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Binding a carbon nanotube to the Si(100) surface using ion irradiation—an atomistic simulation study

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Abstract. Using carbon nanotubes (CNTs) as building blocks in silicon-based electronics requires good electric contacts between the tubes and other devices. Recent experimental and theoretical works have shown that irradiation can be used to modify both the structure and the electrical properties of nanotubes, and also to create new covalent bonds to different nanotube structures. In this study, we have used atomistic computer simulations with analytical, empirically fitted interaction models, to examine the possibility to enhance binding between a CNT and a silicon substrate with C, Si and Ne ion irradiation. Low irradiation doses ($<2.8\times10^{14}$ ions/cm^2) and energies (0.2–2.0 keV) were used, to ensure that the irradiated nanotube will not be destroyed. Our results indicate, that ion irradiation can be used to create new covalent bonds, and also to increase the binding energy between these structures, when the irradiation doses and energies are carefully chosen. We found that a typical number of created new covalent C–Si bonds is 0.5–0.9 (10^{14} ions/cm^2)$^{-1}$, and a typical increase in the binding energy between the structures is 100–400% for moderate irradiation doses.

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1. Introduction

Because the traditional silicon technology is reaching its limit in miniaturization, alternative materials have to be considered for future electronics. Carbon nanotunes (CNTs) [1] are one of the most promising ways to further decrease the device sizes [2]. Because of the metallic or semiconducting nature of CNTs, depending on the atomic structure of each tube, they can be used as interconnects or as devices in nanoelectronics (see e.g. [3]–[8]). One possible way for the transition to nanotube-based electronics would be to integrate CNTs to the cheap and well-established silicon technology. One of the remaining problems with this approach is the poor electric contact at the interfaces between CNTs and other components, which becomes especially important at low temperatures [9].

Irradiation is a routine way to tailor the electrical properties of materials in today's semiconductor industry [10, 11]. In a similar manner, irradiation with energetic charged particles can be used to tailor both the structure and the electronic properties of CNTs. It has been shown that ion irradiation can introduce dopant atoms into CNTs [12]–[16], and can create new covalent bonds between bundled nanotubes and also in interfaces between CNTs and other materials [17]–[20].

Although some experimental and theoretical studies have been made in an effort to understand the role of sp^2-bonded carbon structures (fullerenes and nanotubes) on silicon surfaces [21]–[24], as far as we know, no work has been done on investigating how this interaction could be enhanced. As the effect of irradiation with the same energy differs between suspended CNTs and CNTs on a substrate [18], irradiation might offer a way to tailor the conductivity between CNTs and other devices, without destroying the suspended parts of the CNTs. In this study, we have, with atomistic computer simulations, examined the possibility to use low-energy ion irradiation to enhance the binding between a single-walled CNT (SWCNT) and a silicon substrate with the (100) surface towards the SWCNT.

2. Simulation methods

We have studied ion irradiation-induced enhancing of the binding between a (10,0) SWCNT and a Si(100) surface with atomistic computer simulations. We created a trench to the Si substrate

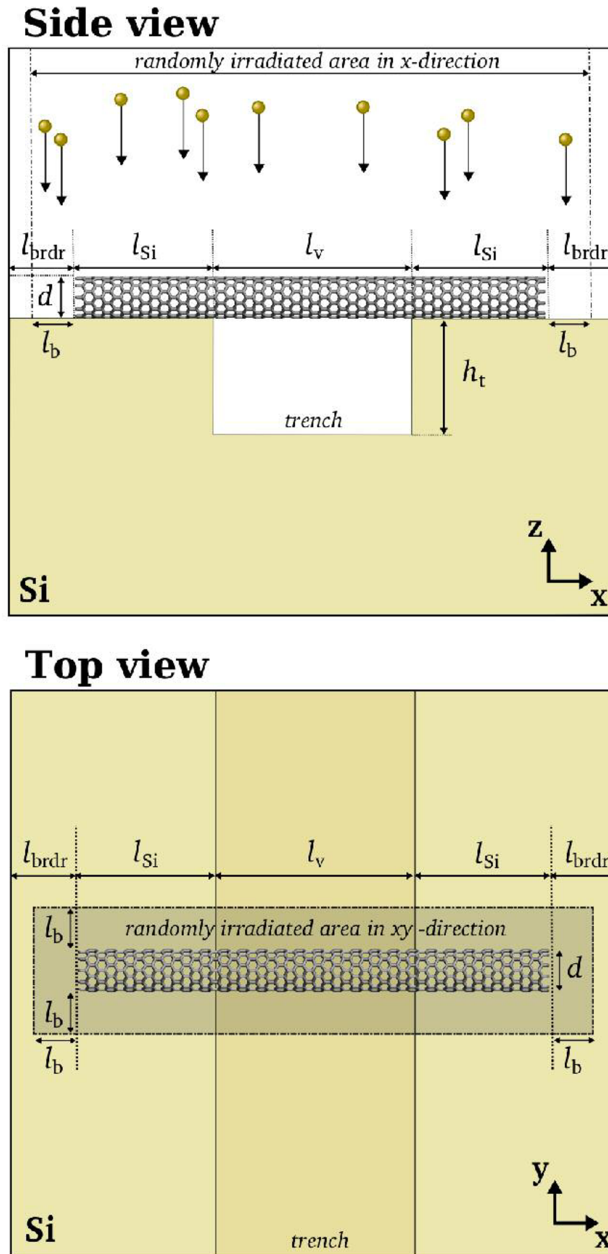

Figure 1. Geometry of the studied system. Diameter of the (10,0) SWCNT $d \approx 8.6$ Å; other presented lengths are approximately as follows: $h_t = 2d$, $l_{Si} = 1.5d$, $l_v = 3d$, $l_b = d$ and $l_{bdr} = 1.7d$.

in the y-direction (see figure 1), perpendicular to the dimer ridges of the Si(100) surface. The nanotube was deposited over it, in a direction perpendicular to the trench length and parallel to the dimer ridges. This direction, parallel to the dimer ridges, has been experimentally found to be one of the preferred directions of nanotubes on the Si(100) surface [22].

The equilibrium position for the CNT was found by minimizing the energy of the system. This position is exactly in between two dimer ridges of the surface (see figure 2), as also presented

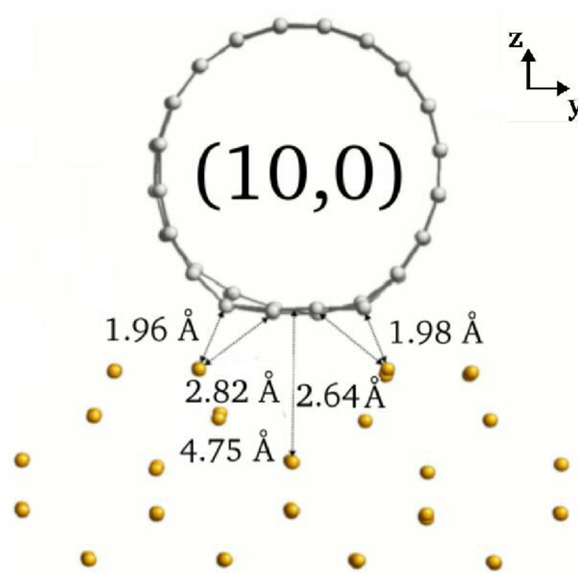

Figure 2. Equilibrium position of the (10,0) SWCNT on a Si(100) surface.

in [24, 25].[2] The studied structure can be fabricated for example by growing CNTs on a silicon substrate as presented in [22, 26], etching straight trenches, and then pulling a nanotube over the trench using the tip of an atomic force microscope.

To model the irradiation of the described structure with low-energy carbon, silicon and neon ions, we used the classical molecular dynamics (MD) approach. Because our method has been extensively described in previous publications [18, 27], we present here only the essential aspects for this study. We used an analytical, empirically fitted, C–Si potential [28] to describe the interactions in our system. The binding energy per unit length between the SWCNT and the Si substrate predicted by this method is in the same range as given by first principles calculations [24], although the bond lengths are $\sim$10% shorter, due to fitting of the potential to the properties of bulk SiC. The motivation for our choice was based on this agreement, which was clearly the best for this potential among the possibilities. The details on the comparison are presented with our preliminary results in [25]. At low inter-atomic distances, this potential was smoothly joined to a repulsive potential [29], to realistically simulate the energetic collisions.

To avoid the unphysical melting of the system due to bombarding with energetic ions, caused by the finite size of the system, we used the Berendsen thermostat [30] to transfer heat realistically from the system outside the impact volume. The simulation temperature was chosen to be 300 K. Periodic boundary conditions were used in the x- and y-directions. Our simulation cell consisted of 15 840 silicon atoms and of 500 carbon atoms. For each ion species and irradiation energy, we carried out from a few up to 30 simulations to obtain reasonable statistics. In each simulation, we bombarded the structure cumulatively with 50 ions, which corresponds to an irradiation dose of $\sim 2.8 \times 10^{14}$ ions cm^{-2} . The simulation time per irradiation event was chosen so that the temperature of the system converged at the end of the simulation, and was therefore different

[2] The minor differences between the values of the preliminary data presented in [25] and those presented in the present study are mostly due to differences in definitions of the interface area and the length of the suspended part of the SWCNT.

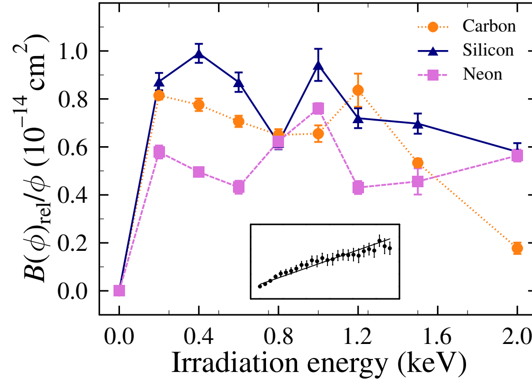

Figure 3. Relative number of created bonds per irradiation dose, due to C, Si and Ne ion irradiation, as a function of the irradiation energy. The inset presents an example of the fitting for carbon ions with an irradiation energy of 1.0 keV.

for each irradiation energy. For the highest energies, the simulation time per each incoming ion was about 0.07 ns, after which the system was relaxed for another 0.07 ns. Impact points were randomly chosen in the area shown in figure 1.

3. Results and discussion

3.1. Enhanced binding

Enhancing the binding between the SWCNT and the silicon substrate was first analysed by counting the number of irradiation-induced carbon–silicon bonds with lengths <2.6 Å in the interface area. These bonds can be expected to have a covalent nature according to first principles calculations [24]. The relative number of created bonds was defined as

$$B(\phi)_{\rm rel} = [N(\phi)^{\rm C-Si} - N(0)^{\rm C-Si}]/N(0)^{\rm C-Si}, \tag{1}$$

where $N(\phi)^{\rm C-Si}$ is the number of C–Si bonds shorter than 2.6 Å, after an irradiation dose of ϕ. We found that, for the energies and doses studied, the relationship between $B(\phi)_{\rm rel}$ and ϕ is highly linear. Therefore, we fitted the data to a linear function to get the ratio of $B(\phi)_{\rm rel}/\phi$ as a function of the irradiation energy $E_{\rm irr}$. These results are presented in figure 3.

Because our goal was to find irradiation parameters, which give the highest enhancement of the binding, damaging the SWCNT at the same time as little as possible, we also calculated the irradiation-induced damage to the system as a function of the irradiation dose. The damage after irradiation dose ϕ was defined as the number of C atoms with coordination number $N_{\rm nbr} \neq 3$, divided by the total number of C atoms:

$$D(\phi) = N(\phi)^{\rm C}_{N_{\rm nbr}\neq 3}/N(\phi)^{\rm C}_{\rm tot}. \tag{2}$$

The damage analysis was done only in the suspended part of the SWCNT, because this part has the main role in carrying the current through the SWCNT, if good electrical contacts have been formed to the interfaces. Although also the damage data can be fitted to a linear function, with

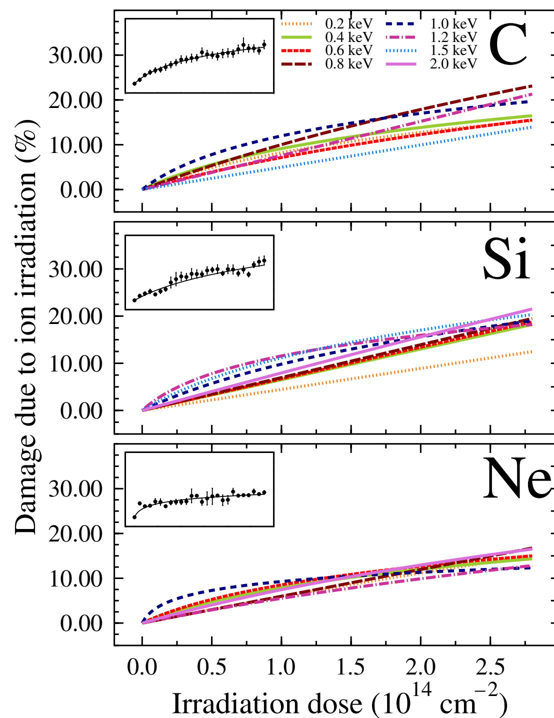

Figure 4. Damage caused to the suspended part of the SWCNT by ion irradiation with C, Si and Ne ions, using irradiation energies E_{irr} = 0.2–2.0 keV. Presented graphs are best fits of the data to equation (3). Insets in the graphs present the data with fitted equation, for each ion species with E_{irr} = 1.0 keV.

relatively small error estimates, as presented in [25], a better fit for a larger range of energies can be obtained using a logarithmic function

$$D(\phi) = a \log(b\phi + 1), \tag{3}$$

where a and b are the fitting parameters. The results of the fits of the damage data to this function are presented in figure 4. We were not able to reliably fit the data for carbon with E_{irr} = 2.0 keV or for neon with E_{irr} = 1.5 keV, because of large statistical fluctuations. The damage caused by the carbon irradiation with E_{irr} = 2.0 keV was the same order as that caused by E_{irr} = 0.2 keV and E_{irr} = 1.5 keV. For the neon irradiation with E_{irr} = 1.5 keV, the caused damage was in the same order as that caused by E_{irr} = 2.0 keV.

3.2. Energy dependence

Interestingly, it can be seen from figure 3 that the increase in the number of new bonds starts to decrease as the irradiation energy increases, except for neon. For neon, the binding energy increase starts increasing again with the highest studied energy, but the behaviour can be expected to be similar to other ions with even higher energies. Furthermore, all the graphs have a clear minimum with the intermediate energies, although the absolute energy which gives this minimum varies.

This can be explained in terms of the energy transfer from the incoming ion to the system. With low energies the ion transfers all its energy to the upper part of the SWCNT, and the effect to

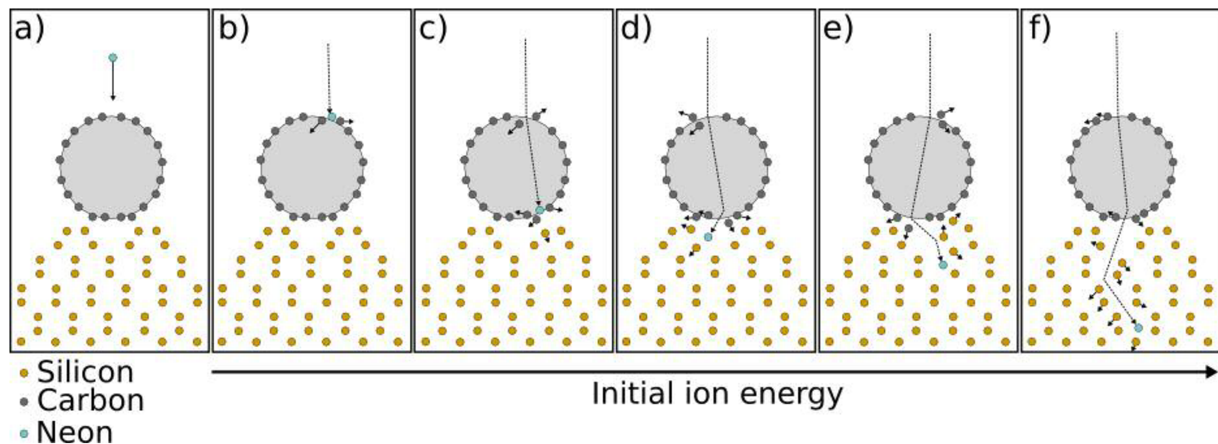

Figure 5. Schematic presentation of the dependence of the effect of the impacting ion to the bonding between the SWCNT and the silicon substrate on the irradiation energy. Panel (a) presents the initial set-up, and panels (b)–(f) present the possible effects. The energy increases from left to right.

the interface area is low (see figure 5(b)). Because of the low energy, not much damage is caused to the SWCNT. As the energy increases, the ion can pass through the upper graphite layer of the SWCNT. While the energy is not high enough for the ion to penetrate the second graphitic layer, it only pushes the atoms of the SWCNT towards the substrate, thereby increasing the number of bonds (figure 5(c)). With a little higher energy, the ion can penetrate both layers, and push the substrate atoms away from the tube (figure 5(d)). When the energy increases further, most of the energy is transferred to the substrate atoms when the ion is bouncing below the Si surface (figure 5(e)). This energy causes sputtering from the substrate towards the SWCNT. With even higher energies, the energy is mainly transferred to the silicon atoms deep in the substrate (figure 5(f)).

The damage caused to the nanotube remains roughly constant after the threshold energy for creating defects is reached. This can be clearly seen from the graphs for silicon and for neon in figure 4. These results agree well with the results found in the literature (see e.g. [18]). For carbon also the ions with the highest irradiation energies cause less damage than those with the intermediate energies around 1.0 keV.

The number of new C–Si bonds is obviously not the whole truth about the binding between the SWCNT and the Si surface, because also the lengths of these bonds and new C–C and Si–Si bonds between the structures, which are formed due to mixing of the structures, have a significant role in the binding. Therefore, we also calculated the force needed to tear off the SWCNT from the surface. This was done by applying an artificial force, directed away from the substrate, to all atoms in the nanotube. By varying this force, we were able to find the limiting force for every irradiated structure, which was enough to remove the nanotube from the substrate. Unfortunately, although we also saw high increases per incoming ion of this threshold force (20% in the best case), this force is more related to the random defects in the atomic structure of the SWCNT, than to the increased binding between the structures.

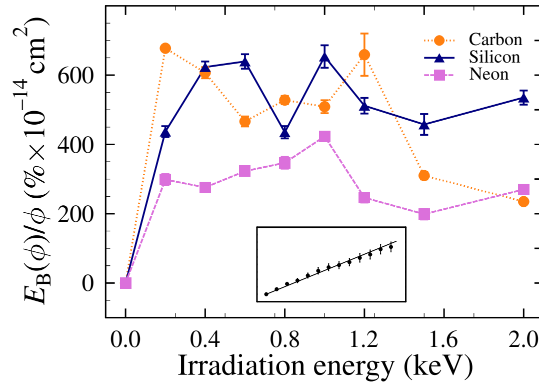

Figure 6. Increase in the binding energy E_B between the SWCNT and the substrate divided by the irradiation dose ϕ, after irradiation with C, Si and Ne ions as a function of the irradiation energy E_{irr} . The inset presents an example of the fitting for carbon ions with an irradiation energy of 1.0 keV.

3.3. Binding energy

We also calculated the binding energy between the structures as a function of the irradiation dose for all energies and ions. This energy was defined as the difference between the total potential energy of the system and sum of the potential energies of the individual structures

$$E_B = E_{total} - (E_{SWCNT} + E_{substrate}). \tag{4}$$

We found that the increase in E_B due to irradiation is significant (typically 100–400% for moderate irradiation doses and low energies). Because the increase in the binding energy is a linear function of the irradiation dose we did a similar fit as presented in figure 4. The increase in the binding energy divided by the irradiation dose is presented for all the ions in figure 6 as a function of the irradiation energy.

The binding energy increases with all of the studied ions and energies, although the dependency of this increase on the irradiation energy varies. For neon, the increase is practically independent of the irradiation energy. With high irradiation doses the nanotube is destroyed and therefore the binding energy eventually starts to decrease. For silicon, this energy seems to be higher than the highest studied irradiation energy (2.0 keV). By comparing figures 3 and 6, it is clear that the increase in the binding energy is related to the number of introduced new C–Si bonds between the structures. However, the number of the introduced bonds does not directly give us the increase in the binding energy.

3.4. Electrical properties

A recent study [31] shows that the increase in resistance of irradiated nanotubes is mainly due to di-vacancies, and can be calculated using the equation

$$R(L) = R_c + \frac{1}{2}\left(\frac{h}{2e^2}\right) e^{L/(4.1\langle d\rangle)}, \tag{5}$$

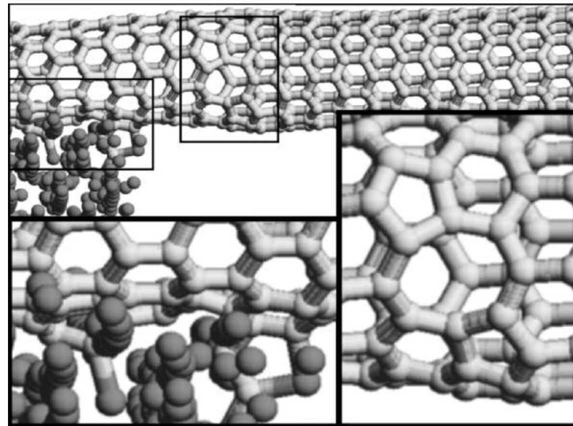

Figure 7. Ball-and-stick presentation of a part of the structure after carbon irradiation with energy of $E_{\mathrm{irr}} = 2.0$ keV and an irradiation dose of $\phi = 0.55 \times 10^{14}$ ions/cm^2. Light atoms are carbon and dark atoms are silicon. Irradiation has created a (5-8-5) di-vacancy to the suspended part of the tube (right-hand-side zoom-in), and also new bonds between the structures at the contact areas are evident (left-hand-side zoom-in).

where R_c is the contact resistance, $h/2e^2$ is the inverse of the quantum of conductance, L is the length of the measured nanotube and $\langle d \rangle$ is the average distance between two di-vacancies. Using this equation, we estimated the maximum increase in the resistance of the suspended part of the SWCNT in our study. We found that, for low irradiation doses ($\phi < 1.0 \times 10^{14}$ ions/cm^2), and those energies producing the lowest damage, this increase is negligible, because practically no di-vacancies are introduced to the structure.

The situation is different for higher energies, because they produce more complex defects. An example of the structure after carbon irradiation with the highest studied energy ($E_{\mathrm{irr}} = 2.0$ keV) and an irradiation dose of $\phi = 0.55 \times 10^{14}$ ions/cm^2 is presented in figure 7.

3.5. Choosing the ion species

Based on the above analysis, it is clear that the ion species has a significant role on the obtained results. Because also the irradiation energy and dose affect the results, it is not a simple task to choose between the C, Ne and Si ions. However, using carbon as the irradiating ion is motivated both because it introduces new carbon atoms to the system and can therefore assist in self-healing of the nanotube, and also because it can lead to a high mixing of carbon and silicon atoms at the interface area, which can lead to formation of small SiC substructures in the substrate.

4. Conclusions

We have used classical MD to study the low-energy ion irradiation as a method to enhance binding between an SWCNT and a silicon surface. Our results indicate that this method can be used both to create new covalent bonds between these structures and to shorten the existing bonds, thereby enhancing the electrical conduction properties of the interface.

When the irradiation energies are kept lower than those causing the maximum damage to the nanotube (0.8–1.0 keV for C and 1.0–1.5 keV for Si; for Ne all the energies produce nearly equal amount of damage), the nanotube is not severely damaged, and good electrical properties can likely be maintained. A typical number of created new covalent C–Si bonds is 0.5–0.9 (10^{14} ions/cm^2)$^{-1}$, and a typical increase in the binding energy between the structures is 100–400% for moderate irradiation doses.

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