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Making junctions between carbon nanotubes using an ion beam

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Abstract

Making use of empirical potential molecular dynamics, we study ion bombardment of crossed single-walled carbon nanotubes as a tool to join the nanotubes. We demonstrate that ion irradiation should result in welding of crossed nanotubes, both suspended and deposited on substrates. We further predict optimum ion doses and energies for ion-mediated nanotube welding which may potentially be used for developing complicated networks of joined nanotubes.

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The possibility for joined nanotubes to be the building blocks of various nanoscale electronic devices [1] has triggered a considerable interest [1–7] to the problem of connecting single-walled carbon nanotubes (SWNTs). Two-terminal heterostructures formed by end-to-end connections between nanotubes with different chiralities have been shown to work as quantum dots [4,5] or diodes [6,7], and multi-terminal heterostructures (''Y'' and ''T'' nanotube junctions) as nanoscale transistor devices [8].

However, experiments on two-terminal heterostructures have been carried out on specific samples in which the connections between nanotubes accidentally appeared at the stage of nanotube growth. It is not quite clear yet how nanotubes of predetermined lengths and chiralities can experimentally be joined. The same problem exists in making multi-terminal heterostructures. Although a high-yield fabrication of multi-walled nanotubes with ''Y'' junctions has been reported [9–11], the growth technique used does not allow one to make a more complicated network of joint nanotubes with predetermined positions of junctions between nanotubes.

Connections between nanotubes have also been made by chemical functionalization [12] or by nanotube soldering [13] using scanning electron microscope to provide deposition of carbon selectively at nanotube junctions. It has also been suggested [14] to use a low energy (3 eV) bombardment of crossed nanotubes with carbon ions to form carbon chains between the nanotubes and,

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thus, solder them. However, the mechanical stability of these junctions and the control over the electrical properties of such heterosystems is still an open question.

A fundamentally different approach to making connections between nanotubes was recently put forward [15]. It has been demonstrated that crossed SWNTs can be welded together by irradiating the junction in a transmission electron microscope (TEM). The junctions were created due to defects (vacancies and interstitials) induced by a high energy (1.25 MeV) focused electron beam.

In this work, making use of molecular dynamics [16] with empirical potentials to model the defect production under argon ion irradiation, we theoretically study ion irradiation of crossed SWNTs as an alternative technique to form nanotube junctions.

To model carbon–carbon covalent interaction, we used the Brenner II interatomic potential [17]. van der Waals-type interactions between carbon atoms in different nanotubes were described by a potential [18] which had been developed earlier by us for simulating the interlayer interaction in graphite. We stress, however, that the intertube van der Waals interaction is essential only between *pristine* nanotubes where all the carbon atoms are in the sp^2 hybridization.

We used open boundary conditions. To cool down the system and damp pressure waves at the borders of the system, the Berendsen temperature control [19] was used at the borders for the first 10 ps after ion impact. Similar to experiments [15] on electron irradiation of crossed carbon nanotubes, the system temperature was chosen to be 1000 K. In order to estimate the defect annealing during macroscopic times between ion impacts onto a system of about 100 nm^2 (time intervals between ion impacts are longer than microseconds even for the highest irradiation currents experimentally attainable), we simulated the system evolution over 100 ps at 2000 K. After this the temperature was everywhere scaled down to the irradiation temperature (1000 K) at a rate of 1 K/ps. This computational technique made it possible to gain an idea of the behavior of defects on macroscopic time scales. Some other details of our simulations can be found in [20,21].

We considered crossed 100 Å-long SWNTs of different chiralities and diameters implying that they are fragments of much longer nanotubes (see Fig. 1). In our simulations, we assumed that our theoretical setup corresponded to either suspended (free standing) crossed nanotubes or those lying on a substrate.

The first situation has been studied by Terrones et al. [15] for the case of electron irradiation. The crossed nanotubes have been deposited on the specimen grid of a TEM, and they did not interact with the environment near the crossing point.

For the suspended nanotubes, we kept the nanotube ends fixed during ion impact simulations, but during the annealing all the atoms were allowed to move. Because we were interested in irradiation-induced phenomena near the tube contact, we irradiated only the contact area, as shown in Fig. 1(b).

However, for supported nanotubes, the presence of the substrate is quite important, since ion-irradiation results in irradiation-induced pinning of nanotubes to the substrate [21] and, hence, in some extra force exerted by the upper SWNT on the lower one.

Due to computational limitations, we were unable to account explicitly for effects of a substrate and irradiation-stimulated nanotube–substrate interaction. However, we estimated the force which should exert the upper nanotube on the lower by simulating the behavior of an interface between a platinum substrate and a nanotube with one elevated end. Typical values of the irradiation-induced force were in the range 10–40 nN (the actual value depends on tube diameters, defect distribution and other factors). To account for this pressing, after every ion impact (before running the annealing simulations) we moved down the boundary atoms at the ends of the upper nanotube by 0.05 Å.

As for extra damage in nanotubes created by the sputtered substrate atoms, this damage can anneal quite easily [21] provided that the ion energy is not too high (<1 keV). This is because backward sputtered substrate and carbon atoms are much less energetic than the incident Ar ion and create mostly close Frenkel pairs (for SWNTs, a vacancy and carbon adatom adsorbed onto the

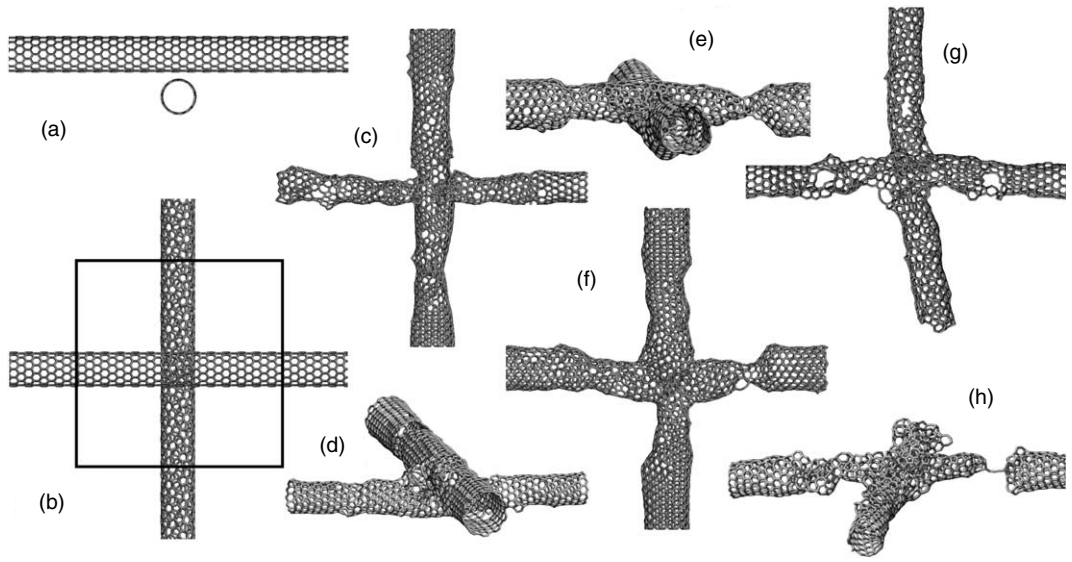

Fig. 1. Molecular models of crossed carbon nanotubes in the stick representation. Two nanotubes before ion irradiation (a) and (b). The box indicates the irradiated area. Top (c) and side (d) view of the interface of suspended $(10, 10)$ and $(12, 0)$ nanotubes after irradiation dose $\Phi = 0.5 \times 10^{15}$ cm^{-2}. Ion energy $E_i = 0.8$ keV. The same for the interface of supported $(10, 10)$ and $(10, 10)$ nanotubes, $\Phi = 0.9 \times 10^{15}$ cm^{-2}, $E_i = 1$ keV. Crossed nanotubes under low temperature irradiation (g). The amount of defects is much higher in this case since the defect annealing practically does not occur. Example of a nanotube break-up and strong amorphization of the carbon network (h) when the irradiation dose is higher than actually needed.

nanotube wall) which anneal due to adatom migration.

We carried out simulations of Ar ion bombardment of crossed SWNTs characterized by the chiral indices as follow: $(10, 10)$–$(10, 10)$; $(12, 0)$–$(10, 10)$; $(12, 0)$–$(10, 3)$; $(16, 0)$–$(16, 0)$. Although the choice of the nanotube chirality was somewhat arbitrary, the expectation is that the simulation results are qualitatively correct for any SWNTs with diameters in a range of from 8 to 20 Å and weakly depend on the chiralities of crossed nanotubes. For every pair of nanotubes, we irradiated the system with Ar ions having energies $E_i = 0.4$, 0.8 and 1 keV.

Typical atomic configurations of crossed nanotubes with various chiralities after ion bombardment are shown in Fig. 1(c)–(f). A molecular model for $(10, 10)$–$(12, 0)$ suspended crossed SWNTs is presented in Fig. 1(c) and (d) with the irradiation dose $\Phi = 0.5 \times 10^{15}$ cm^{-2}. Only the contact area was irradiated, as described above. It is seen that covalent bonds between nanotubes have been formed during the irradiation. These bonds appeared near irradiation-induced defects, mostly vacancies, due to dangling bond saturation. Formations of these bonds always resulted in lowering the total potential energy of the system with defects, when a number of carbon atoms have been removed from the interface region by incident ions.

Fig. 1(e) and (f) shows the interface of $(10, 10)$–$(10, 10)$ supported crossed SWNTs, $\Phi = 0.9 \times 10^{15}$ cm^{-2}. For the nanotubes on a substrate, the extra pressure at the crossing point originating from the nanotube–substrate interaction resulted in almost complete merging of nanotubes at the crossing point. The suspended SWNTs were soldered together rather than welded by forming the real "X"-junction. We stress, however, that the experimentally observed merging [15] of nanotubes under electron irradiation occurs on time scales of minutes. This time scale cannot be achieved in present-day atomistic simulations due to computational limitations. Thus, these atomic configurations should be considered as intermediate states, which, nevertheless, outline the route to the

complete merging of nanotubes by forming an interface between two nanotubes consisting only of hexagon and pentagon rings.

The bombardment also resulted in sputtering of a substantial amount of atoms from the nanotubes, amorphization of the atomic networks and the shrinkage of the apparent nanotube diameter. This reduction in the nanotube diameter is due to the healing of irradiation-induced vacancies through dangling bond saturation. A similar behavior of nanotubes under electron irradiation has been reported by Ajayan et al. [22] Note that at the irradiation doses used in our simulations, the SWNTs preserved tubular form and remained hollow.

In spite of defect annealing at elevated temperatures between ion impacts, a large number of defects are clearly evident in the nanotube network. A complete annealing of defects did not take place due to the above mentioned limitations on the simulation time. Most irradiation-induced defect should disappear after high-temperature annealing. Thus, although ion bombardment creates damage not only in the junction area but also far from it, irradiation of nanotubes combined with high-temperature treatment can be used to weld nanotubes together preserving, at the same time, their tubular form. We found that the irradiation-induced welding occurs for nanotubes having any chirality, although the mechanical stability and the welding time should depend on the chirality because of different number of pentagons needed to join the networks of nanotubes with different chirality.

Having demonstrated a principal possibility for nanotube welding with the help of ion beams, we proceed to the issue of the optimum range of ion energies. If ion energies are too low, very few defects in the interface region will be formed. On the other hand, highly energetic ions can give rise to formations of severely damaged regions (or to a complete break up of a nanotube), especially for nanotubes on substrates. For supported nanotubes, high energy ions will inevitably result in sputtering of a substantial number of energetic substrate atoms, which will pose considerable problems for the damage control.

One can expect that the criterion for the optimum energy of an Ar ion is that the energy of an incident ion should enable the ion to penetrate through the upper nanotube and displace one or two carbon atoms in the lower nanotube. Carbon atoms can be knocked off from the lower nanotube by not only Ar ions, but also carbon recoils.

We simulated impact events of Ar ions with energies E_i up to 0.6 keV on SWNTs with various chiralities. The impact points were randomly chosen over the upper SWNT surface in the junction area. For every ion energy considered, we carried out 400 independent runs and averaged the results.

We found that, independent of the nanotube chirality, if E_i was in a range of $0.3 < E_i < 1$ keV, it produced one–two energetic recoils (both Ar and C atoms) below the nanotube and less then one recoil if $E_i < 0.3$ eV. At energies higher than 1 eV the number of recoils does not depend on E_i, due to a decrease in the probability [21] to create a defect in nanotube. Since the Ar ion should have an energy of at least 34 eV to displace a carbon atom from a graphitic network (and roughly the same energy for a carbon recoil [1]), by an energetic recoil we imply an atom/ion with a kinetic energy higher than 34 eV.

The average energy of the recoils is plotted against E_i in Fig. 2. It is evident from this figure that the average energy increases with E_i and is independent of the nanotube chirality. Given that the number of energetic recoils below the upper nanotube should not be too small (a very high irradiation dose is needed in this case for welding) and, on the other hand, E_i should be not too high, as discussed above, we can conclude from graph 2 that the optimum ion energy should be in a range of 0.4–0.6 keV.

The next point to be addressed is the optimum irradiation dose. Even if the energy of incident ions is right, an excessive irradiation dose will result in a total destruction of irradiated nanotubes by the ion beam. In Fig. 1(h) we present an example of highly damaged crossed nanotubes after an irradiation dose of $\Phi = 2 \times 10^{15}$ cm^{-2}. It is seen

[1] Despite the difference in the masses of C and Ar atoms, and, hence, different maximum energy transferred in a binary collision, the threshold energy for a displacement is roughly the same due to chemical interactions between carbon atoms in the nanotube.

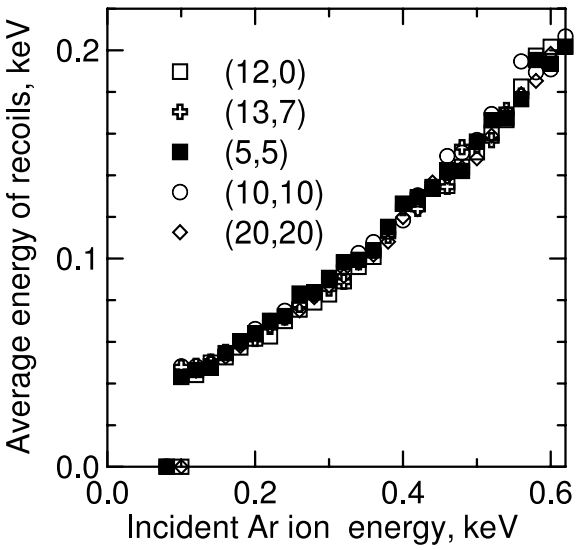

Fig. 2. Average energy of energetic recoils (both Ar and C atoms) below a nanotube as a function of incident ion energy.

that this irradiation dose gave rise to break up of nanotubes, strong amorphization and loss of the tubular shape. Irradiation of crossed nanotubes with various chiralities gave qualitatively similar results, although we found that the maximum permissible irradiation dose depends on the tube diameter. Based on our results, we predict that for SWNTs with diameters less than 1 nm the optimum dose ($E_i = 0.5$–1 keV) for welding should be about $\Phi = 0.5$–0.7×10^{15} cm^{-2}, whereas for thicker nanotubes with diameters larger than 1 nm the optimum dose is $\Phi \approx 1 \times 10^{15}$ cm^{-2}. This irradiation dose roughly corresponds to 10 ion impacts onto the junction area.

To emphasize the importance of maintaining high temperatures during irradiation, in Fig. 1(g) we also show the atomic configuration of crossed intact nanotubes after irradiation dose $\Phi = 0.5 \times 10^{15}$ cm^{-2} but at zero temperature. It is evident that the number of defects, especially large vacancies, is much higher than that for the case of high-temperature irradiation considered above, since high temperatures made it possible for the defects to migrate and anneal.

In order to clarify the role of irradiation-induced defects in nanotube welding, we also simulated the behavior of crossed pristine nanotubes at high temperatures and when a force pushes one nanotube to the other. The structure of crossed nanotubes under the applied force (to mimic attraction between a nanotube and substrate) and zero temperature has been studied by first-principle methods by Yoon et al. [23] Similar to that work, to estimate the force at a given tube separation, we slightly reduced the intertube distance and then relaxed the system while keeping fixed the boundary atoms at the nanotube ends.

We found that a force of about 30 nN results in a substantial decrease in the intertube separation and nanotube flattening near the junction area. We further found that elevating the temperature up to 2000 K in the strained system did not break up the carbon network of these intact nanotubes, nor gave rise to formations of any bonds between the nanotubes. Thus, we can conclude that welding of nanotubes is not possible without defects even if a force which presses one nanotube to the other is applied and that the reorganization of the carbon network near the junction point occurs via defect annealing and migration.

To conclude, we simulated the irradiation of crossed SWNTs, both suspended and deposited on substrates, with 0.4–1 keV Ar ions using empirical potential molecular dynamics. We found that ion irradiation and high temperatures can be employed for nanotube welding which is mediated by dangling bond saturation and carbon network reconstruction near the irradiation-created vacancies in the junction area. We further predict that the optimum Ar ion energies should be in a range of 0.4–0.6 keV, whereas the optimum irradiation dose should be about 10^{15} cm^{-2}. Thus, given that carbon nanotubes can potentially be positioned on a substrate quite accurately using an atom force microscope, ion irradiation may be used to produce a mechanically stable network of joined nanotubes with predetermined positions of junctions between nanotubes.

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