

Relative abundance of single and double vacancies in irradiated single-walled carbon nanotubes

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Double and single vacancies differently affect the conductance of carbon nanotubes [G. Gómez-Navarro *et al.*, *Nat. Mater.* **4**, 534 (2005)], so that the exact knowledge of the abundance of these defects is mandatory for an unambiguous interpretation of irradiation-induced changes in nanotube conductance. We calculate concentrations of defects produced by Ar ions using the molecular dynamics method combined with kinetic Monte Carlo simulations. Carefully taking into account the annealing of defects, we show that the ratio of single to double vacancies has a minimum at ion energies of about 0.5 keV and that the ratio saturates toward a constant value at high ion energies. © 2007 American Institute of Physics. [DOI: 10.1063/1.2800807]

The remarkable electronic properties of carbon nanotubes^{1,2} combined with their inherent nanometer sizes have stimulated a vast amount of research work aimed at developing all-carbon nanoelectronics.³ A possible route toward designing nanotube-based circuitry and achieving the desired functionality of elementary electronic devices is to use beams of energetic particles such as electrons^{4,5} or ions⁶⁻⁹ to change the structure, morphology, and the local electronic properties of nanotubes in a controllable manner (see Ref. 10 for an overview). In particular, spatially localized ion irradiation was shown to result in the formation of quantum dots^{11,12} and inverters¹³ in nanotubes. Electron and ion beams can be used to cut nanotubes^{14,15} or weld them together^{14,16} to provide interconnections between the transistors implemented in semiconducting nanotubes.

As a side effect, ion and electron bombardment gives rise to irradiation-induced damage in nanotubes. Thus, considerable amount of attention has been paid to electronic transport in defected single-walled nanotubes,¹⁷⁻²⁰ (SWNTs) as even a small number of defects may dramatically change conductance of the nanotubes due to their quasi-one-dimensional structure. In calculations of transport properties of defected nanotubes, the following approach^{17,20} has been used: the conductance of a short section of the nanotube with only one defect was calculated; then, the conductance of the whole system was computed by summing up and averaging over different distributions of defects. Such an approach requires knowing not only how a certain type of defects changes the conductance but also the relative abundance of defects.

The most prolific defects which appear in SWNTs under ion irradiation are single and double vacancies (SVs and DVs, respectively) as well as adatoms.¹⁰ Although a lot of theoretical work has been done to get insight into defect production under ion irradiation,²¹⁻²⁴ the exact ratio between concentrations of SVs and DVs is unknown: previous works^{21,24} concentrated more on the total amount of damage expressed in terms of the atoms with coordination different from that in pristine nanotubes. Yet this information is critical in conductance calculations, as SVs and DVs have different effects on the electronic transport in nanotubes.¹⁷

In this work, we theoretically study this issue. We simulate impacts of Ar ions onto SWNTs and calculate the relative abundance of SVs and DVs as a function of ion energy. Moreover, using the kinetic Monte Carlo (kMC) code recently developed by us,²⁵ we carefully take into account annealing of defects on the macroscopic time scale, which has never been done before.

In our simulations, we used classical molecular dynamics (MD) with analytical potentials, the only computational approach which is fast enough to realistically simulate impacts of energetic ions onto nanoscale systems while explicitly taking into account their atomic structure. We addressed the limit of low irradiation doses and low ion energies, when nonadiabatic effects are not important.²⁶ Our simulation method has been described at length elsewhere²¹⁻²⁴ and, hence, only the details specific to this study are presented below.

Impacts of Ar ions with initial energies ranging from 25 to 10 keV onto individual 200-Å-long SWNTs were modeled. The majority of the simulations were carried out with a (8,8) SWNT, with a diameter of ~11 Å—typical for SWNTs produced by the high-pressure carbon monoxide decomposition method.²⁷ Simulations were also done for (12,0)

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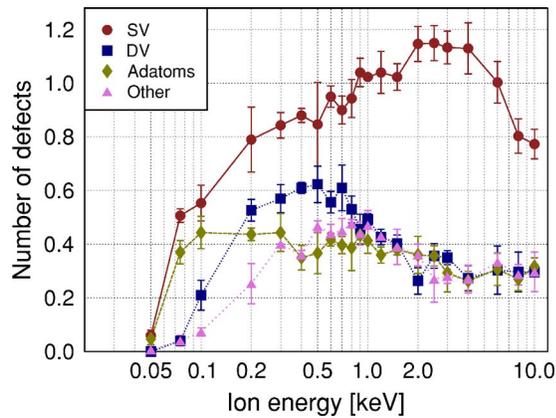


FIG. 1. (Color online) Average numbers of single and double vacancies, adatoms, and other defects per Ar ion impact as functions of ion energy. The symbols are simulation results, lines are guides for the eye.

and (10,4) SWNTs with similar diameters to assess the chirality dependence on the results.

The system temperature was chosen to be equal to zero, as previous studies^{21,24} showed that the production of defects is essentially the same at zero and room temperatures. In order to avoid spurious effects caused by pressure waves developed after ion impacts, temperature control of Berendsen *et al.*²⁸ was used at the SWNT border areas for the first 5 ps after ion impacts followed by quenching the temperature to 0 K. For every energy, 300 independent runs with randomly chosen impact parameters were carried out and the results were averaged. After each irradiation event the atomic structure was analyzed in order to identify the irradiation-induced defects. Each defect was categorized as a SV, DV, or a more complex defect, including multivacancies (three and more atoms missing),^{29,30} by ring analysis.

As the time scale in the conventional or even accelerated^{31,32} MD simulations is, in practice, too short to take into account annealing of irradiation-induced defects, the kMC method²⁵ was used for this purpose. In the kMC approach, a fixed atomic lattice is assumed, on which the defects are allowed to migrate via a discrete set of temperature activated events. The defects created by irradiation were allowed to migrate until they annihilated or the maximum simulation time (10 s) was reached.

The average number of defects in a (8,8) SWNT per ion impact is presented in Fig. 1. The total number of defects reaches its maximum at an ion energy of about 0.7 keV. At higher energies the number of SVs increases slightly (up to ~2 keV), while the number of DVs drops. The number of other defects is maximal at 1.0 keV and slowly decreases at higher energies. Such a behavior originates from a drop in the cross section for defect production at high ion energies.^{21,24} We found that the number of multivacancies is less than 10% for all ion energies. Multivacancies normally appear when the ion tangentially hits the sides of the tubes. The abundance of multivacancies does not seem to correlate with their relative stability^{29,30} at room and lower temperatures, but at temperatures above 300 °C, multivacancy abundance may be affected by their energetics.

The kMC simulations showed that adatoms *inside* the SWNTs are mobile at room temperature and that all of them quickly recombine with vacancies. Because roughly 45% of the adatoms produced by the ion impact are inside the tube, the annealing significantly changes the absolute numbers of

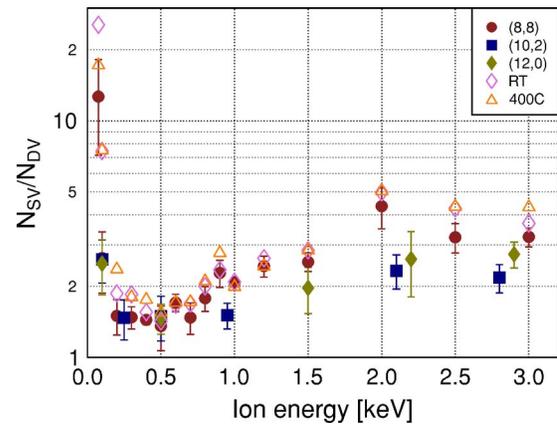


FIG. 2. (Color online) Ratio of the number of single to double vacancies N_{SV}/N_{DV} calculated at zero temperature for (8,8), (10,4), and (12,0) SWNTs as a function of ion energy. For (8,8) nanotubes, the results after annealing obtained by the kMC method at finite temperatures are also shown.

SVs and DVs. For adatoms *outside* the tube, the annihilation probability within the simulation time (10 s) was found to be ~5%. Thus, one can expect that at room temperature, nearly all adatoms will recombine with vacancies during several hours after irradiation. We also repeated kMC simulations at higher temperatures and found that at 400 °C, it takes about 10 s for complete annihilation of adatoms.

As a considerable number of C atoms are sputtered from nanotubes, and in part due to clustering of the adatoms, the complete annealing of vacancies due to adatom-vacancy recombination is not possible. The kMC simulations showed that the numbers of SVs and DVs decrease at 400 °C by about 20%. The effect is somewhat higher at lower irradiation energies due to a smaller number of sputtered atoms. SVs are not mobile enough³³ at room temperature to form DVs for the low dose irradiation limit studied in this work.

The ratio of the number of SVs to DVs N_{SV}/N_{DV} in the (8,8) SWNT at different temperatures is plotted in Fig. 2 as a function of ion energy. It is evident that annealing slightly increases the ratio, as the number of DVs decreases quicker as that for SVs because annihilation of adatoms with DVs creates SVs. For low ion energies the ratio is increased by ~10% at room temperature and at 400 °C by ~20% as compared to the zero temperature result. The effect is weaker for high ion energies.

At energies below 0.1 keV, N_{SV}/N_{DV} goes to infinity as the impact energy gets closer to the threshold for producing a double vacancy. At energies from 0.4 to 0.7 keV, the ratio is minimal (about 1.5), while at higher energies, it is saturated toward SV/DV ~3.

We also calculated analytically the average number of SVs and DVs within the binary collision approximation (BCA). We assumed that the number of defects N_d is proportional to the cross section σ for displacing a carbon atom,²⁴ $N_d = A\sigma$, where the proportionality coefficient A is the same for any type of defects. The threshold displacement energy for C atom was chosen to be $E_{th} = 25$ eV, as in our MD simulations. For double vacancies we used $E_{th} = 50$ eV. Fitting the BCA result to the MD data gave $A = 0.32 \text{ \AA}^{-2}$. The comparison of the average number of defects obtained from the MD and BCA simulations and presented in Fig. 3 indicates that at small ion energies, the BCA approach reproduces well the MD results for both SVs and DVs, while at higher energies, the number of SVs is larger due to vacancies

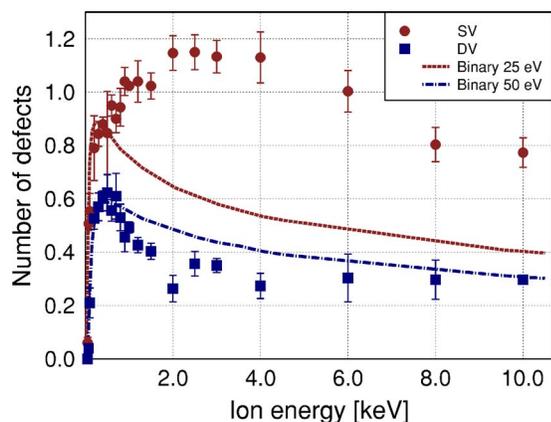


FIG. 3. (Color online) Number of single and double vacancies in a (8,8) nanotube as a function of ion energy as given by the MD and analytical binary collision calculations.

produced by secondary recoil atoms. However, at low energies, the BCA approach can be used to estimate the relative abundance of SVs and DVs.

To sum up, in this letter, we calculated the relative abundance of various types of irradiation-induced defects created by energetic Ar ions as a function of ion energy. Carefully taking into account the annealing of defects, we showed that the ratio of single to double vacancies can be infinitely large at small ion energies. The ratio has its minimum (1.5) at ion energies of about 0.5 keV and with increasing ion energy, it saturates toward 3. Our simulation results make it possible to quantitatively estimate the relative abundance of defects in irradiated nanotubes and thus, predict irradiation-induced changes in nanotube conductance in a wide range of ion energies.

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