Multiwalled carbon nanotubes as apertures and conduits for energetic ions

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(Received 3 February 2005; published 16 June 2005)

We perform molecular dynamics simulations to study motion of heavy ions with kilo-electron-volt energies through multiwalled carbon nanotubes. We show that under certain conditions on the tube alignment with respect to the ion beam and on ion energies, the ions can efficiently channel through the empty cores of the nanotubes. We demonstrate that the dependence of the critical angle on ion energy obeys a simple continuum-theory-based equation. We further discuss making a nanotube-based conduit for energetic ions, which should work as an aperture and allow one to manipulate ion beams at the nanoscale.

DOI: 10.1103/PhysRevB.71.245408 PACS number(s): 81.07.De, 61.80.Az, 61.85.+p

Channeling of energetic ions through solids is a phenomenon which is highly important for the present-day semiconductor technology.[1,2] Basically, when an energetic ion moves nearly parallel to a major axis or plane in a single crystal, it can be steered down the open channel between the aligned rows of atoms, thereby avoiding violent collisions with the host atoms and giving rise to deeper implantation and less lattice disorder. On the other hand, such a behavior also complicates obtaining shallow junctions and reproducible range profiles.

The channeling effects are particularly important for materials with high crystallinity and anisotropic atomic structure. One can expect that the effective channeling of ions is possible in carbon nanotubes[3] (CNTs), as they have hollow cores, a high aspect ratio, and a low concentration of defects.

The motion of light ions (protons) through single-walled nanotubes (SWNTs) has received considerable attention,[4,5] as SWNT bundles were suggested for steering the beams of high-energy [giga-electron-volt (GeV)] protons. However, it is not clear at all if CNTs can in practice be used for this purpose, because the bundles will quickly be destroyed by the beam as experiments on proton irradiation of SWNTs indicate.[6]

Contrary to light ions, channeling of heavy ions through CNTs has not yet been studied. At the same time, this issue is of fundamental interest, as the energy transfer mechanism is absolutely different in this case (nuclear stopping dominates over electronic stopping) and the well-controlled atomic structure of CNTs makes it possible to check (e.g., by the transmission electron microscope) the fundamentals of the heavy ion channeling theory for solids, and specifically for graphitic systems.[7] Besides this, as CNTs can easily be bent and manipulated at the nanoscale, developing a CNT-based conduit for energetic ions could be an advance in spatially localized shallow ion implantation, which might be particularly important for the further progress in the solid-state quantum computing.[8]

In this work, we theoretically study channeling of heavy ions with keV energies through multiwalled nanotubes (MWNTs). We further discuss making a MWNT-based conduit for energetic ions, which should work as an aperture and allow one to manipulate the beam at the nanoscale.

Effects of ion irradiation on nanotubes have been studied both experimentally[6,9–12] and theoretically.[13,14] However, when estimating the ion ranges, it has been assumed that the beam direction is perpendicular to the tube shells. Now, to address channeling through the tubes, we must consider the opposite case: the ion beam direction is nearly parallel to the tube axis, see Fig. 1(a).

It is intuitively clear that an energetic ion propagating through the tube empty core can travel very far, provided that the angle between the tube axis and ion velocity is vanishingly small. However, the situation is not so straightforward when the tube is bent or the beam alignment with respect to the tube axis is not perfect. To understand the nature of ion interactions with MWNTs, we considered first the collision of the ion with the inner shell of a MWNT, see Fig. 1(a). The neglect of all other MWNT shells is well motivated in this case as the shells are spatially separated by 3.2 Å and they are only weakly bounded to each other via van der Waals (vdW)-type forces.[3]

To describe collisions of energetic ions with the nanotube, we employed molecular dynamics[15] (MD) with analytical

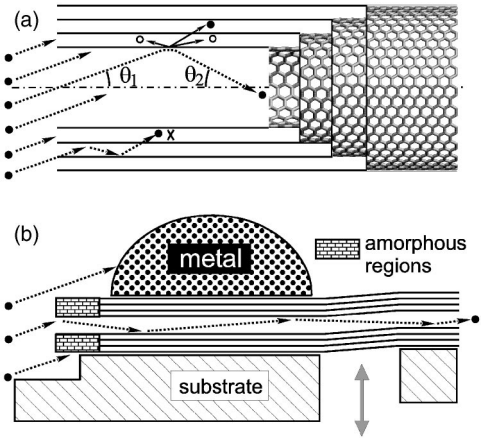

FIG. 1. (a) Schematic representation of a beam of Ar ions colliding with a multiwalled carbon nanotube with an open end. Depending on ion energy, impact point, and angle Θ_1, the ion hitting the inner shell of the tube can either remain in the core region or go through the shell. (b) The basic idea for a nanotube-based ion aperture.

potentials. The MD method can describe well both chaotic and coherent many-body atomic collisional processes[16] and it has been demonstrated to reproduce very accurately experimental channeling results in Si.[17] The simulation method has been described at length in other publications[13,14] and therefore we present here only the details essential for this study. To model carbon-carbon interactions, we used the Brenner II interatomic potential.[18] We chose Ar as the typical heavy ion. The interaction between Ar ions and C was modeled with the Ziegler-Biersack-Littmark universal repulsive potential.[19] A very large cutoff range of 4 Å was used for the Ar—C interaction, as we found that shorter cutoff ranges effected the results. We did not account for the electronic stopping as the ion energies considered were low and the nuclear slowing down completely governed the collisional phase. Besides this, the electron density in the MWNT cores is very low. We considered both zero and finite (room) temperatures.

We started with the following question: What happens during the collision of an Ar ion with a SWNT and how does the ion trajectory depend on the ion energy E and the incidence angle Θ_1 [the angle between the tube axis and the original ion velocity vector, see Fig. 1(a)]? We considered ions with energies of 0.1–20 keV and $\Theta_1 = 8° - 20°$. For each ion energy and angle we simulated 100 impacts and collected the statistics. The polar angle (the projection of the ion velocity vector onto the plane perpendicular to the tube axis) and the impact points were randomly chosen. To understand the role of the tube atomic structure we considered (10,10) armchair, (17,0) zigzag, and (12,8) chiral SWNTs with diameters of 1.3–1.4 nm.

We found that at low energies the ion is always bounced back by the wall without creating any damage to the tube. At higher energies the ion can sputter 1–4 carbon atoms from the tube, but it still remains inside the tube, as schematically shown in Fig. 1(a). At a certain energy E_{dc} (the dechanneling energy—the maximum energy for channeling; in practice, we defined E_{dc} as an energy at which the ion remains inside the tube with a probability of 95%) which depends on Θ_1, the ion goes through the wall. The probability of dechanneling (the number of dechanneled ions per incident ion) as a function of ion energy is shown in Fig. 2 for the zigzag SWNT. It is seen that E_{dc} is critically dependent on the angle, but even when ion energy is higher than E_{dc}, the ion has a finite probability to stay inside the tube after the collision.

We obtained qualitatively similar results for the armchair and chiral tubes. Using the data presented in Fig. 2, one can plot E_{dc} versus the angle, or the other way around, one can present the maximum, or critical, angle ψ_c as a function of ion energy, see Fig. 3. The results for zigzag and chiral tubes are very close to each other. However, as seen from Fig. 3, for a given angle the ions start penetrating through the armchair tube at lower energies than for other SWNTs. This can be associated with the orientation of the graphene network with respect to the ion beam direction. For armchair SWNTs, the C—C bonds are oriented perpendicular to the ion beam, see the inset in Fig. 3. Due to a larger projected distance between the atoms in the armchair tubes, the ion can more easily go through the middle of the bond than in all other SWNTs.

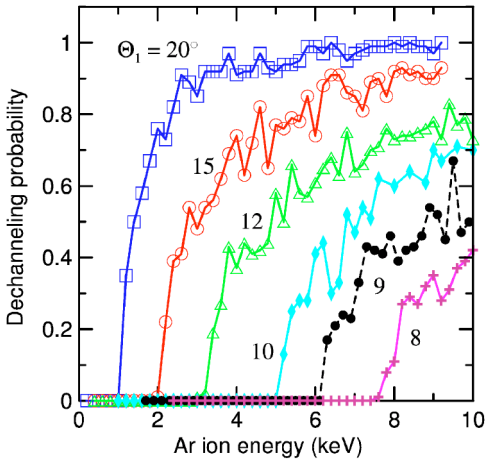

FIG. 2. (Color online) Dechanneling probability as a function of Ar ion energy at different angles of incidence Θ_1 for a zigzag (17,0) SWNT.

The simulations results shown in Fig. 3 can be described by a universal curve fit to the data. We found that the results can well be reproduced by an equation $\psi_c = \text{const}/\sqrt{E}$, see also Fig. 3. This is in line with a general equation[1] $\psi_c = \sqrt{U(r_c)/E}$, where $U(r_c)$ is the ion potential energy at the critical approach distance r_c. The latter equation has been derived within the framework of the continuum theory of channeling, and it is of limited validity (see, e.g., Ref. 1, and references therein), as only one row or plane of atoms is taken into account to calculate $\psi_c(E)$. However, the open structure of SWNTs motivates well this approximation for evaluating the critical angle.

Because lattice vibrations play a significant role in ion channeling,[1] we further simulated collisions of Ar ions with nanotubes at room temperature. The critical angle as a function of ion energy is shown in Fig. 3 at room temperature for the chiral SWNT. As expected, for a given Ψ_c finite temperatures resulted in a decrease in maximum ion energies, but the

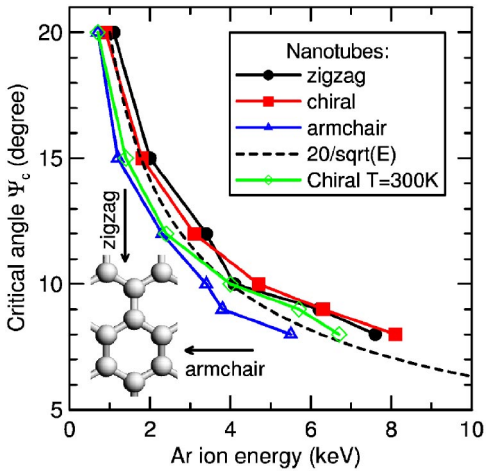

FIG. 3. (Color online) Critical angle as a function of ion energy for nanotubes with various chiralities. The dashed line is a fit to the data. The inset shows the orientation of the armchair and zigzag nanotube atomic network with respect to the ion beam direction.

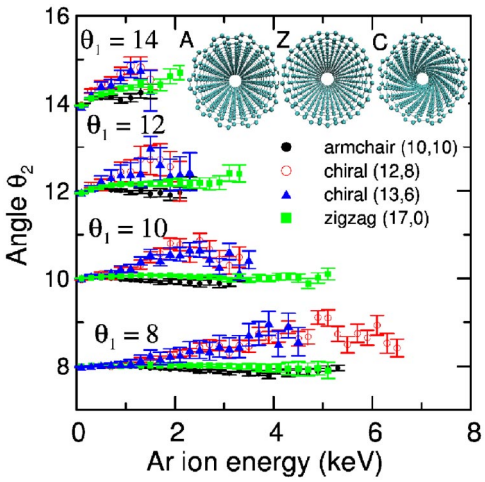

FIG. 4. (Color online) Scattering angle Θ_2 as a function of ion energy at different angles of incidence Θ_1 for various SWNTs. The inset shows the atomic networks of armchair (*A*), zigzag (*Z*), and chiral (*C*) SWNTs. Finite angles between the rows of atoms and ion trajectories increase ion scattering angles in chiral nanotubes.

effect was small—about 10%–20% of the corresponding values at $T=0$. Qualitatively the same results were obtained for other tubes considered. The relatively weak influence of finite temperatures can be understood in terms of small atom vibration amplitude as compared to the inner diameter of the tubes.

The next highly important issue to be addressed is the average scattering angle Θ_2 of the ion, see Fig. 1. One can expect that an ion propagating through the MWNT core will collide many times with the inner wall of the MWNT. Thus, if Θ_2 quickly grows after each impact, this should inevitably result in ion dechanneling.

Figure 4 shows Θ_2 as a function of ion energy at different Θ_1 for various SWNTs. It is evident that for armchair and zigzag tubes $\Theta_2-\Theta_1$ at smaller values of Θ_1 and lower energies, when the energy losses are small, which means that the ion trajectories are nearly reversible.[20] However, at larger angles of incidence ($>10°$), $\Theta_2>\Theta_1$, as the ion loses a substantial part of its kinetic energy and thus it is not possible to reverse the ion path.

For chiral tubes Θ_2 is always larger than Θ_1. The reason for that is clear from the inset in Fig. 4 showing the atomic networks of armchair (*A*), zigzag (*Z*), and chiral (*C*) SWNTs. In chiral tubes, the rows of atoms are not parallel to the ion direction, which gives rise to enhanced scattering and energy losses. This result indicates that effective channeling of heavy ions is possible only through achiral tubes. Finite temperatures were found to slightly increase scattering angles (by 1%–4% at $T=300$ K). We received similar results for the ions colliding with flat graphene planes.

Because for ion energies lower than E_{dc}, the ion trajectories are close to reversible, the number of collisions governed by the total length of the tube will determine the ion energy at the output from the other tube end and set the lower limit on the initial energy of the ion to go through the tube of a given length. As our simulations indicate, energy losses at $E=E_{dc}/2$ are 0.05–0.1 keV per single collision. Assuming that $\Theta_2=\Theta_1$ one can estimate the averaged number of collisions and the final energy of the ion. For example, if $\Theta_{ini}=8°$ and $E_{ini}=12$ keV, the ion should go through a micron-long SWNT with an inner diameter of $d=1.5$ nm and have at least 7 keV at the output from the other end of the tube.

As mentioned above, in our simulations we did not account for the electronic stopping of the ions, as in the energy range considered the nuclear stopping dominates. For higher ion energies, when the electronic effects become more important, our model can be augmented with the formalism developed in a recent work[21] on propagation of particles through cylindrical nanochannels. In that work, the interaction of ions and neutral particles with the channel was modeled within the framework of the classic electromagnetic theory. It was concluded that the particles can be transmitted through nanochannels with lengths up to hundreds of microns without significant energy losses. However, for carbon nanotubes these estimates seem to be too optimistic, as nuclear stopping was not properly taken into account, while our simulations indicate that every collision with the nanotube wall gives rise to energy losses.

Having analyzed propagation of energetic ions through SWNTs, we moved on considering MWNTs. Simulations for double-walled and triple-walled MWNTs with account for vdW interactions between shells[22] gave basically the same results for single ion impacts.[23] We also simulated effects of the high-dose irradiation on the atomic structure of the MWNT for $\Theta_{ini}=5°-15°$ and an ion energy of 1 keV. To account for annealing of defects at the microscopic time scale (several microseconds or more at the typical ion currents) between ion impacts but at low temperatures, we first simulated the collisional phase at room temperature, then kept the system at 500 K for 0.1 ns, after which the system was quenched down to 300 K before the impact of the next ion. We found that the open end of the irradiated tube becomes completely amorphous at an irradiation dose of $\Phi\sim10^{15}$ cm^{-2}, but for MWNTs with inner diameters of about 1.5 nm the inner core remained open ut to $\Phi=4\times10^{15}$ cm^{-2}. This means that MWNTs, especially the MWNTs with larger inner cores can survive "shooting" about a hundred ions with higher energies before the end of the tube is completely destroyed and closed. Amorphization of the atomic structure near the end will also decrease the number of ions channeling between the shells, although one can expect that even without account for this effects the ranges of ions between the shells will be much smaller than in the core due to higher electron density and larger number of collisions with the walls. At the same time, a substantial part of defects in the central part of the MWNT should anneal due to the migration of carbon interstitials[24] and by saturating vacancy dangling bonds.[14]

The efficient channeling of ions through achiral MWNTs can be employed to make a MWNT-based apertures to make a nanobeam and to steer the beam. Such an aperture can be produced by employing a combination of techniques routinely used nowadays for handling supported CNTs. A MWNT deposited on a substrate can be straightened[25] and cut[26] to open its ends by the tip of the atomic force microscope, then by applying a combination of etching and

electron-beam lithography techniques[27] the metal shield can be produced, see Fig. 1(b). The beam can be steered by moving the whole unit or, ideally by bending the MWNT. Thus, the target can be irradiated in predetermined positions by a beam just several nanometers across. Such a device can be used for implanting ions or even single ions, which is highly important for the further progress in the solid-state quantum computing.[8] As channeling is possible through bent tubes, the technique should make it possible to direct ions onto the regions unattainable by direct ion irradiation. Note also that CNTs have been suggested as possible conduits for atoms and molecules with thermal energies.[28–30] Extensions to higher energies of the particles might also result in developing other promising applications in biology and materials science.

To conclude, we theoretically studied channeling of Ar ions through carbon nanotubes. We found that the ions can channel through the empty cores of the MWNT with a very low probability of dechanneling if the inner shell is an achiral tube. We showed that the dependence of the critical angle on ion energy obeys a simple universal equation. As interactions of energetic ions with the target are well described by the universal repulsive potential,[19] such a behavior should be general for not only Ar but also other heavy ions. We finally suggested making a nanotube-based conduit for energetic ions, which should work as an aperture and allow one to manipulate the beam at the nanoscale.

We would like to thank Professor G. Hobler, Professor F. Banhart, and Professor Zh. Zhu for fruitful discussions. The research was supported by the Academy of Finland under Project Nos. 48751, 50578, and 202737. Grants of computer time from the Center for Scientific Computing in Espoo, Finland are gratefully acknowledged.

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