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Nitrogen-doped carbon nanotubes under electron irradiation simulated with a tight-binding model

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Experiments show that nitrogen-doped carbon nanotubes subjected to the electron beam in a transmission electron microscope can easily lose dopant atoms and that overall they are less stable under electron irradiation than the pristine tubes. To understand the lower stability of nitrogen-doped nanotubes we use a density-functional-theory-based tight-binding model and simulate impacts of energetic electrons onto the nanotubes. We show that the dopant atom displacement energy and thus the electron threshold energy is lower for nanotubes with smaller diameter and that, independent of the nanotube diameter, the dopant nitrogen atoms can be displaced more easily than the host carbon atoms. Our results set a limit on the threshold electron energy for damage production in N-doped tubes and indicate that spatially localized electron irradiation of doped nanotubes can be used for local atomic and band structure engineering.

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Chemical doping of nanostructured carbon systems such as carbon nanotubes, fullerenes, and peapods is a possible route toward controllable modification of their structural, mechanical, and, first of all, electronic properties. Doping may be implemented by intercalating foreign atoms into the open space in the carbon network or by substituting the host atoms with impurities.

Both approaches have been effective for carbon nanotubes. The intercalation of alkali-metal and bromine atoms into bundles of single-walled carbon nanotubes has been shown^{1,2} to increase the carrier concentration and to decrease the tube resistivity at 300 K by up to a factor of 30. Even larger decrease in resistivity has been reported for nanotube mats doped with Cs and K atoms.³

As for substitutional doping, much attention has recently been given to the doping of single- and multiwalled nanotubes (SWNTs and MWNTs) with boron and nitrogen atoms.^{4–12} This is a natural choice of the dopant, as B and N atoms are the neighbors of C in the periodic table and thus have roughly the same atomic radius as C, while they possess one electron less or more than C, respectively. N doping has received particular attention (see Ref. 13 for a recent review), as, in addition to the changes in the electronic properties, N impurities have been shown to affect the nanotube morphology,^{6,7} reactivity,⁵ as well as nanotube field emission properties.¹⁰

In spite of substantial experimental progress in N doping, there remain many open important questions, e.g., the existence and the reason for fundamental limits on the maximum nitrogen concentration in nanotubes. The maximum concentration of N in SWNTs was reported to be about 1%, while in MWNTs the average concentration can reach 15–20%, and the local concentration can be as high as 25–30%.¹⁴ Moreover, it is not clear why nitrogen was detected only in MWNTs with diameters over 10 nm, despite the presence of tubes with diameters down to 5 nm in the samples.⁸

The nitrogen concentration and distribution is frequently probed by electron energy loss spectroscopy (EELS) in the

transmission electron microscope (TEM). Unfortunately, studies on nitrogen-doped nanotubes are complicated by a lower stability of doped nanotubes under electron irradiation as compared to the pristine tubes: The experiments^{13,15,16} showed that interaction of energetic electrons in TEM with N-doped tubes gives rise to a quick loss of N-doped atoms, which means the results on N concentration may be affected by the technique used. This is particularly important for SWNTs, as even very quick examination of doped SWNTs in the TEM may result in complete loss of nitrogen, which has even given rise to doubts of the existence of N-doped SWNTs.¹⁶ To some extent, loss of N atoms under irradiation is a counterintuitive result, as one might expect that heavier N atoms (as compared to C atoms) will acquire less kinetic energy after the electron impact. Hence, in this naive picture, it should be more difficult to displace N atoms and the relative concentration of N should increase in irradiated tubes.

The main goal of this work is to study the stability of N-doped carbon nanotubes under electron irradiation and to assess the loss of N atoms due to the energetic electrons. By employing atomistic computer simulations we estimate the threshold electron energy required to displace a dopant N atom from the nanotube atomic network and show that it is lower than that for the host C atoms. Lower threshold electron energies result in a higher cross section, and thus N atoms should indeed be lost more quickly than C atoms from the nanotubes probed by the TEM. We further demonstrate that the threshold energy depends on the tube diameter, but for a given diameter, it is always less than the threshold energy for C atoms.

To simulate impacts of energetic electrons onto N-doped SWNTs, we employed the nonorthogonal density-functional-theory-based tight-binding (DFTB) method.^{17,18} As we recently showed,^{19,20} the structures and energetics of defects in nanotubes and graphite calculated with the DFTB method are in excellent agreement with those obtained with first-principles methods, which provides strong evidence for the adequacy of the DFTB method for the simulations. We fur-

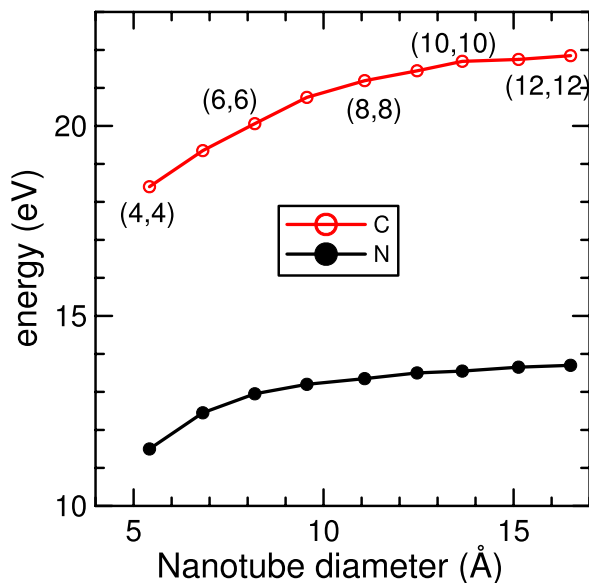


FIG. 1. (Color online) Threshold energy T_d needed to displace a dopant nitrogen atom from armchair single-walled carbon nanotubes calculated dynamically as a function of tube diameter. The threshold energy for host C atoms is also shown for comparison. The lines are guides for the eye.

ther compared the geometry and substitution or adsorption energy of N atoms to the results²¹ obtained by the plane-wave DFT theory code VASP,²² and found good agreement.²³

It is well known^{24,25} that the primary cause of electron irradiation damage of nanotubes in vacuum is knock-on collisions of electrons with atomic nuclei, as electronic effects are not important for damage production in either metallic or semiconducting nanotubes. The reason for that is the very high conductivity of metallic nanotubes and high charge mobility in semiconducting tubes.²⁶ As the role of electronic effects in damage production is smaller for metals than for semiconductors, one can expect that the main source of irradiation damage in N-doped nanotubes should be the same as in pristine tubes, because N doping increases the metallicity of the tube. We stress that this damage mechanism is different from low-energy electron-beam-stimulated etching of nanotubes in a scanning electron microscope when foreign molecular species are present.²⁷

We used the same simulation setup as in previous studies on effects of electron irradiation on pristine tubes.^{28,29} Because the electron-atom collision time is very short as compared to the characteristic times of the atomic motion,²⁵ in our dynamical simulations we assumed that a N dopant atom had instantaneously acquired some kinetic energy due to electron impact and then treated the motion of atoms adiabatically by running free molecular dynamics. The initial momentum vector was perpendicular to the nanotube surface.

We defined T_d as the minimum initial kinetic energy of a N atom to leave its position in the nanotube atomic network and not recombine before the energy is redistributed among other atoms in the system. We used the self-consistent-charge (SCC) modification of the DFTB method for static calculations and the non-SCC version of the method for dynamic

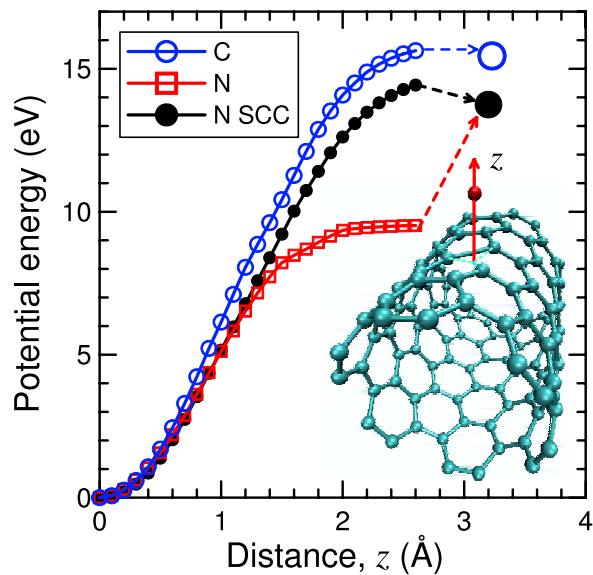


FIG. 2. (Color online) Potential energy of a dopant N atom and a host C atom as a function of the separation between the atom and the tube as calculated by the SCC and non-SCC DFTB methods. Zero energy corresponds to the equilibrium position of the atoms in the nanotube atomic network. The lines are guides for the eye. The big symbols stand for the energy of the tube with a vacancy and the isolated atom ($z=\infty$). The inset shows the simulation setup used in these calculations.

calculations. We were unable to run SCC dynamical calculations due to a very slow convergence of the electronic density at large separations between the recoil atom and the nanotube, as the precise energy conservation was critical for accurate determination of T_d . All other details of the dynamical simulations were identical to those used in Ref. 29.

T_d as a function of tube diameter for armchair SWNTs with various chiral indices is shown in Fig. 1. It is evident that (i) T_d decreases as the tube diameter becomes smaller; and (ii) T_d is always smaller for N than for C. The difference between the threshold energies proved to be over 6 eV. However, the difference may have been overestimated, as the use of non-SCC DFTB method resulted in spurious charge transfer from the tube to the N atom at separations between the nanotube and the dopant atoms exceeding 2.5 Å.

To understand the role of the charge transfer, we calculated the total energy of a (6,6) SWNT as a function of the separation between the moving atom and its substitutional equilibrium position in the nanotube network. In practice, we moved the N atom up and relaxed the system with constraints: the N atom was fixed, while the nearest neighbors of the N atom were allowed to move in the x - y plane (see the inset in Fig. 2).

At large separations the system energy for the non-SCC mode proved to be different from the sum of energies of the isolated SWNT and an isolated N atom due to spurious charge transfer: the bigger symbols in Fig. 2 stand for the sum of the energy of the tube with a single vacancy and the energy of an isolated N atom. The SCC DFTB simulations

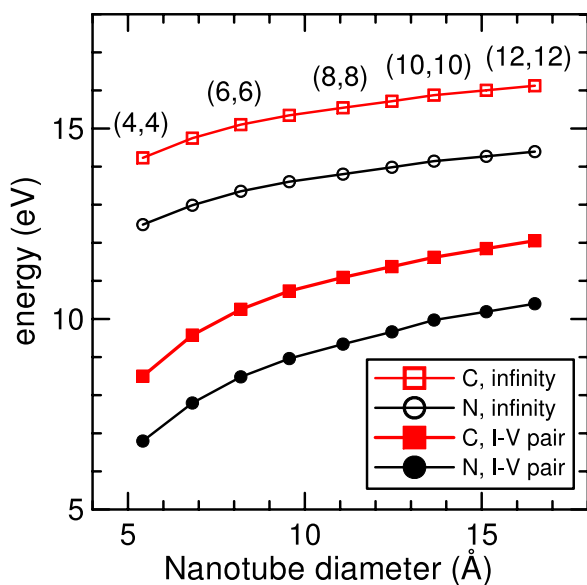


FIG. 3. (Color online) Energy required to take the dopant N atom or host C atom to infinity and the energy required to create a spatially separated vacancy-interstitial pair. These energies can be considered as lower bounds on the displacement energy T_d .

gave the correct behavior (the energy at large separations is slightly overestimated due to constraints applied to the nanotube atoms), as there was no extra negative charge on the N atom at large separation.

As the N ion with one extra electron is stable, in experiments the recoil atom can be sputtered as a negatively charged ion, and thus the true threshold energy in our model should lie between the value given by the SCC and non-SCC modes. Because for any separation the energy of both neutral and charged N atoms is lower than that for C atom (note that charge transfer problem is not relevant to monoatomic systems), one can expect from Fig. 2 that it would cost less energy to displace a N atom than a C. We stress that the dynamics and the charge state of the sputtered species can be studied more accurately only by time-dependent DFT methods beyond the Born-Oppenheimer approximation. This can hardly be done in practice even on massive parallel computers due to the extremely high computational cost of such simulations.

We also used the static approach to assess the effect of nanotube curvature on T_d for dopant atoms. We assumed that T_d is proportional to the energy required to make a vacancy in the nanotube atomic network by moving the dopant or host atom to infinity. The energies for N and C atoms are shown in Fig. 3 for armchair tubes as functions of tube diameter (open circles and open squares, respectively). It is evident that, as in dynamical simulations, (i) the energy is smaller for tubes with smaller diameters; and (ii) it is always smaller for N than for C, with the difference between the energies being 4–6 eV.

As in experiments the sputtered atom can be immediately absorbed on the tube surface, we finally estimated T_d as the energy required for making a spatially separated vacancy-interstitial pair.²⁹ In SWNTs, the adatoms play the role of interstitials,^{30,31} so that in this approach T_d is related to the

adatom adsorption energy which decreases with the tube diameter.³² The energy for creating a vacancy and a N atom is also shown in Fig. 3 for armchair tubes as a function of tube diameter (filled circles). The corresponding results²⁹ for C are also shown in Fig. 3 for comparison (filled squares). As in other simulation setups used in this work, (i) the energy increases with tube diameter; and (ii) for a certain diameter it is always lower for N than for C. The difference between the energies proved to be around 5 eV.

Thus all the simulation approaches indicate that it is easier to displace a N atom from nanotubes with small diameter, and for any diameter, the displacement threshold energy for N atoms is lower than that for C atoms by 2–4 eV. Lower values of T_d for N atoms can be associated with weaker bonds between N and C atoms as compared to the pristine tubes: it costs 1–2 eV to substitute the host C atom with a N atom.³³ As for the dependence on tube diameter, the drop in T_d is due to two factors: the strain in the carbon network and the ability of the nanotube to reconstruct by saturating dangling bonds.²⁹

The lower values of T_d correspond to lower electron energies E_{kin}^e , or equivalently to lower voltages in the TEM. Within the binary collision approximation,²⁵ the minimum (threshold) electron energy E_N^e required to displace a N atom can be estimated as

$$E_N^e = m_N \left(\frac{E_C^e}{m_C} - \frac{T_d(C) - T_d(N)}{4m_e} \right)$$

where E_C^e is the threshold electron energy for the pristine C system, m_e is the electron mass, m_C (m_N) and $T_d(C)$ [$T_d(N)$] are the atomic masses and atom threshold kinetic energies for C and N, respectively. Assuming that $E_C^e = 86$ keV for graphite and nanotubes with large (>2 nm) diameters,³⁴ the difference $T_d(C) - T_d(N) \sim 3$ eV would give $E_N^e \sim 66$ keV.

The drop in T_d also points to different displacement cross sections, i.e., how frequently the atoms are displaced during the irradiation. Within the McKinley-Feshbach formalism,³⁵ the difference in T_d of 2–4 eV would give for N a cross section that is higher by almost a factor of 2 than that for C. Thus, N atoms will be displaced more frequently than the host atoms, in accordance with the experimental results. As the barrier (and thus the cross section) depends on the tube diameter, this means that SWNTs are indeed more sensitive to electron irradiation than MWNTs, especially given that the N atoms displaced from inner shells in MWNTs may migrate back and annihilate with the vacancy while N atoms knocked out from SWNTs leave the system.

To conclude, we have shown that the displacement energy for N dopant atoms in carbon nanotubes is lower than that for host carbon atoms, which gives rise to a higher displacement rate and thus quick loss of dopant atoms, especially in SWNTs. Our quantitative results for electron threshold energy and displacement cross section set the limit on the threshold electron energy for damage production in N-doped tubes and should provide a better understanding of how the experimental setup in TEM affects the results of measurements of nitrogen concentration by EELS and thus may help to minimize the spurious effects. Our results further indicate that

spatially localized electron irradiation can be used for changing locally the concentration of N and thus for the local atomic and band structure engineering of nitrogen-doped nanotubes,¹³ nanotubes with nitrogen-molecule-functionalized groups,³⁶ B-C-N nanotubes,³⁷ and other nanotube composite systems.³⁸

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