

Effects of ion irradiation on supported carbon nanotubes and nanotube-substrate interfaces

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ABSTRACT

We employ molecular dynamics to study the effects of ion irradiation on carbon nanotubes lying on different substrates. We show that defect production depends on the type of the substrate and that the damage is higher for metallic heavy-atom substrates than for light-atom substrates, since in the former case sputtered metal atoms and backscattered recoils produce extra damage in the nanotube. We further study the behavior of defects and demonstrate that although ions may severely damage nanotubes in a local region, the nanotube carbon network can heal such a strong localized damage due to defect migration and dangling bond saturation. Finally, we predict the pinning of nanotubes to substrates by forming nanotube-substrate bonds which appear near irradiation-induced defects.

INTRODUCTION

Recent experiments [1–6] on the irradiation of carbon nanotubes (NTs) with energetic particles revealed many new interesting phenomena, e.g., the coalescence [1] and welding [2] of NTs under electron irradiation, ion irradiation-induced changes in electrical coupling between NTs [3], surface reconstructions [4, 5], and modifications of mechanical properties [6]. Experiments also provide evidence that ion irradiation of nanotubes may be employed for fabricating metal nanowires on insulating substrates using the carbon tubes as masks [7].

These examples illustrate the demand for microscopic understanding of defect formation mechanisms in supported NTs (i.e., nanotubes on different substrates). Note that apart from the fact that supported NTs can be used as mask for making nanowires, tubes may be utilized in various key experiments. This may include scanning tunneling microscopy probing of the irradiated NTs [8] to locate and characterize irradiation-induced defects, or electronic transport studies on quasi-one-dimensional systems with disorder [9–11]. The presence of a substrate may play a dominant role on the damage production in supported NTs since in that case the nanotubes can be damaged by backscattered impinging particles or by atoms sputtered from the substrate.

In this work, we study the ion irradiation of single-walled NTs on different substrates. For qualitative understanding of the physical processes involved, we considered two limiting cases: a heavy-atom metallic substrate and a light-atom substrate with covalent bonds between atoms. The former was chosen to be a platinum (111) surface, the latter a Bernal graphite (0001) surface. Noble metals [12, 13] and graphite [13, 14] have repeatedly been used as substrates in experimental studies on carbon NTs.

SIMULATION METHOD

The method used in this study has been described in detail in other publications [8, 15] and so only a brief outline will be given here. We used classical molecular dynamics [16] to model defect production in NTs under argon ion irradiation. This is the only method fast enough for both simulating realistically energetic collisional processes and achieving representative statistics. To model C-C interaction, we used the Brenner II interatomic potential [17]. For simulating the irradiation of a NT lying on a heavy-atom metal substrate, we chose platinum as a substrate material since an interatomic potential was recently developed to describe Pt-C systems [18]. Although gold is usually used as a nanotube substrate material, we believe that in both Pt-C and Au-C systems the defect formation mechanism in NTs on such substrates is essentially the same, in view of a similar behavior of collision cascades and heat spikes in these metals [19]. The Pt-C interatomic functional form and parameter values used in our simulations as well as the results of extensive tests are given elsewhere.[18]

We considered individual single-walled 100 Å-long (10,10) armchair NTs on Pt and graphite substrates. The original geometry for the Pt substrate is shown in Fig. 1 a). The incidence of argon ions with energies from 100 up to 2000 eV was perpendicular to the substrate surface. The original temperature of the system was equal to zero. To prevent spurious reflection of pressure waves from the borders of the system, the Berendsen temperature control [20] was used at the borders for the first 20 ps after ion impact, then the temperature was scaled down everywhere to zero at a rate of 1 K/ps. For every energy considered, we carried out 100 independent runs and averaged the results.

In order to simulate defect annealing (which inevitably occurs on a macroscopic time scale at finite temperatures), we heated the system up to high temperatures (1500 K), but for a comparatively short time of 100 ps with a subsequent quench to the zero temperature.

RESULTS AND ANALYSIS

We firstly consider a NT lying on the Pt substrate. Having optimized the geometry of the NT-substrate system by minimizing its energy, we irradiated the NT with argon ions as described above. The optimization resulted in a partial distortion of the *pristine* carbon network (i.e., without dangling bonds), but we did not observe formation of any substrate-NT bonds for intact carbon nanotubes.

The typical defect creation mechanism was as follows. The impinging Ar ion usually created a single vacancy (or multi-atom vacancy) in the uppermost part of the NT wall as well as some primary carbon recoils which, along with the ion, produced defects in the lower part of the tube and in the substrate. A part of the recoils (or the Ar ion) were reflected back from the substrate surface producing some additional damage in the NT. The characteristic time of these processes was about 0.1 ps. At high ion energies (more than 1 keV), up to 3 carbon atoms were sputtered from the NT.

Visual analysis of the final atom positions indicated that, similar to the irradiation of suspended NTs [8], single vacancies (and vacancy-related defects [4] which single vacancies can turn into) were the most prolific defects in nanotubes which appear after ion

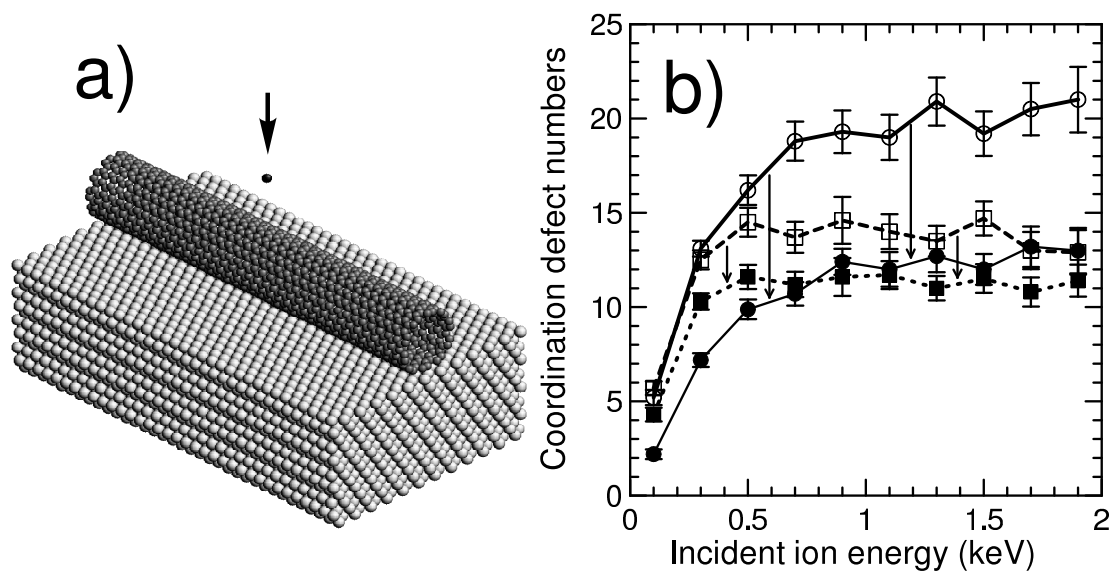


Figure 1: Original atom configuration of the nanotube-Pt substrate system for ion impact simulations (a). The initial movement direction of the impinging Ar ion is designated by the arrow. Average coordination defect numbers for a nanotube lying on Pt substrate as a function of incident Ar ion energy (b). Open/full circles stand for the number of C atoms with a coordination other than three before/after annealing for a nanotube lying on Pt substrate, open/full squares for a nanotube lying on graphite substrate. Arrows visualize the relationship between the curves before and after annealing.

impact.

In order to quantitatively characterize the damage in the NT at different energies of incident Ar ions, in Fig. 1 b) we plot the number of C atoms with a coordination other than three (i.e., atoms in defect configurations) as a function of ion energy (open circles). This quantity may be considered as a characteristic of the overall damage in the NT produced by an ion.

It can be seen from Fig. 1 b) that if the energy of the incident ion is higher than the defect creation threshold energy (about 50 eV, see Ref. [8]), then the number of defects increases with the energy up to roughly 600 eV, after which it remains practically constant. The reason for such behavior is that at low energies the damage production grows with energy, because there is more energy available for it. At higher ion energies, although defect production in the NT drops as the nuclear collision cross section decreases [8], there are more reflected C recoils and Pt atoms sputtered from the substrate, all of which damage the tube. At very high energies (several keV), the ion penetrates into the substrate rather deeply, which results in a drop in the sputtering yield and, respectively, in NT damage due to this mechanism. The decrease in damage from diminution in the cross section and the damage enhancement from the sputtered atoms approximately counterbalance each other at energies higher than 1 keV.

The annealing of defects (as described above) gave rise to a substantial drop in the defect numbers. In Fig. 1 b) we also present the overall damage after annealing as a

function of ion energy (full circles). Although about 40% of defects annealed, a substantial amount of defects remained in the system. The ratio of annealed defects can be larger on longer time-scales, but total annealing of defects is not possible since a number of atoms were sputtered from the NT.

We found that two mechanisms gave rise to defect annealing. The first mechanism is a recombination of vacancies with C adatoms on the NT walls due to the migration of the adatoms. The second mechanism of annealing is a mending of vacancies through dangling bond saturation and by forming non-hexagonal rings and Stone-Wales defects. An illustration of this mechanism is given in Fig. 2 where the front walls of one and the same NT just after ion impact (a) and after annealing (b) are shown.

The latter mechanism has been also found to be important for the defect annealing upon electron irradiation [4]. We emphasize here that ion irradiation creates more severe local damage than electron irradiation, since in the former case a vacancy cluster may be easily formed by an energetic ion impact, whereas in the latter case the predominant defects are single vacancies. Thus, carbon NTs have surprisingly high ability to heal the damage, although topological defects still remain in the carbon network.

Another interesting effect observed in our simulations is the saturation of irradiation-induced carbon dangling bonds by forming comparatively strong bonds (typical energies of about 1 eV) between the nanotube and substrate atoms. We stress once more that we did not observe formation of any bonds between intact NTs and Pt substrates. Thus, the ion irradiation pins the nanotube to the substrate. We also noticed that sputtered Pt atoms sometimes became stuck to defects in the nanotube walls and remain in these positions even after the annealing of NTs at elevated temperatures. This finding is corroborated by experiments in which Pt clusters have been observed near defects on carbon NT surfaces [21].

Having considered NTs on heavy-atom metallic substrates, we now proceed to the other limiting case: NTs on graphite. The original atomic configuration was similar to that given in Fig. 1 a) for the Pt substrate. The number of irradiation-induced coordination defects in a NT on graphite is presented in Fig. 1 b) (open squares) as a function of the incident ion energy. Analogous to the case of the Pt substrate, the defect number grows with the energy up to roughly 600 eV, after which remains practically constant. Note that the total damage is lower than in the case of Pt due to an absence of atoms sputtered from the substrate and a lower probability of energetic recoil backscattering. As in the case of the Pt substrate, the annealing of defects also gave rise to a drop in defect numbers (full squares).

The defect coordination numbers after annealing proved to be roughly the same for NTs on both Pt and graphite substrates. Although the radiation damage in tubes on heavy-atom substrates is much higher than for graphite, the ability of carbon NTs to heal the defects in the carbon network due to dangling bond saturation and adatom migration gives rise to a similar amount of defects in the NTs after annealing. Since for all the NT substrates the number of sputtered C atoms (created predominantly by the first impact of the ion) was the same, the extra damage created by energetic substrate atoms and backscattered C atoms in NTs on heavy-atom substrates may be annealed rather easily. This is in part due to the comparatively low energies of such atoms, which always are

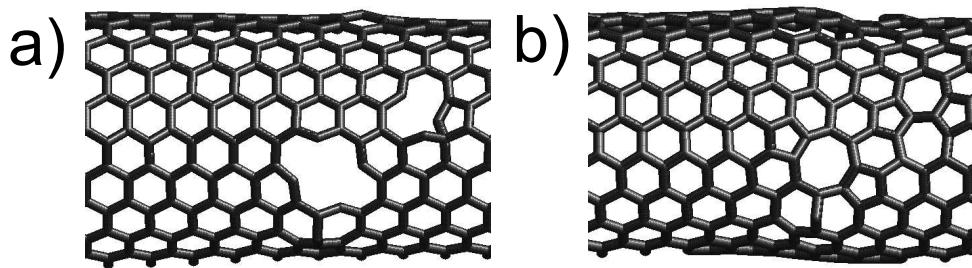


Figure 2: Front walls of one and the same nanotube just after ion impact (a) and after annealing (b). During annealing the double vacancy in the middle of the carbon network transformed to an agglomeration of non-hexagonal rings. The single vacancy and the nearby C adatom in the upper right-hand corner of the network transformed to a Stone-Wales defect.

much less energetic than the incident ion.

This ability of NTs to mend irradiation-induced defects in the carbon network is important for using them as masks against ion bombardment in the production of metal nanowires. Since the sputtering yield is higher for metals than for carbon [22], even single-walled NTs may potentially be used for making extra narrow metal wires (multi-walled NTs have been used in the experiments [7]). We note, however, that further studies on the irradiation of the NT-substrate interface are clearly needed to ascertain what the optimum conditions and limitations of this technique are.

CONCLUSIONS

In this paper, we used molecular dynamics simulations to examine both the irradiation of carbon nanotubes lying on different substrates and the behavior of irradiation-induced defects under annealing. We showed that at low temperatures the defect production depends on the type of the substrate and that the damage is higher for metallic substrates composed of heavy atoms due to sputtered substrate atoms and backscattered carbon recoils. The number of defects increases with the energy of the incident ions (up to roughly 600 eV), then it remains practically the same because of a decrease in the nuclear collision cross section at higher ion energies. We further demonstrated that the carbon network can heal ion-induced damage due to defect migration and dangling bond saturation. The residual damage in NTs after annealing is independent of the substrate type. We finally predict a pinning of nanotubes to both metallic and graphite substrates upon ion irradiation. This should happen through a formation of chemical bonds between the tube and substrate atoms near the irradiation-induced defects.

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