs for the stability of dissimilar tube joints. As shown in this work, some T-junction joints can even be made without the incorporation of pentagons. The presence of large localized states in the gap that can pin the Fermi level has interesting implications for complex device modeling. Furthermore, the T junctions can be used as "universal joints" for forming a 2D network of tubes in which conduction pathways can be controlled.

In summary, we have proposed a new type of metal-semiconductor-metal T junction made up only of carbon atoms. The two different configurations were chosen to illustrate the fact that such junctions can be created with an excess of heptagons which provide almost all the curvature needed. Both structures were found to be stable under molecular dynamics relaxation employing quantum mechanical methods showing them to be minima of the total energy. We have also calculated the LDOS using the tight-binding method and observed the presence of localized defect states. Unlike the simple tube bends, the T junction is in reality a quasi-2D junction. If produced, these junctions could be the prototypes of nanoscale tunnel devices.

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Note added.—Some time after the submission of this Letter we became aware of an experimental observation of a junction with a sharp 90° bend in a pure single wall carbon nanotube [17]. This shows that such 90° bends are now possible under the regular growth conditions and postulates the exciting possibility of realizing 2D molecular networks of nanoscale electronic devices.

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