Adsorption and migration of carbon adatoms on carbon nanotubes: Density-functional *ab initio* and tight-binding studies

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We employ density-functional plane-wave *ab initio* and tight-binding methods to study the adsorption and migration of carbon adatoms on single-walled carbon nanotubes. We show that the adatom adsorption and migration energies strongly depend on the nanotube diameter and chirality, which makes the model of the carbon adatom on a flat graphene sheet inappropriate. Calculated migration energies for the adatoms agree well with the activation energies obtained from experiments on annealing of irradiation damage in single-walled nanotubes and attributed to single carbon interstitials.

The methods of single-walled carbon nanotube (SWNT) mass production have been the subject of intensive research. However, despite a considerable effort, there is still a lack of control over SWNT chiralities and diameters at the growth stage. This is in part due to the insufficient understanding of the SWNT growth mechanisms.

Many microscopic SWNT growth models have been developed[1–6] with growth taking place either at the nanotube edge[1–3] (capped or open) or its root.[4–6] However, whatever the mechanism is, the quantitative understanding of the synthesis process is not possible without knowing how the "building blocks"—carbon atoms and clusters—are supplied to the place where the SWNT growth occurs.

Carbon atoms coming from the feedstock (plasma, gas, etc.) can be captured directly at the end of the SWNT (Ref. 3), especially if dangling covalent bonds are present. However, it seems to be more plausible that the atoms first absorb onto the SWNT surface and then they migrate to the SWNT growing end.[1,2] The adsorbed atoms (adatoms) can also aggregate and form clusters (amorphous carbon) and detach from the nanotube surface. Thus, knowing the adatom migration mechanism and such key quantities like adsorption and migration energies is indispensable for the comprehensive theory of SWNT synthesis.

At the same time, there exists very little knowledge about how carbon adatoms migrate over the SWNT surface. There have been studies on the migration of carbon adatoms on a graphene (flat) surface[1,7] but the effects of SWNT surface curvature on the carbon adatom diffusion have not yet been studied by proper methods.[8] The reported values of the adatom migration barriers (about 0.1 eV) for graphene[1,7] seem to be much lower than the migration energies (~ 0.8 eV) of single carbon interstitials obtained in experiments on the annealing of the irradiation-induced damage in SWNT's.[9] Carbon interstitials can be considered as adatoms in SWNT samples.[10] Thus, the curvature effects appear to be important.

In this work we study the adsorption and diffusion of carbon adatoms on SWNT's. By using two different computational techniques we evaluate the adatom adsorption energy E_a and migration barrier E_m for SWNT's with various chiralities. We show that E_m is much higher for SWNT's

than for graphene, which implies that some theories of SWNT growth must be revisited.

We employed the nonorthogonal density-functional-based tight-binding (DFTB) method.[11] In this approach the parameters of the Hamiltonian are derived from *ab initio* density-functional theory (DFT) calculations. We also used the "real" DFT implemented in the plane-wave (PW) basis set VASP[12] code. Although the PW DFT method is at the leading edge of electronic structure calculations, we were unable to carry out all simulations using this method because of computational requirements of this study (large unit cells, complex diffusion geometries, etc.). Therefore we mainly used the PW DFT method for validating the DFTB results. As shown below, the DFTB method works well, thus offering a good compromise between accuracy and computational efficiency.

In DFT calculations, we used projector augmented wave potentials[13] to describe the core electrons and the generalized gradient approximation (GGA)[14] for exchange and correlation. A kinetic energy cutoff of 400 eV was found to converge the total energy of our system to within meV. The same accuracy was also achieved with respect to the **k**-point sampling of the Brillouin zone. The adatom diffusion paths were calculated in a static approximation using the nudged elastic band method.[15] Other details of our DFT PW calculations can be found in Ref. 16.

To check the applicability of DFTB to the problem of adatom migration, we first calculated E_a and E_m for the adatom on a graphene sheet. The DFTB method gave the same equilibrium position of the adatom (a bridgelike structure with the adatom being above the middle of the carbon-carbon bond) as our DFT PW calculations.[16] E_a (with account for the spin-polarization energy correction[17]) was found to be ≈ -2 eV, which is in line with the *ab initio* data reported in other studies (-1.78 eV,[1] -1.35 eV,[7] -1.4 eV,[16] -2.04 eV Ref. 18).

We further calculated the adatom migration path and barrier statically and dynamically by performing molecular dynamics for 0.2 ns at temperatures in the range of 700–1500 K. In perfect agreement with our DFT PW calculations,[16] the
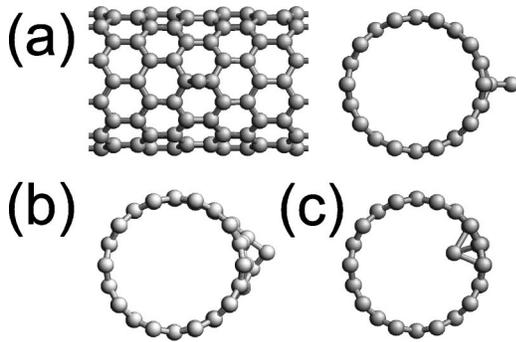
FIG. 1. Ball-and-stick representation of a (10,0) single-walled zigzag nanotube with a carbon adatom, as calculated by the DFTB method. (a) The adatom is above a bond parallel to the tube axis (top and side views). (b) The adatom is on top of a bond perpendicular the tube axis (side view). (c) Adatom is inside the tube.

diffusion path was found to be a nearly straight line between two equivalent adjacent sites bridging carbon atoms. Static and dynamical simulations gave $E_m = 0.4 \pm 0.1$ eV, which is in a very good agreement with a DFT PW value of 0.45 eV. From our molecular dynamics simulations we also evaluated the adatom jump frequency $\nu_0 = (3.7 \pm 0.7) \times 10^{12} \text{sec}^{-1}$ which proved to be about the experimental value ($4 \times 10^{12} \text{sec}^{-1}$) for the jump frequency of the carbon interstitial in graphite.[19]

Our previous DFT PW calculations[16] showed that the adatom has a finite magnetic moment, but the difference between the spin-polarized and nonpolarized ground-state calculations is quite small, about 0.04 eV. Magnetic effects also proved to be of minor importance for the diffusion.[16] Thus, we can conclude that the DFTB model, although being unable to account for magnetic effects, captures the main physics of the carbon adatoms on graphitelike surfaces.

We started with zigzag SWNT's. In our DFTB calculations, finite SWNT's (having a length of 12.7 Å and composed of up to 200 atoms) with periodical boundary conditions were considered. The same systems were used for the DFT PW simulations. To check how the results depend on the tube length, we also repeated DFTB calculations for (8,0) and (9,0) SWNT's with doubled length. We found no qualitative difference for the absorption geometry, nor the adatom diffusion path. E_a and E_m were dependent on the tube length, but the difference never exceeded 10% of the value.

Similar to adsorption of a carbon atom onto graphene, the adsorption onto a SWNT proved to be exothermic. The adatom on the outer surface of the SWNT occupies the bridge position above the C—C bond. However, due to the SWNT curvature, the adatom adsorption onto sites above C—C bonds being parallel and perpendicular to the nanotube axis results in different adsorption energies and local atom arrangements, see Figs. 1(a) and 1(b). Both the TB and PW DFT methods gave essentially the same adatom geometry. Adatoms inside the SWNT [Fig. 1(c)] are displaced a little from the bridge position due to curvature-enhanced interactions with the neighbor atoms.

In Fig. 2(a) we plot adsorption energies as functions of nanotube diameters for zigzag SWNT's. For adatoms on the
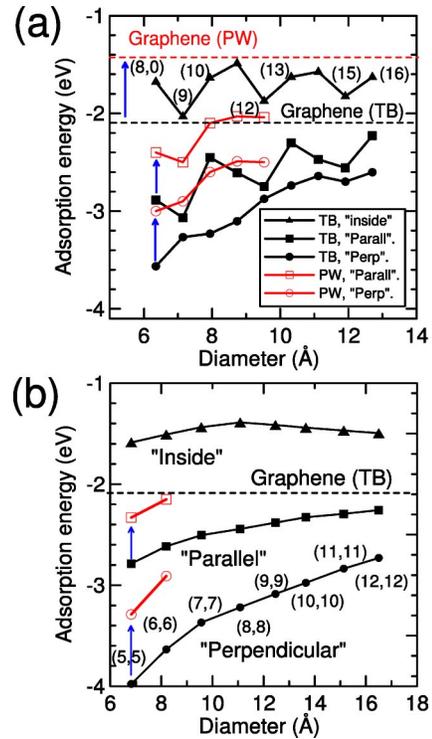
FIG. 2. (Color online) Adsorption energies of carbon adatoms on zigzag (a) and armchair (b) single-walled nanotubes as functions of tube diameters. The arrows visualize the relationship between the corresponding TB and PW results. The numbers stand for the tube chirality indices. The symbol legend for armchair tubes is the same as for zigzag ones.

outer surface the absolute value of E_a decreases with an increase in the SWNT diameter. This seems to be a general tendency: similar behavior of Al, H (Ref. 20), and N (Ref. 21) adatoms on SWNT's has been reported. The adsorption energy is always lower for configurations when the adatom is above the C—C bond oriented perpendicular to the SWNT axis than for the ''parallel'' configuration. This can be understood from simple carbon bonding considerations: in the ''perpendicular'' case it is easier for the adatom to pull the two adjacent nanotube atoms apart [note that the bond is actually broken, see Fig. 1(b)] thus avoiding the energetically unfavorable four-coordinated atom configurations. GGA *ab initio* simulations for small SWNT's gave qualitatively similar results, but, analogously to the case of the flat graphene sheet, the absolute values are shifted by about 0.5 eV. This difference may be due to fitting the TB parameters to local-density approximation (LDA) DFT data, since LDA calculations of adatom adsorption energy also gave a lower value for graphene[18] than with GGA. E_a are much higher for adatoms adsorbed onto the inner surface due to energetically unfavorable bonding geometry, see Fig. 1(c). Qualitatively similar behavior was obtained for armchair SWNT's, see Fig. 2(b).

It is interesting that the dependencies shown in Fig. 2(a) for zigzag SWNT's proved to be nonmonotonic. The curves for the parallel and ''inside'' configurations have sawtooth shapes with the minima corresponding to $n = 9, 12, 15$.
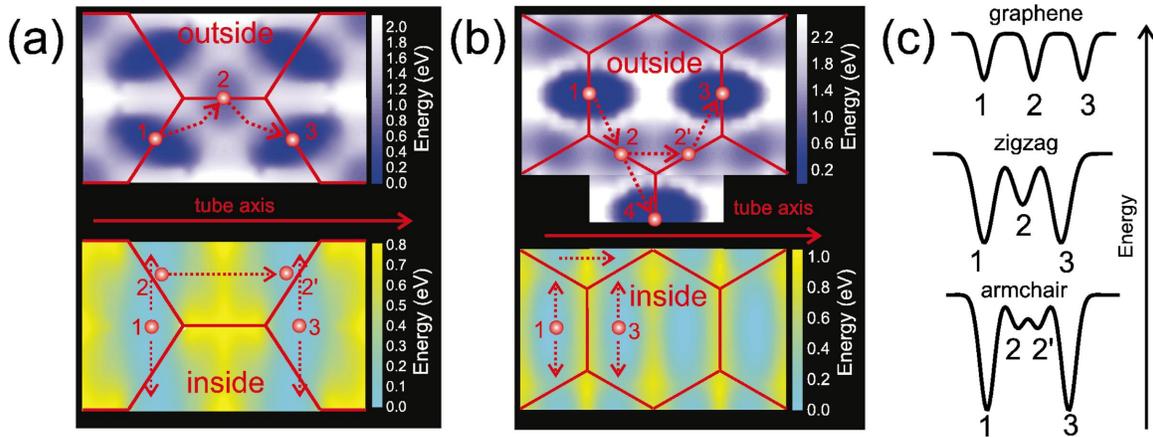
FIG. 3. (Color) Potential energy surface as a function of the adatom position on a zigzag (8,0) nanotube (a) and a (5,5) armchair SWNT (b) as calculated by the DFTB method. Circles stand for stable/metastable adatom positions, dotted lines show migration paths. Schematic energy diagrams for adatoms outside the tube (c).

SWNT's with these indices have metallic properties, whereas the rest are semiconductors. Note that the dependencies were smooth for armchair SWNT's which are always metals (within the TB picture). Our analysis of the local density of states and orbital electronic population indicates that the increase in bonding may be due to an additional overlap of the adatom electronic states with the electronic states of metallic SWNT's near the Fermi energy. PW DFT calculations also gave a lower adsorption energy for metallic (9,0) SWNT's than for semiconducting (8,0) and (10,0) SWNT's. Likewise, E_a was slightly (0.01 eV) lower for (12,0) than for (11,0) tubes. This effect is present only in parallel configurations, since the perpendicularly bonded adatom strongly distorts the atomic configuration such that it is no longer locally metallic.

Having evaluated the adatom adsorption energy, we proceeded to migration barrier calculations. Analogously to the case of graphene, we evaluated E_m by calculating the total energy of the system as a function of adatom position with constraints. The adatom was allowed to move only in the radial direction, all other atoms were free to move (except for fixed boundary atoms).

We found that adatoms on the SWNT outer surface can migrate between equivalent perpendicular positions (1) and (3) via intermediate parallel positions (2) and (2′), see Fig. 3, with E_m being dependent on the SWNT diameter. Results of DFTB simulations were corroborated by PW simulations for the smallest SWNT's.

E_m between positions (1) and (2) as a function of the SWNT diameter is presented in Fig. 4. E_m is higher for SWNT's than for graphene due to curvature-induced lower values of E_a corresponding to perpendicular adsorption configurations, see Fig. 3(c). Since the difference between the adsorption energies in perpendicular and parallel positions is larger for nanotubes with small diameters, E_m decreases with the tube diameter D approaching the corresponding value for graphene. The difference is larger for armchair than for zigzag SWNT's resulting in larger values of E_m.

We stress that adatoms are highly mobile at typical growth temperatures. The time τ needed for the adatom to

move a distance L can be evaluated as $\tau = L^2/D_0$,[22] where $D_0 = \nu_0 a^2 \exp[-E_m/kT]$, a is the elementary jump length. Thus if $L = 1$ μm, $T = 600\,°C$, $E_m = 0.8$ eV, then $\tau \approx 1$ sec.

Note that the adatom migration mechanism as calculated by the DFTB and *ab initio* methods is fundamentally different from the kick-out mechanism[6] derived from the analytical potential calculations. We believe that the latter is an artifact of the analytical method resulting from the use of the interaction range cutoff functions and the general transferability problem of analytical potentials.

We would also like to point out that the adatom can quickly form dimers and SWNT growth may be due to diffusion of not only single adatoms but also dimers. Further studies will quantify the dimer behavior.

For all SWNT's considered, adatoms inside the SWNT can easily spiral along the nanotube circumference (along the dark "trenches" of roughly the same potential energy in Fig. 3) with an energy barrier of 0.1–0.3 eV. This is in part due to a weaker bonding to the SWNT and shorter curvature-mediated "jump length" than on the outer surface. The barriers for migration along the tube also depend weakly on the SWNT diameter and are 0.5–0.7 eV.
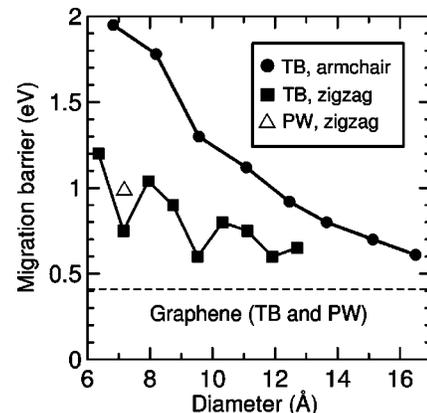
FIG. 4. Energy barrier for adatom migration on the outer surface of nanotubes as a function of nanotube diameters. The graphene migration barrier is the same in both PW and TB calculations.

To conclude, using tight-binding and density-functional *ab initio* methods we studied the adsorption and migration of carbon adatoms on armchair and zigzag SWNT's. We found that the adatoms form strong bonds with the nanotubes and that the migration is highly anisotropic. The adatom adsorption energy and migration barrier depend on the nanotube diameter and chirality, which should be taken into account in models of nanotube growth and radiation damage annealing. The migration barriers, being in the range 0.6–1 eV for SWNT's with typical diameters of 1–1.4 nm, are in a good agreement with the experimental values (about 0.8 eV) reported in the literature. Since, for a given tube diameter, migration barriers are governed by the orientation of the C—C bonds with respect to the tube axis, migration barriers for all chiral nanotubes should be between the values for armchair and zigzag SWNT's.

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