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

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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. The examples are graphite-to-diamond transformations in carbon onions under irradiation, irradiation-induced carbon nanotube welding, and cross linking, 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. 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 SiO₂ substrate. 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 an 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 molecular dynamics (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 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 \( a_e = 0.34 \text{ nm} \). 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 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 \( E_i = 0.1 \text{--} 1.5 \text{ keV} \) 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 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

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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.
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).

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

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

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 $Y_C/Y_{Au} \approx 0.05$ at $E_i = 0.2 \text{ keV}$ and $Y_C/Y_{Au} \approx 0.25$ at $E_i = 1 \text{ keV}.^{13}$ Thus, $E_i$ should be rather low, in a range of $0.1$–$0.5 \text{ keV}$. 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 $\Phi$ needed to sputter the layer

$$\Phi = n_m h / Y_m, \quad (2)$$

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

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 $\Phi = 1.6 \times 10^{15} \text{ cm}^{-2}$. $E_i = 700 \text{ eV}$ 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 $N_{c}(\Phi)/N_{c}(\Phi = 0)$ of the energetic recoils below the MWNT as a function of irradiation dose $\Phi$. Surprisingly, $N_c$ remained after this irradiation dose roughly the same. At low irradiation doses $N_c$ 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 $N_c$ at higher $\Phi$ 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 $D > 3 \text{ nm}$ (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 $E_i < E_{th}$. Notice that $Y_{NT}$ is almost one order of magnitude larger than $Y_C$. 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

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

Having calculated $Y_{NT}$, we can estimate the minimum...
width $W$ of a metal wire which can be made using MWNTs as masks (we assume that $W=D$) from the carbon atom balance equation:

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

where $N[D] = 0.5D\pi(3/2a^2_{gr}a^2_{as})^{-1}$ is the number of atoms (per cm$^2$) in a MWNT with the outer diameter $D$, $a_{gr} = 0.142$ 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 $h$:

$$W(h,E_i) = A_1E_{i} + A_2n_{nt}hY_{NT}(E_i)/Y_{ns}(E_i)$$

where the constant $A_1 = 5.6$ nm/keV, $A_2 = 0.13 \times 10^{22}$ cm$^3$, $Y_{NT}(E_i)$ 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) and $E_{i} = 0.2$ keV, we obtain $W = 3$ 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 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, 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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12 In most common FCC metals, close Frenkel pairs annihilate at or even below room temperature, see, e.g., Landolt-Börnstein, New Series III Vol. 25 edited by H. Ullmaier (Springer, Berlin, 1991), Chap. 2, p. 88.
14 J. F. Ziegler and J. P. Biersack, Program trimp (1996) The displacement energy (34 eV) was taken from MD simulations (Ref. 9) other parameters had default values. We calculated sputtering yield from amorphous carbon at different angles of ion incidence and integrated over the MWNT surface.
15 The total number of atoms in a MWNT with outer diameter $D$ and length $L$ (composed of armchair single-wall nanotubes) is $N_{nt} = \pi(3/2a^2_{gr}a^2_{as})^{-1}L(D+2a_2)$, as simple calculations indicate. Because inner shells with smallest diameters are frequently absent in MWNTs (Ref. 10), we decreased the number of atoms by a factor of 2 and left out the $2a_2$ term.