NANO
LETTERS

2007
Vol. 7, No. 8
2459−2462

Divacancies in Graphene and Carbon Nanotubes

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Received May 23, 2007

ABSTRACT

Divacancies are among the most important defects that alter the charge transport properties of single-walled carbon nanotubes (SWNT), and we here study, using ab initio calculations, their properties. Two structures were investigated, one that has two pentagons side by side with an octagon (585) and another composed of three pentagons and three heptagons (555777). We investigate their stability as a function of tube diameter, and calculate their charge transport properties. The 585 defect is less stable in graphene due to two broken bonds in the pentagons. We estimate that the 555777 becomes more stable than the 585 for a diameter of about 40 Å (53 Å) for an armchair (zigzag) SWNTs, indicating that they will prevail in large diameter multiwalled carbon nanotubes and graphene ribbons.

Even though pristine single-wall carbon nanotubes (SWNTs) have exceptional material properties,[1] defects can be used to tailor or improve their mechanical[2,3] and/or electrical characteristics. In particular, the presence of defects in these one-dimensional systems can dramatically change the charge transport properties due to disorder and localization. Understanding the properties of the relevant defects becomes thus a crucial issue in the field of SWNTs. Recent works have shown that divacancies are the most important ones regarding the changes in transport properties:[4,5] a low concentration, about 0.03%, can change the SWNT conductance by about 3 orders of magnitude. Moreover, divacancies have formation energies that are smaller than a single vacancy itself. Therefore, the detailed microscopic understanding of divacancies in SWNT becomes a fundamental issue for the use of these tubes in devices and interconnects.

Irradiation[6] of SWNTs by Ar ions has been recently used[4] to alter their electrical characteristics. Measurements of the low voltage resistance as a function of tube length led to an exponential behavior, indicative of strong Anderson localization regime. Simulations have shown[7,8] that the most likely defects to be formed under Ar^+ irradiation are vacancies and divacancies, the latter appearing in about 30−40% of the impacts. The divacancy structure considered in these studied had carbon atoms arranged in a geometry with two pentagons side by side with an octagon, a configuration that we will refer from now on as a 585 divacancy. A recent tight-binding molecular dynamics study of two initially isolated vacancies in a graphene layer[9] has shown that they coalesce into the 585 structure. This configuration, however, reconstructs further into a distinct and a bit more complex structure, composed of three pentagons and three heptagons, which will be called 555777 from now on. Ab initio calculations from the same group have shown that the 555777 structure is 0.9 eV more stable than the 585.

Considering the general relevance of divacancies to charge transport in nanotubes, and the fact that the 555777 structure is more stable in graphene than the 585, it becomes very important to know the following: (i) Is this also the most stable configuration in nanotubes, and (ii) if not, why this is so and for what SWNT diameter the crossover will occur, since graphene can be viewed as infinite diameter tubes? (iii) How does the 555777 divacancy affect the transport properties?

We provide, using state of the art ab initio calculations, the answer to all these questions. We show that the 585 defect is more stable than the 555777 by approximately 0.7 eV (1.7 eV) in armchair (zigzag) SWNTs, for a diameter range of 7−14 Å. We estimate that the 555777 becomes more stable than the 585 for a diameter of about 40 Å (53 Å) for an armchair (zigzag) SWNTs. Finally, we calculate that the charge transport properties of both defects are quite similar close to the Fermi energy for metallic nanotubes.

All our results are based on ab initio total energy density functional theory[10] calculations.[11] For the transport calcula-

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10.1021/nl071217v CCC: $37.00

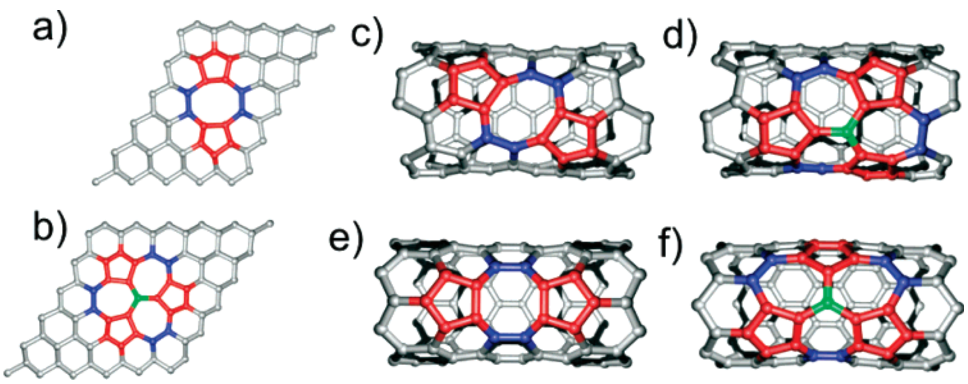

Figure 1. Ball and stick models for the final geometries of the defects: (a) 585 and (b) 555777 in graphene; (c) 585 tilted and (d) 555777 in the (5,5) armchair nanotube; (e) 585 parallel and (f) 555777 in the (8,0) zigzag nanotube. The carbon atoms in pentagons are marked in red, the ones that complete either the octagons or the heptagons are colored in blue, and the ones at the center of the *C*3 symmetry operation in the 555777 defects are colored green. All the others are colored gray.

tions we have used a code that we have written in our group,[14,15] which is based on the nonequilibrium Green's function-density functional theory (NEGF-DFT) approach and the SIESTA code.[16] For details, see refs 14 and 15.

In parts a and b of Figure 1 we present the 585 and 555777 defects in graphene, respectively. We calculated the formation energies for these structures and obtained that the 555777 is more stable than the 585 by 0.8 eV, in agreement with previous results.[9] We performed calculations for a diameter range of 7−15 Å, for six (*n*, *n*) armchair tubes and eight (*n*, 0) zigzag tubes (see Figure 2). The 585 defect in SWNTs has two possible orientations relative to the tube axis: perpendicular and tilted in armchair and parallel and tilted in zigzag. For the (5,5) nanotube, the perpendicular orientation is less stable by approximately 3.5 eV, whereas in the (8,0) tube the tilted is the less stable one by 2.7 eV.

The results for the armchair tubes are presented in Figure 2a. As it can be seen, the general features are (i) contrary to what happens in graphene, the 585 defect is always more stable than the 555777 defect; (ii) both defects are more stable in the tube than in graphene; (iii) there is basically a monotonic increase in the formation energy as the diameter increases, with a variation of approximately 0.8 eV going from the (5,5) to the (10,10) tube; (iv) in this diameter range the slopes of the formation energy curves as a function of diameter are roughly the same for both defects (with a constant energy difference[17] of ∼0.7 eV), and the curves are basically linear in this diameter range. This indicates that the stability crossover between the defects will probably happen at relatively large diameters, which is confirmed below.

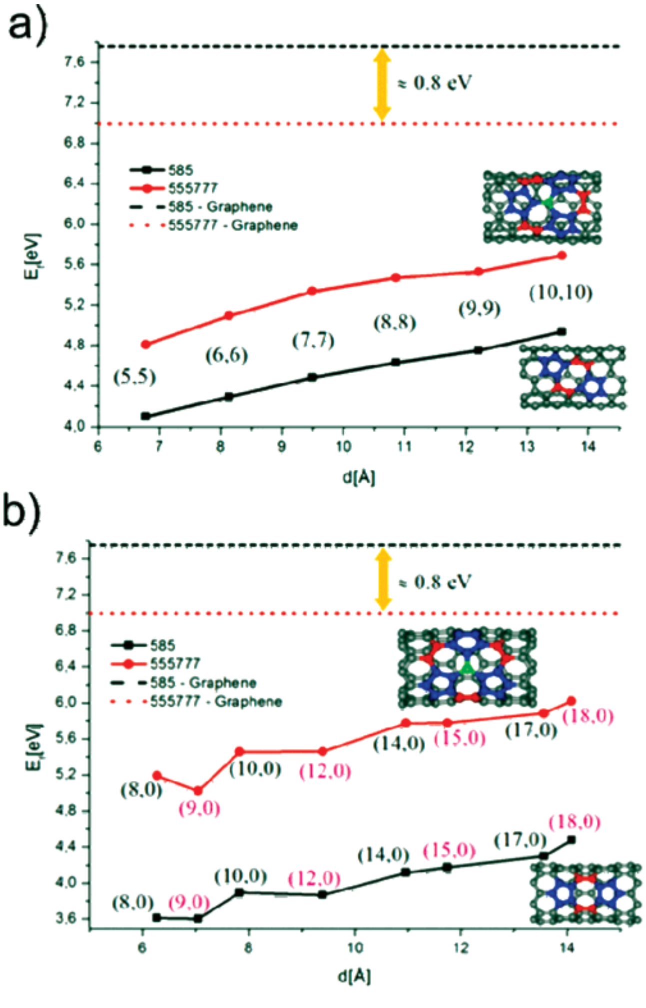

Figure 2. Formation energy vs diameter for the 585 and 555777 defects in (a) armchair and (b) zigzag SWNTs. In both figures we also present their graphene limits.

In Figure 2b we present similar results for the zigzag tubes, and we observe that, basically, all the general features mentioned above are also valid here. There are two distinct features, one quantitative and the other qualitative. The quantitative difference is the larger stability of the 585 defect in the zigzag tubes when compared to the armchair ones (the energy differences between the 555777 and 585 defects are ∼1.6 eV). This is related to a much larger relaxation of the atoms around the defect. The qualitative changes are the oscillations in the formation energies. These oscillations are related to the alternation between semiconductor and metallic character of the tubes (for (*n*,0) tubes, they are metallic if *n* is a multiple of three), and similar features have been observed for other defects.[18]

The important question is why the behavior of the defects is different in graphene when compared to that in the tubes. In Figure 3 we plot histograms for the carbon−carbon

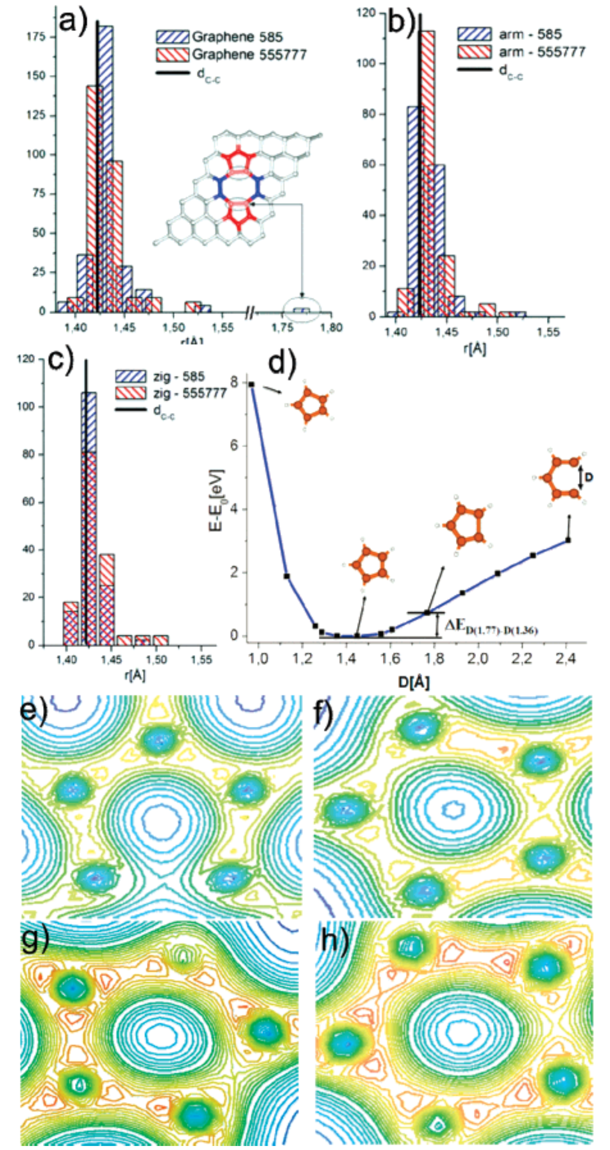

Figure 3. Histogram of C−C distances for the 585 and 555777 structures in: (a) graphene, (b) (5,5) armchair SWNT, and (c) (8,0) zigzag SWNT. The equilibrium C−C distance, d_{C-C}, for the pristine systems are also shown. In (d) we present the total energy of a cyclopentadienyl (C_5H_5 as a function of a C−C distance). Charge density plots in planes that passes through the C atoms in the pentagons for the defects (e) 585 in graphene, (f) 555777 in graphene, (g) 585 in (5,5), and (h) 585 in (8,0).

Table 1. Elastic (harmonic) and ab Initio Energy Differences As Defined in Ref 19

S	$\Delta E^{S}_{\mathrm{harm}}$ (eV)	$\Delta E^{S}_{\mathrm{ai}}$ (eV)
(5,5)	0.6	0.7
(8,0)	2.0	1.7
graphene	1.0	−0.8

distances in graphene and in the (5,5) and (8,0) nanotubes, for both types of defects. As it can be seen, there is a distribution of values around the equilibrium C−C distances of ≅1.42 Å, mostly within ±0.2 Å, and a few close to 1.50−1.52 Å. In graphene, however, there are two very large C−C distances of ≅1.77 Å for the 585 defect (Figure 3a). These distances are related to the pentagons formed after the removal of the C atoms in order to form the vacancies. The planar constraints of the graphene prevent the carbon atoms from approaching each other.[3] No other defect has such large distances. This indicates that this is probably the reason why the 585 defect is less stable in graphene.

To confirm this idea, we have investigated a very simple model. We first estimated the elastic harmonic energy difference ($\Delta E^{S}_{\mathrm{harm}}$) between the two defects in each structure using a simple molecular mechanics Hamiltonian[19,20] for the C−C bonds and angles. The results are shown in Table 1, together with the ab initio total energy difference[19] ($\Delta E^{S}_{\mathrm{ai}}$). The ab initio results contain both harmonic (elastic) and nonharmonic contributions. The nonharmonic terms are mostly related to the very stretched, almost "broken bonds". We will thus refer to this contribution as a chemical one. We can thus say that (i) the elastic contribution always favors the 585 defect, (ii) the elastic contribution accounts for the majority of the ab initio energy difference for the nanotubes, and (iii) there must be chemical contributions that cause the inversion of stability in graphene, most likely related to the pentagons in the 585 defect.

To check this latter hypothesis, we have analyzed electronic charge density distributions for these pentagons in all the systems (Figure 3), and we have identified a much smaller charge density distribution between the two large C−C bonds in the 585 defect in graphene. In order to estimate this chemical contribution, we have considered a cyclopentadienyl molecule (C_5H_5) as a model system for the local bonding in these pentagons. In Figure 3d we plot the change in total energy as the length of one of the C−C bonds is varied. The energy difference between the configuration with a C−C distance of 1.77 Å and the equilibrium (1.36 Å) is ≅0.75 eV. As we have two large bonds in the 585 defect in graphene, their contribution to the total energy would be ≅1.5 eV. Thus, in graphene, the elastic energy contribution makes the 555777 defect less stable than the 585 by approximately 1.0 eV (as it does in all systems), whereas the chemical contribution due to the planar constraints renders the 585 defect less stable by approximately 1.5 eV. This gives a total energy difference of $\Delta E^{\mathrm{graphene}} = \Delta E^{\mathrm{graphene}}_{\mathrm{harm}} - \Delta E^{\mathrm{graphene}}_{\mathrm{chem}} = 1.0 - 1.5 = -0.5$ eV, which is now similar to the $\Delta E^{S}_{\mathrm{ai}} = -0.8$ eV. In other words, the 585 defect is less stable only in graphene due to the two broken bonds in the pentagons, that is, the chemical contribution dominates the elastic one.

We estimate[21] the diameters d where the 555777 becomes more stable than the 585 to be $d \cong 40$ Å for the armchair and $d \cong 53$ Å for the zigzag nanotubes, which correspond to (30,30) and (117,0) tubes, respectively, which are relatively large tubes, as expected.

Finally, we calculated the charge transport properties for both structures in a (5,5) SWNT, using a central region with three bulk unit cells connected to a middle region with seven unit cells, where the defects are placed.[14] Using the NEGF formalism described above, we calculated the transmittance, T(E) (Figure 4). For a pristine tube T(E) has a value of $2G_0$, where $G_0 = 2e^2/h$, and both defects give a significant reduction of this value at the Fermi energy, E_f, as has been

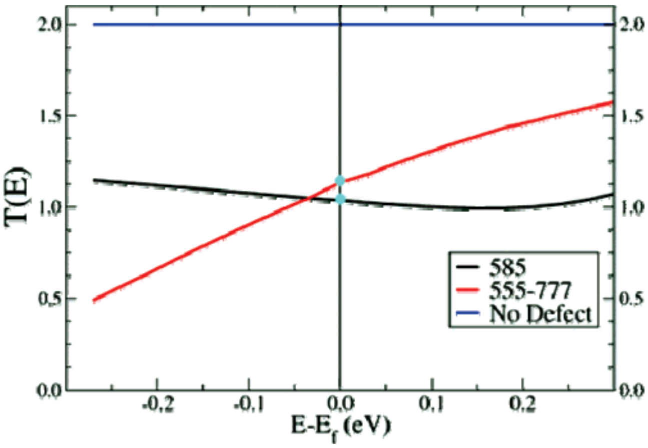

Figure 4. Transmittance $T(E)$ for the two defects in a (5,5) SWNT, in units of G_0.

observed for the 585 defect before.[5,8] Low-voltage measurements[5] would probably not be able to distinguish the two structures, but as the 555777 has a slightly different behavior of T(E) as a function of voltage, they may provide distinct signals. A more detailed analysis where disordered effects are taken into account[8] would have to be carried out to answer such questions.

In summary, we have investigated in great detail the divacancies in carbon nanotubes. We have shown that the 585 structure is more stable than the 555777 defect for a large range of diameters. Eventually, for large enough tubes, the chemical cost of increasing the C−C bonds in some pentagons causes an inversion of stability. The divacancies are quite important defects since they have extremely small formation energies, significantly smaller than two isolated vacancies, leading to their coalescence, but also smaller than a single vacancy itself (the formation energy for an isolated vacancy in a (5,5) tube is ≅6 eV whereas in a graphene sheet it is ≅8 eV). Moreover, they significantly affect the charge transport properties of these materials, and both types of divacancies do so in a similar way. We expect that these defects will also be relevant in the newly discovered graphene sheets, as well as in graphene ribbons. Moreover, the 555777 defects may play an important role in multiwalled carbon nanotubes since diameters up to 350 nm for the outermost tube have been observed.[22]

Acknowledgment. We acknowledge support from the Brazilian Agencies FAPESP (2004/08928-3 and 2005/59581-6) and CNPq, and CENAPAD-SP for computer time.

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NL071217V