Ion irradiation-induced welding of a carbon nanotube to a Si (100) surface

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ABSTRACT

Carbon nanotubes (CNTs) are one of the possible building blocks for electronic devices in the transition phase from traditional silicon-based microelectronics towards the few-nanometer regime. Remaining problems in integrating CNTs to the existing technology is the low reactivity of the CNT walls which leads to low conductance between CNTs and the other components. Because recent studies have shown that ion irradiation can be used to modify both the electrical and structural properties of CNTs, we propose that it could also be possible to use ion irradiation with low energies to enhance the conductance of these connections. We have used classical molecular dynamics simulations with empirically fitted potentials to examine this possibility by irradiating a single-walled carbon nanotube (SWCNT) on a silicon substrate at room temperature. The nanotube was deposited over a trench created to the silicon substrate so that the nanotube was partly suspended. Low irradiation doses and low energies (0.2 keV–1.2 keV) were used to ensure that the irradiated CNT will not be destroyed. The simulations were carried out for silicon, carbon and neon ions. Our simulations indicate that ion irradiation will increase the number of covalent bonds between the CNT and the Si substrate. When the irradiation dose and energies are low, the damage caused to the SWCNT atomic network can be tolerable when compared to the improvement in the conductance of the contact regions. Furthermore, as the CNTs have high ability to heal the irradiation-induced damage, it is possible that the irradiation will not have a significant negative effect to the conductivity of the CNT in a system of this type.

INTRODUCTION

Carbon nanotubes (CNTs) [1] are one of the alternatives to help the existing semiconductor technology decrease the device sizes towards the desired nanometer-range [2, 3]. Due to their semiconducting and metallic nature, which depends on the atomic structure of each CNT, they can be used either as building blocks for new nanometer-size devices or as wires connecting other devices. Best means towards the transition from the micro to nano scale would be to integrate the existing, cheap and well established, silicon technology and the CNT-based devices. One of the problems in this process is the poor electrical connection between the CNTs and the other devices, which becomes especially important at low temperatures [4–6].

Irradiation with energetic ions has been routinely used in the semiconductor industry to introduce dopants into silicon [7, 8]. Electron and ion irradiation with high energies can also be used to modify the atomic structure of the materials. Similar to conventional

materials, irradiation with ions and electrons can also be used to tailor the properties of CNTs. It has for example been shown that, by using irradiation, it is possible to bend CNTs [9], weld CNTs together [10–12], strengthen CNT bundles [13, 14] and to cause other interesting structural modifications [15–18].

Irradiation can also be used to introduce dopant atoms into CNTs and for CNT functionalization [19, 20]. Furthermore, we have recently shown that ion irradiation is also a promising method to introduce boron and nitrogen dopants into nanotubes [21, 22], which is especially interesting because B/N atoms can serve as electron acceptors/donors in carbon structures. We showed that, by choosing the energies carefully, it is possible to get up to 40% of the dopants into substitutional lattice sites in the CNT atomic network. We have also shown that it is possible to introduce K clusters into multi-walled carbon nanotubes by using ion irradiation [23]. This might offer a way to get only metallic CNTs, if desired, because alkali-metal doped CNTs are found to be metallic [24, 25]. The fact that K and Rb doped C_{60} are superconducting at 19.3 K [26] and 28 K [27], respectively, further increase the interest on alkali-metal doped CNTs. It has also quite recently been shown that it is possible to control the resistivity of CNTs by using irradiation [28].

Irradiation has therefore clearly been shown to be a promising method for tailoring both structural and electrical properties of CNTs. As the effects of irradiation with the same energy differs between suspended CNTs and CNTs on a substrate [29], this might offer a way to enhance the conductivity between CNTs and other electronic devices without destroying 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 bonding between a single-walled carbon nanotube (SWCNT) and a silicon substrate with (100) surface on top.

SYSTEM

The system to study was a (10,0) single-walled carbon nanotube (SWCNT) on a silicon (100) surface. A trench was created to the substrate in the y-direction, perpendicular to the dimer ridges of the Si (100) surface, and a nanotube was deposited over it in 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 the preferred direction of nanotubes on this surface [30]. The equilibrium structure of the system was found by minimizing the cohesive energy. The position of the nanotube with the lowest energy was exactly between two dimer ridges of the surface (see Fig. 1). The outer dimensions of the silicon substrate after the relaxation were roughly 80 Å × 80 Å × 50 Å, the length of the SWCNT was about 50 Å and the trench was about 17 Å deep.
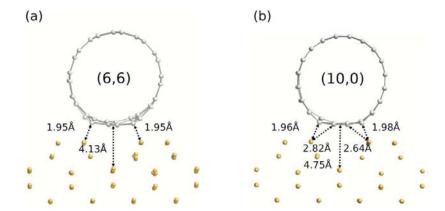
Figure 1: Minimum energy configurations for (6,6) and (10,0) SWCNTs on Si (100) surface as predicted by the Erhart-Albe potential. The corresponding binding energies and comparison to the energies found for different SWCNTs in Refs. [30, 31] are listed in Table 1. The values of the distances found with first principles calculations [31] for the (6,6) SWCNT corresponding to values presented in this figure (1.95 Å and 4.13 Å) are 2.11 Å and 4.31 Å.

METHODS AND SIMULATIONS

Simulations were carried out using classical molecular dynamics (MD) method. Our simulation method has been described in previous publications [29, 32] and thus only aspects essential for this study are presented below. The interactions between the particles were described with analytical, empirically fitted, potentials. We considered two different potentials which both include the interactions between carbon and silicon, specifically the C-Si-H potential by Beardmore and Smith (BS) [33] and the C-Si potential by Erhart and Albe (EA) [34]. To make a choice between these potentials, we relaxed our system with both and compared the binding energies and bond lengths predicted by them to each other and to values found from the literature [30, 31]. We defined the binding energy per length of the contact area to be

$$\frac{E_B}{l_B} = \frac{E_{\text{system}} - (E_{\text{CNT}} + E_{\text{Si}})}{l_B} \tag{1}$$

where E_{system} is the cohesive energy of the whole system, E_{CNT} is the cohesive energy of the CNT and E_{Si} is the cohesive energy of the silicon substrate. The minimum energy structures predicted by EA are presented in Fig. 1 for both (6,6) and (10,0) SWCNTs and the binding energy comparison is presented in Table 1.

Based on the binding energy comparison, it can be concluded that the BS potential underestimates the strength of the C-Si bond when compared to all the other methods, whereas the values predicted by the EA potential are in line with the results from other

Method	SWCNT	d [Å]	E_B l_B [eV/Å]
EF	(18 0)	8.1	-0.34
EF	(10 10)	7.8	-0.34
FP	(6 6)	4.7	-0.21
EA			-0.31
BS			-0.06
EA	(10 0)	4.5	-1.12
BS			-0.16

Table 1: Comparison of the binding energies of SWCNTs with different chiralities to the Si (100) surface per the length of the contact area E_B l_B, as predicted by empirical force potential (EF) [30], first principles calculations (FP) [31], the Erhart-Albe potential (EA) and the Beardmore-Smith potential (BS). d is the diameter of the SWCNT in question.

methods. Also the bond lengths predicted by EA potential agree well with those given by first principles calculations [31], although they are 0.1–0.2 Å shorter. This agrees well with the result from first principles calculations of C_{60} binding to the Si (100) surface [35], which show that the C-Si bond length is about 0.1 Å longer for C_{60} on Si (100) than in bulk CSi, to which the EA potential has been fitted.

Because of the better agreement with the predictions found from the literature, we decided to use the EA potential for this study. At low inter-atomic distances the potential was smoothly joined to a repulsive potential [36], to realistically simulate the energetic collisions.

To avoid the effect of melting the structure due to bombarding with energetic ions, we used the heat transfer method by Berendsen et al. [37]. Temperature was scaled in the regions outside the impact volume to avoid un-physical effects on the energetic events. The simulation temperature was chosen to be 300 K, because the choice of temperature can be essential for the interaction between carbon and silicon atoms. No pressure control was used during the simulations.

For each ion and irradiation energy we carried out 10–20 independent simulations. In each simulation we irradiated the structure cumulatively with 50 ions. The simulation time per ion was chosen so that the temperature of the system converged at the end of the simulation. Impact points were always randomly chosen.

RESULTS

Enhancing of the bonding between the SWCNT and the silicon substrate in the contact areas was studied by counting the number of C-Si bonds with length $<$ 2.6 Å, which can be expected to have covalent nature according to the first principles calculations [31]. We

first studied the relative number of created bonds

$$B(\phi)_{rel} = \frac{N(\phi)^{C-Si} - N(\phi = 0)^{C-Si}}{N(\phi = 0)^{C-Si}} \tag{2}$$

where $N(\phi)^{C-Si}$ is the number of those C-Si bonds in the contact area with length < 2 6 Å after irradiation with dose ϕ, as a function of the dose for each ion and energy combination. We found that, for the studied doses and energies, the relationship is nearly linear. Therefore, we fitted the data to a linear function to get the ratio $B(\phi)_{rel}$ ϕ for each ion and energy. An example of the fitting process is presented in Fig. 2 for carbon ion and energies of 0.2, 0.8 and 1.2 keV. The results of the fitting are presented in Fig. 3 as a function of the ion energy.
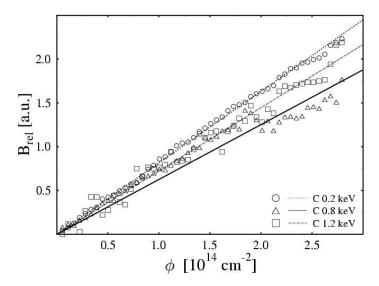

Figure 2: Example of the linear fitting: Relative number of created bonds (in arbitrary units) as a function of the irradiation dose. Lines are best fits for linear approximations for the data. Obtained ratios for all ions and energies are plotted in Fig. 3.

The damage caused to the CNT was studied by counting the number of carbon atoms which have a different number of neighbours than in the perfect system. The damage was calculated by dividing this number of atoms with the total number of carbon atoms left in the analysed volume. Damage analysis was carried out in the suspended part of the SWCNT since it should have the main role in current carrying process for this structure. Again, we first studied the damage as a function of the irradiation dose

$$D(\phi) = \frac{N(\phi)^C_{N_{nbr}=3}}{N(\phi)^C_{total}} \tag{3}$$

where $N(\phi)^C_{N_{nbr}=3}$ is the number of those carbon atoms with number of bonds $N_{nbr} = 3$ after irradiation with dose ϕ. We found that, for the studied doses and energies, also this
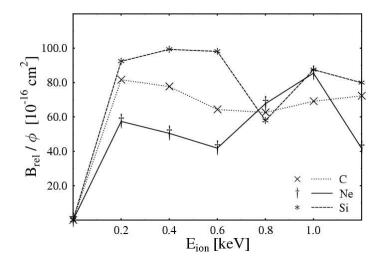
Figure 3: Relative number of created bonds per irradiation dose as a function of the irradiation energy. Standard deviations in the values are in order of the sizes of the markers and are therefore not shown.

relationship is nearly linear. Therefore, we again fitted the data to a linear function to get the ratio $D(\phi)$ ϕ for each ion and energy. An example of the fitting process is presented in Fig. 4 for carbon ion and energies of 0.2, 0.8 and 1.2 keV. The results of the fitting are presented in Fig. 5 as a function of the ion energy.
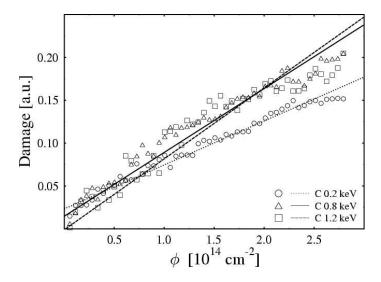

Figure 4: Example of the linear fitting: Damage (in arbitrary units) as a function of the irradiation dose. Lines are best fits for linear approximations for the data. Obtained ratios for all ions and energies are plotted in Fig. 5.
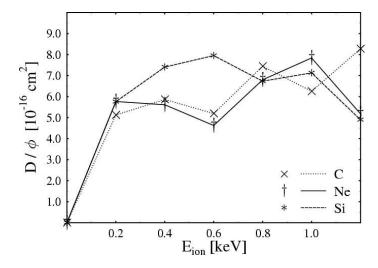
Figure 5: Damage caused to the SWCNT per irradiation dose as a function of the irradiation energy. Standard deviations in the values are in order of the sizes of the markers and are therefore not shown.

It is interesting to note that the graphs in Figures 3 and 5 have a local minimum in the middle. This can be understood by considering the penetration of the ion through the CNT. The minima correspond to the situation, where the ion has just enough energy to penetrate through the CNT. For the suspended parts of the CNT this decreases the damage because the ion leaves the structure (when compared to a bit lower energy) and for those parts on the substrate this decreases the number of created bonds because the ion pushes the substrate atoms a bit downwards, away from the CNT.

DISCUSSION AND CONCLUSIONS

In this study, we have shown that ion irradiation can be used to increase the number of covalent C-Si bonds between carbon nanotubes deposited on silicon surfaces. The increase in the number of bonds is dependent both on the ion species used and on the irradiation energy. Because we calculated only the number of C-Si bonds, it is clear that this does not give the whole picture of the bonding between the nanotube and the substrate, because irradiation removes carbon atoms from the nanotube and silicon atoms from the substrate. Therefore, to some extent the bonds between the nanotube and the substrate can also be between two carbon or two silicon atoms.

To take also these bonds into account, we calculated the binding energies for the system irradiated with carbon ions and energies of 0.2 keV and 0.4 keV. After irradiation with the dose $\phi \approx 1\ 17 \times 10^{14}$ ions/cm^2 the relative number of created bonds $B(\phi)_{rel}$ was about 95% and 90% for energies of 0.2 keV and 0.4 keV, respectively. For the same dose, the binding energies E_B had increased by about 170% and 400%, respectively. It is therefore

clear that also C-C and Si-Si bonds have a significant role on the binding, and that this role increases with the irradiation energy, because ions with higher energies tear the CNT more and also cause more sputtering from the substrate.

Similar to the relative number of created bonds, also the damage caused to the CNT is dependent on both the ion species and the irradiation energy. If the resistance increase due to ion irradiation is really primarily dependent only on the number of divacancies, as suggested by Gómez-Navarro *et al.* [28], the irradiation energies should be kept as low as possible, because the ratio of the number of created divacancies per the number of created single vacancies can be expected to increase with the irradiation energy.

As a conclusion, to enhance the binding between single-walled carbon nanotubes and silicon substrates, we would suggest using irradiation with energies less than about 0.4 keV to keep the damage as low as possible. The best choice for the irradiation ion can be assumed to be carbon, because for low energies it seems to introduce nearly as many new C-Si bonds between the CNT and the substrate as silicon, but with less damage. The choice of carbon as the irradiating ion is even more motivated by the fact that the carbon atoms which stay within the CNT after the irradiation event can greatly decrease the damage due to adatom migration [38] at room temperature.

ACKNOWLEDGEMENTS

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