Carbon nanotubes as masks against ion irradiation: An insight from atomistic simulations

A. V. Krasheninnikov,[a] K. Nordlund, and J. Keinonen
Accelerator Laboratory, P.O. Box 43, FIN-00014 University of Helsinki, Finland

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Recent experiments show that carbon nanotubes can be used as masks against ion irradiation to make metallic nanowires of a few nanometers in width. In order to ascertain the limitations of this technique, we use molecular dynamics and simulate ion irradiation of multiwalled nanotubes. We derive an equation which for a given nanowire material allows one to estimate the theoretical limit on the minimum width of the wire which can be made using this technique. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1499224]

The rising interest in irradiation effects in carbon nanostructures is triggered by recent observations of intriguing irradiation-induced phenomena.[1–3] The examples are graphite-to-diamond transformations in carbon onions under irradiation,[1] irradiation-induced carbon nanotube welding,[2] and cross linking,[3] just to mention a few.

Experiments also show that ion bombardment and carbon nanotubes may be employed for fabricating metal nanowires using multiwalled nanotubes (MWNTs) as masks.[4] By irradiating with 300 eV Ar^+ ions, a Au/Ti wire about 10 nm in width has been formed underneath a MWNT lying on a thin Au/Ti layer deposited earlier on a SiO_2 substrate.[4] The key idea is illustrated in Fig. 1. Because carbon nanotubes are micrometer-long and nanometer-wide objects and since they can be positioned very accurately using atomic force microscope (AFM), the described technique may potentially be employed for developing a large and complicated network of metal nanowires.

In this letter, we report on empirical potential[5,6] molecular dynamics[7] (MD) simulations of the MWNT irradiation with energetic ions. With a knowledge of a MWNT behavior under irradiation, we derive an equation which allows one to estimate the theoretical limit for the minimum width of a metal nanowire, which depends on metal layer characteristics.

The method used in this study has been described at length in other publications[6,8,9] and so we will discuss only the details important for these simulations. We considered 6-nm-long MWNTs composed of (5-10-15- etc.) armchair single-walled nanotubes with the intershell distance $a_s = 0.34$ nm.[10] All the ion impact simulations were carried out at zero temperature. To prevent spurious reflection of pressure waves from the borders of the system, the Berendsen temperature control[11] was used at the borders of the MWNT for the first 20 ps after ion impact, then the temperature was scaled down everywhere to room temperature at a rate of 1 K/ps.

We started with the question: What is the maximum energy E_{th} of incident Ar ions for a MWNT with an outer diameter D at which no damage is created in the metal layer below the MWNT? To address this issue, we simulated impact events of Ar ions with energies $E_i = 0.1-1.5$ keV on MWNTs with various number of shells. The impact points were randomly chosen over the MWNT surface. We assumed normal (relative to the substrate surface) incidence of Ar ions. For every ion energy considered, we carried out 100 independent runs and averaged the results.

Our simulations showed that the irradiation resulted in the sputtering of carbon atoms from the MWNT, formation of vacancies on the MWNT walls, and interstitial atoms between the shells. In Fig. 2(a), we plot the number N_r of energetic recoils (both Ar and C atoms) which hit the metal layer below a MWNT as a function of E_i. By an energetic recoil, we imply an atom/ion with a kinetic energy higher than 50 eV. At lower energies, even if a recoil gives rise to the displacement of a surface metal atom below the MWNT, this damage should anneal[12] easily, since the MWNT prevents metal atom sputtering and the defects, if formed, are close Frenkel pairs. It is seen from Fig. 2 that energetic recoils below a MWNT appear at a certain ion energy E_{th} which depends on the number of shells, i.e., on D.

Figure 2(b) shows a plot of E_{th} versus D. It is evident that the plot may be well approximated with a straight line. We suggest that this linear dependence is also valid for nanotubes with larger diameters. Thus, by measuring the diameter of a MWNT by AFM, one can calculate the upper bound on

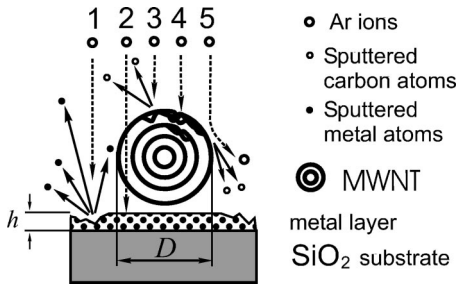

FIG. 1. Schematic illustration of the setup for using MWNTs as masks against ion bombardment. Trajectories (1–5) of incident ions correspond to the following events: (1) sputtering of metal layer atoms; (2) channeling of the ion across the MWNT through the spatial regions with a low atom density; (3) backward carbon atom sputtering from the MWNT and creation of vacancies in the carbon network; (4) amorphization of the MWNT; and (5) sideward carbon sputtering.

[a]Electronic mail: akrashen@beam.helsinki.fi

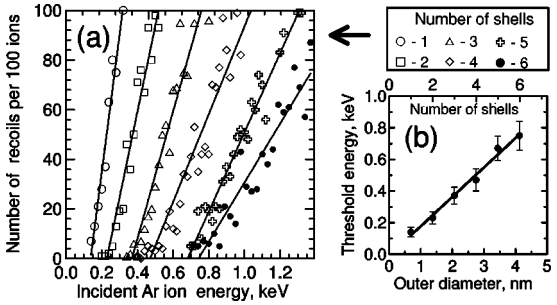

FIG. 2. (a) Number of energetic recoils (both Ar and C atoms) which hit the metal layer below the nanotube as a function of incident ion energy for MWNTs composed of different numbers of shells. (b) Threshold energy E_{th} of incident ions (the maximum energy at which no energetic recoil hit the area below the nanotube) as a function of tube outer diameter (number of shells).

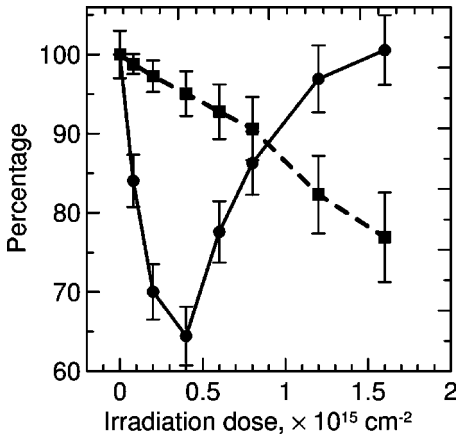

FIG. 3. Reduced number of energetic recoils below the MWNT (circles) and reduced number of carbon atoms left in the nanotube (squares) as a function of irradiation dose. $E_i = 700$ eV.

the ion energy at which no damage is created in the layer below the MWNT. Alternatively, for given E_i, one can estimate the smallest outer diameter D^* of the MWNT. A fit to the data in Fig. 2(b) gave

$$D^* = A_1 E_i, \quad A_1 = 5.6[\mathrm{nm/keV}]. \tag{1}$$

The next issue to be addressed is the choice of the optimum ion energy, which should be much lower than E_{th}. One can expect that the optimum energies should be in a range where the ratio of carbon sputtering yield Y_{C} to metal sputtering yield Y_m is small. For gold $Y_{\mathrm{C}}/Y_{\mathrm{Au}} \approx 0.05$ at $E_i = 0.2$ keV and $Y_{\mathrm{C}}/Y_{\mathrm{Au}} \approx 0.25$ at $E_i = 1$ keV.[13] Thus, E_i should be rather low, in a range of 0.1–0.5 keV. We stress that E_i should always be less than E_{th} to preserve the crystalline perfection and avoid carbon implantation into the metal below the MWNT.

With a knowledge of E_i, Y_m, and metal layer thickness h we can estimate an irradiation dose Φ needed to sputter the layer

$$\Phi = n_m h / Y_m, \tag{2}$$

where n_m is the metal atom concentration. For gold $n_{\mathrm{Au}} = 6 \times 10^{22}$ cm^{-3}, $Y_{\mathrm{Au}}(E_i = 0.2\ \mathrm{keV}) \approx 1$. Thus, for $h = 10$ nm $\Phi \gtrsim 10^{17}$ cm^{-2}.

Such relatively high irradiation doses will inevitably result in a strong amorphization of the nanotube and sputtering of a large amount of carbon atoms. Thus, proper allowance should be made for the ability of amorphized MWNTs to stop energetic ions and for carbon atom sputtering.

To model a high-dose irradiation of MWNTs and defect annealing over macroscopic times between ion impacts, we carried out simulations as follows: An ion impact was modeled as described herein, then, to overcome potential barriers between metastable atom configurations, the system was gradually heated up to 2000 K and maintained at this temperature for 200 ps with a subsequent quench to zero temperature. After that, the procedure is repeated until the desired dose is reached.

We simulated 200 consecutive ion impacts onto a three-walled MWNT, which corresponded to $\Phi = 1.6 \times 10^{15}$ cm^{-2}. $E_i = 700$ eV was deliberately chosen to be above the threshold value to monitor the ability of MWNTs to stop energetic particles under these ''extreme'' conditions. The irradiation resulted in the sputtering of about 25% of carbon atoms and complete amorphization of the MWNT, as the structure and angle analysis of the carbon network indicated.

Figure 3 shows the reduced number $N_r(\Phi)/N_r(\Phi = 0)$ of the energetic recoils below the MWNT as a function of irradiation dose Φ. Surprisingly, N_r remained after this irradiation dose roughly the same. At low irradiation doses N_r even decreases. This can be associated with the irradiation-induced amorphization of the nanotube, which made ion ''channeling'' through the regions of a low atomic density impossible (cf. trajectory 2 in Fig. 1). The increase in N_r at higher Φ is related to the drop in the total atom density due to sputtering. We qualitatively obtained similar results for nanotubes with other number of shells.

The role of absorbed Ar atoms in stopping Ar ions was negligible. Although some Ar ions got stuck in the MWNT, the majority of them left the nanotube during the annealing through vacancies in the nanotube walls. Thus, reasoning from Fig. 3, one can expect that high-dose irradiation of nanotubes practically does not affect their ability to work as masks unless a substantial part of the nanotube is sputtered.

To quantitatively characterize the loss of atoms during irradiation, we calculated Y_{NT} for large MWNTs with $D > 3$ nm (as will be clear from the following discussion, these are the smallest MWNTs which can be used for making nanowires). Y_{NT} is plotted against E_i in Fig. 4. Because at such energies, sputtering occurs mostly from the MWNT topmost region which is completely amorphized (see the inset in Fig. 4), we also calculated Y_{NT} using TRIM[14] which treats the irradiated sample as an amorphous structure. Both approaches gave similar results. Since Y_{NT} is independent of the MWNT radius in TRIM simulations, we believe that our results are correct for any MWNTs provided that $E_i < E_{\mathrm{th}}$. Notice that Y_{NT} is almost one order of magnitude larger than Y_{C}.[13] This is due to the sideward sputtering which is absent for macroscopic samples where only the backward yield is measured. A linear fit to the MD data in Fig. 4 gave

$$Y_{\mathrm{NT}}(E_i) = A_2 E_i - 0.14, \quad A_2 = 2\,\mathrm{keV}^{-1}. \tag{3}$$

Having calculated Y_{NT}, we can estimate the minimum

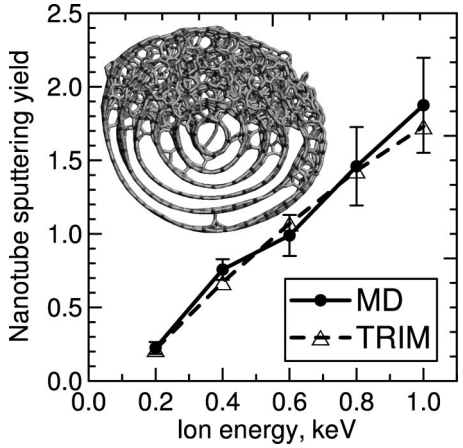

FIG. 4. Sputtering yield from a MWNT vs incident Ar ion energy. A typical atom network of a MWNT under high-dose low-energy ion irradiation is also shown.

width W of a metal wire which can be made using MWNTs as masks (we assume that $W \approx D$) from the carbon atom balance equation:

$$\Phi(h,E_i)Y_{\mathrm{NT}}(E_i)+N[D^*(E_i)]=N[W], \tag{4}$$

where $N[D]=0.5D\pi(3\sqrt{3}a_{gr}^2a_s)^{-1}$ is the number of atoms (per cm^2) in a MWNT with the outer diameter D,[15] $a_{gr}=0.142$ nm. The first summand is the number of carbon atoms sputtered from the MWNT during irradiation, the second one corresponds to the number of atoms in a MWNT with diameter D^* needed for preventing damage creation below the MWNT upon the impact of the last ion, see Fig. 2(b) and Eq. (1).

Combining Eqs. (1)–(4), we arrive at an expression which connects W and h:

$$W(h,E_i)=A_1E_i+A_3n_mhY_{\mathrm{NT}}(E_i)/Y_m(E_i), \tag{5}$$

where the constant $A_1=5.6$ nm/keV, $A_3=0.13\times10^{22}$ cm^3, $Y_{\mathrm{NT}}(E_i)$ is given by Eq. (3), and E_i is in the range 0.1 keV $<E_i<0.5$ keV. For a 10-nm-thick gold layer (thinner layers could hardly be used due to poor conducting properties)[4] and $E_i=0.2$ keV, we obtain $W\approx3$ nm. Equation (5) is universal and can be used for any layer material provided that we know its sputtering yield.

Note that the minimum width of the wires which have experimentally been obtained[4] is larger than our predicted limit by a factor of 4. This is due to, apparently, a higher irradiation dose used than actually needed, and surface migration of metal atoms at room temperature. To prevent this, the system should be irradiated at low temperatures.

Thus, this technique potentially provides a better resolution than the present-day electron-beam lithography,[16] although a low AFM operation speed prevents mass production of metal wires using nanotubes as masks against ion bombardment. We finally point out that this setup can also be employed for spatially selective ion implantation into the regions of the samples which have not been covered with the nanotubes.

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