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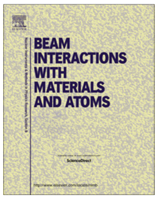

Multiwalled carbon nanotubes as masks against carbon and argon irradiation. A molecular dynamics study

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ABSTRACT

Experiments showed that multiwalled carbon nanotubes (MWCNT) can be used as masks against irradiation to create metallic nanowires in a substrate. In order to understand the limitations of this application, it is interesting to know the energy and number of carbon atoms emerging from the MWCNT after the irradiation and how the structure of the MWCNT is modified. Using a molecular dynamics code that we have previously developed, we have simulated the continuous irradiation of MWCNT with carbon and argon projectiles. We have obtained that the use of carbon instead of argon to irradiate the MWCNT increases de effectiveness of the MWCNTs as masks, due to the ability of the carbon projectiles to be part of the MWCNT structure and partially mend the damage produced during irradiation.

We have analyzed the number, energy, and spatial distribution of the recoils generated during irradiation and the change of the MWCNT structure as a function of the incident energy (100 and 500 eV), fluence (up to $4.5 \cdot 10^{15}$ ions/cm^2), and number of shells (up to 5-shells) of the MWCNT. These results determine the effectiveness of MWCNT as a mask, being useful to understand whether the atoms emerging from the MWCNT produce damage in the substrate or not.

We find that for carbon projectiles the efficiency of MWCNT as masks does not depend much on the fluence, but on the number of nanotube shells and projectile incident energy. On the other hand, for a given nanotube and fluence, we observe a threshold incident energy below which the nanotube acts as a perfect mask.

1. Introduction

Since their discovery in 1991 [1], carbon nanotubes (CNT) have attracted a lot of attention due to their outstanding mechanical and electronic [1–3]. For instance CNT can be metallic or semiconductor depending on the way they are rolled up [1], which make them ideal candidates for their use in nanoelectronics. Many other potential applications of CNT such as electrochemical devices, hydrogen storage, sensors, guide and transport energetic charged particles, etc. have been proposed [2,4–6].

The irradiation of CNT has been shown to be an important tool to modify their structure and properties in a controlled way [7,8]. Using irradiation it is possible to cut or weld the CNT, reduce their diameter, form junctions, produce amorphization in multi-walled carbon nanotubes (MWCNT), etc. [7].

Experimentally it was shown that MWCNT can also be used as masks against irradiation. In this way the substrate under the MWCNT is protected from the sputtering and so this technique can be used to produce ultra narrow metal nanowires [9]. Using molecular dynamics, this was previously analyzed for MWCNTs under argon irradiation [10]. In this work, we suggest that the suitability of MWCNT as masks will depend on the type, fluence, and energy of the projectiles used to irradiate them. Krasheninnikov *et al.* have studied this issue [10], but only for argon projectiles, and derived an equation to calculate the width of the nanowire that can be generated with this technique.

In this work we study the suitability of MWCNT as masks against irradiation with carbon ions using computer simulations, and we compare our results with those obtained when using argon projectiles. We quantify the efficiency of the MWCNT as masks and analyze the dependence of this efficiency on the projectile incident energy and fluence, showing that, unlike what is expected, when using carbon projectiles, the dependence of the mask efficiency on the fluence is not very relevant.

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2. Simulation code

In order to simulate the irradiation of MWCNT by carbon and argon projectiles, we have used a numerical code based on classical molecular dynamics (MD) [11]. In this code, the forces acting on each carbon atom were calculated by means of the Brenner potential [12], but without considering the bond conjugation terms, which are not relevant for energetic collisions [13], smoothly linked [14] to the Ziegler–Biersack–Littmark (ZBL) universal potential at short interatomic distances [15]. On the other hand, the interatomic forces between the argon projectiles and the carbon atoms of the CNT were calculated by means of the Ziegler–Biersack–Littmark (ZBL) universal potential [15].

We have numerically solved the equations of motion of all interacting atoms using the velocity Verlet algorithm [16] with a variable time step Δt, which depends on the maximum velocity and force, to reduce the computing time. In addition, the nanotube temperature is controlled using the Berendsen thermostat [17]. Note that the carbon atoms at both ends of the nanotube are fixed during the simulation, in order to avoid the displacement of the nanotube during the irradiation.

In this work we have simulated the irradiation with carbon and argon projectiles up to $E_0 = 1200$ eV of carbon nanotubes up to 5-shells, armchair (10, 10), (15, 15), (20, 20), etc., with length ~ 100 Å, and with its axis parallel to the z-axis. It is worth to mention that we have neglected the electronic energy-loss in our simulations because of the low projectile incident energies involved. The nanotube radius depends on the number of shells, being $r_{\mathrm{CNT}} \sim 7$ Å for the single-walled carbon nanotube (SWCNT) and $r_{\mathrm{CNT}} \sim 21$ Å for the 5-shells MWCNT. We show in Fig. 1 the longitudinal view of the SWCNT we used in our simulations, which is attached by its ends, both having fixed positions. In addition, we show in Fig. 1 the transversal view of the 5-shells MWCNT we have considered in our simulations. It is worth to mention that the velocity of the carbon atoms located in a region of 5% of the total length of the nanotube, next to its fixed ends, are scaled according to the Berendsen thermostat, as previously mentioned. As it is depicted in Fig. 1, the projectile bombards the nanotube in the x-direction, perpendicular to the nanotube axis, although the exact impact coordinates are randomly distributed on a central region of 10% of the total length of the nanotube. We simulate the bombardment of the nanotube with 200 consecutive projectiles. Our simulation procedure for the bombardment of each projectile is divided on three stages. Firstly, we simulate the collisional stage during 10 ps, then we simulate an annealing stage at temperature $T = 1500$ K during 100 ps, and finally, we simulate the subsequent quenching to ambient temperature during 20 ps. The annealing temperature was chosen in such a manner that it is the highest possible, in order to stimulate the healing of defects, but without producing misleading defects on the CNT [11].

During irradiation, the projectiles transfer energy to the nanotube, which produces the displacement of some of the atoms of the nanotube, resulting on recoils and vacancies generation. In order to evaluate the efficiency of using a nanotube as mask, we analyze the position and energy of the atoms reaching a plane located 2 Å behind the MWCNT, where we assume the substrate is placed (see Fig. 1). Such information provides insight about the damage produced on the substrate behind the nanotube, when using these nanotubes as masks against irradiation.

3. Results

We show in Fig. 2, the number of atoms arriving to a plane placed 2 Å behind a carbon nanotube, with 1, 3, or 5-shells, as indicated in the figure, irradiated with carbon projectiles, for different incident energies and fluences. These curves correspond to an average of the results from 15 different independent runs. Specifically, the graphs of the upper panel show the results for projectile incident energies of 100 eV, whereas the graphs of the lower panel show the results for 500 eV; the labels indicate the fluence values, being (a) $1.1 \cdot 10^{15}$, (b) $2.2 \cdot 10^{15}$, and (c) $4.4 \cdot 10^{15}$ ions/cm^2. The distance between the thin vertical dashed lines represents the diameter of the carbon nanotube. The cyan lines correspond to all atoms and the black lines correspond to atoms with energies higher than $E_{\mathrm{th}} = 37$ eV, those that we assume that can sputter an atom on the metallic substrate. This particular value of E_{th} corresponds to the minimum energy of a carbon atom to produce sputtering in a platinum surface [18,19]. For other metals and for argon projectiles the value of E_{th} is lower, so we can be sure that atoms with energy higher than 37 eV will produce damage in any metallic substrate. As can be observed, the 5-shells nanotube is a good mask against irradiation for all fluences and energies considered, whereas the 3-shells nanotube is a good mask for 100 eV incident energy. In the other cases, CNTs are partial masks or do not act as a mask at all.

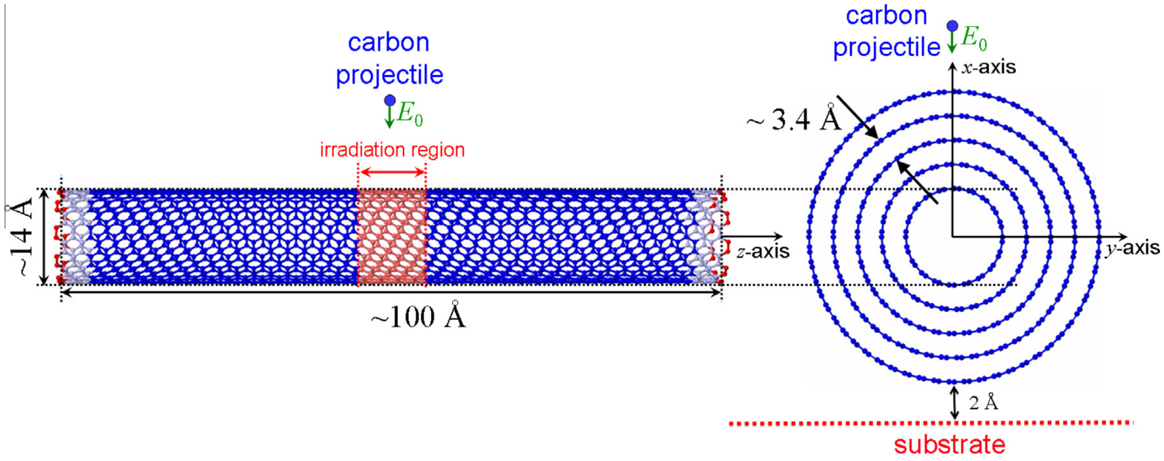

Fig. 1. Scheme of the studied system. A MWCNT is bombarded by carbon projectiles and we analyze carbon atoms reaching a plane located 2 Å below the MWCNT. At the left we observe a lateral view of the inner shell of the MWCNT. Red atoms at both ends are fixed, grey atoms close to both ends act as a Berendsen thermostat. Carbon projectiles bombard the central region of the MWCNT represented by pink atoms. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)