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A molecular dynamics study of the clustering of implanted potassium in multiwalled carbon nanotubes

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Abstract

We have studied the low energy irradiation of carbon nanotubes (CNT) with K ions using classical molecular dynamics simulations with analytical potentials. The studied CNTs had diameters of about 0.5–1.2 nm and single or multiple walls. The average penetration depth and probabilities to introduce an impurity atom into CNT were studied with simulations on irradiating the CNT with single K ion. The number of potassium clusters, their average sizes and the damage produced into the CNT due to the irradiation were studied using multiple K ion irradiations. We found that the K ions are mobile in CNTs right after the implantation event and that they cluster together. For CNTs with 1–3 coaxial tubes, the highest ratio of K atoms in clusters per total number of K ions was obtained by using an irradiation energy of about 100 eV. Also the least damage per K ion was found to be produced into the CNT with this energy when those energies high enough for the ion to penetrate the outermost wall of the CNT were considered.

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Keywords: Nanotube; Ion irradiation; Doping; Potassium; Molecular dynamics

1. Introduction

The unique electronic, mechanical and thermal properties of carbon nanotubes [1] (CNTs) have given rise to a huge body of research work on their characteristics and nanotube applications. Especially the use of CNTs in nanoelectronics has been widely discussed [2] because in addition to their inherent nm-sizes, CNTs can be either metallic or semiconducting depending on the chirality of the tube.

Ropes formed from CNTs have been shown to become metallic at room temperatures when they are doped with alkali-metals such as K, Rb and

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Br_2 [3,4]. Furthermore K and Rb doped C_{60} have been found to be superconducting at temperatures below 19.3 K [5] and 28 K [6], respectively. This has risen interest in the structure and also in other properties of alkali-metal-doped CNTs [7–12] and CNT-C_{60} peapods [13]. Also the interesting results for using alkali-doped CNTs as a hydrogen storage medium [14] has stimulated research on potassium-doped CNTs [15,16].

Potassium-doped CNTs and CNT bundles have been fabricated quite recently with different methods using potassium vapour and high temperature annealing [3,4,11,12,16] or electrochemical methods [8,9,14,15]. A drawback with these methods is that it is only possible for K atoms to get inside CNTs which have open ends.

Irradiation with energetic ions is an alternative method to introduce dopants into materials. It is routinely used in the semiconductor industry to introduce dopants into Si [17,18], and we have recently shown that it is a promising method to dope carbon nanotubes with B or N [19,20]. In this paper, we suggest that ion implantation might offer an alternative way to introduce potassium-impurities into CNTs in a controllable manner and at lower temperatures. Ion irradiation makes it possible to also bring potassium ions inside the CNTs. However, it is not clear what effect the K irradiation has on the CNTs and what would be the optimum irradiation energies for K doping.

When multiple K atoms are introduced into a CNT, they can be expected to cluster together due to the interaction between the atoms. While it is not clear a priori that impurities in materials cluster with each other, in the case of nanotubes such behaviour could be expected because there is plenty of volume where the atoms can move and start to attract each other. Moreover, it is well known that K atoms form clusters in fullerene surroundings [5].

2. Method

We simulated the irradiation process using classical molecular dynamics (MD) with analytical, empirically fitted, potentials. We first determined a reasonable energy range with single K ion irradiations of graphite and CNTs, and then used this range to study the clustering of K atoms in CNTs using multiple K ion irradiation simulations.

Because our simulation method has been described in detail elsewhere [21,22], only the features essential for this study are presented here.

2.1. Interatomic potentials

The interactions between carbon atoms was described by a widely used Tersoff-like parametrization for carbon made by Brenner [23] but without the bond conjugation term.

Since we were not able to find an existing analytical potential to describe the interactions between carbon and potassium, we used a simple pair potential obtained with DMol software[1] [24]. Pair potentials completely neglect the effect of the surrounding bonds, and thus they overestimate the strength of interaction between atoms surrounded by other atoms. Because of this, the model gives a worst case estimate when the mobility of K atoms in CNTs is considered. To understand the effect of this overestimation, we compared our results with similar simulations using the same potential, but with a strength of one third of the original in the potential well region.

The minimum energy distance for a C–K dimer predicted by this potential is $d_{\text{C-K}} \approx 2.4$ Å and minimum energy $E_{\min}^{\text{C–K}} \approx -1.7$ eV. This potential yields a threshold energy of $E_{\text{tresh}}^{\text{p}} \approx 7.2$ eV for a K ion to penetrate through one graphite layer. This threshold is obtained when the impact point is in the center of a hexagon of C atoms. We used a cut-off radius of $r_{\text{cutoff}}^{\text{C–K}} = 5.0\ \text{Å} \approx 2d_{\text{C-K}}$.

In simulations including multiple K ions we used analytic embedded atom method (EAM) potential for bcc metals constructed by Johnson and Oh [25]. With this interaction we used a cut-off radius of $r_{\text{cutoff}}^{\text{K–K}} = 6.0$ Å.

All our potentials were smoothly joined with the ZBL repulsive potentials [26] at short

[1] DMol is a trademark of AccelRys, Inc.

inter-atomic distances to realistically model energetic collisions. Electronic stopping was not taken into account as the ion energies were low and the nuclear slowing down governed the collisional phase.

2.2. Temperature control

Constant temperature was modelled using the Berendsen temperature control technique [27] at the regions outside the impact volume. The simulation temperature was chosen to be 100 K.

To study the effect of the average temperature on the obtained results, also simulations with lower average temperature and longer simulation times were performed with the largest CNT and irradiation energy of 0.5 keV. The obtained results were not found to be affected by these modifications.

2.3. Impact area and periodic boundary conditions

For graphite the impact point was randomly chosen within one unit cell in the central part of the irradiated surface. Periodic boundary conditions were used for graphite in the directions parallel to the irradiated surface. The irradiation direction was perpendicular to the surface of the system.

In all CNT simulations, the irradiation direction was perpendicular to the CNT length direction. For CNTs irradiated with single K ions, the impact points were randomly chosen in the central part of CNTs so that one unit cell length and the whole CNT diameter was sampled. Periodic boundary conditions were used in the direction of the CNT length.

For simulations with multiple K ions, the whole CNT volume was uniformly irradiated. To ensure this, the starting point of the ions was chosen to be $(x = 0\ \text{Å}, y = r_y \in [-d/2, d/2],\ z = 30\ \text{Å})$, where r_y was a random number chosen separately for every ion, and d is the CNT diameter. The irradiation direction was parallel to the negative z-axis and the CNT length direction was parallel to the x-axis. The CNT was centered at the origin in the y- and z-directions. After every impact the structure was moved a random amount $r_x \in [0, l]$ in the x-direction using periodic boundary conditions. l is the CNT length.

2.4. Damage analysis

To study the effect of the K ions to the structure of the CNT we also estimated the amount of damage produced by K ions into the CNT atomic network. We used a damage analysis method based on the structure-factor analysis, which has previously been used with different types of structures [28,29].

In the implementation for graphene layers, which was also found to work well for nanotubes, the three nearest neighbours were considered and atoms with $P_{\text{st}}(i) > 0.14$ were interpreted as defect atoms.

We defined damage to be

$$\text{damage} = \frac{N_{\text{C}}^{\text{sputtered}} + N_{\text{C}}^{\text{defect}} + N_{\text{K}}^{\text{total}} - N_{\text{K}}^{\text{CNT}}}{N_{\text{C}}^{\text{total}} + N_{\text{K}}^{\text{total}}}, \quad (1)$$

where $N_{\text{C}}^{\text{sputtered}}$ is the number of sputtered C atoms, $N_{\text{C}}^{\text{defect}}$ is the number of those carbon atoms not in a perfect lattice site but still remaining in the CNT volume, $N_{\text{K}}^{\text{CNT}}$ is the number of K atoms inside the CNT and $N_{\text{C}}^{\text{total}}$ and $N_{\text{K}}^{\text{total}}$ are the total number of C and K atoms, respectively. This choice of damage seems to agree well with the visual estimation on the produced damage.

3. Results

3.1. Single K irradiation of graphite

To study the effect of CNT's diameter on the penetration depth of the ion and also to get a realistic energy range for CNT simulations, we simulated irradiation of multiple graphitic layers in A–B-stacking. We started simulations with an irradiation energy of 20 eV and then increased it by 20 eV until 500 eV, when on average more than five graphite layers were penetrated. We performed 50 simulation runs with each energy to get representative statistics. The averaged number of penetrated graphite layers are presented in Fig. 1 with standard error estimates.

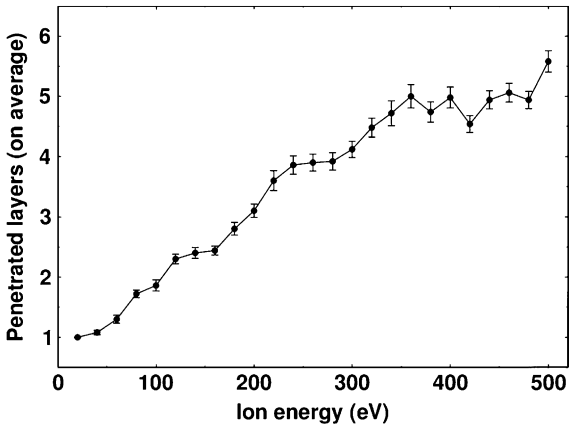

Fig. 1. The averaged number of penetrated graphitic layers as a function of the ion energy.

3.2. Single K irradiation of CNTs

The CNTs we studied were single-walled, double-walled and triple-walled zigzag nanotubes (SWNT, DWNT and TWNT) with the smallest CNT being (5,0) SWNT and the largest (5–10–15,0) TWNT, the outer diameters of which are ~0.5 nm and ~1.2 nm, respectively. The (5–10–15,0) TWNT was chosen because the inter-shell distance in this CNT is nearly 0.3 nm, which corresponds the distance between graphene layers in graphite.

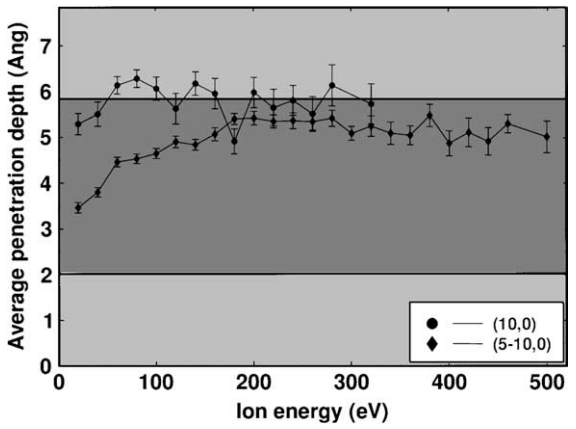

Fig. 2. Averaged penetration depth of K as a function of the ion energy. The (10,0) SWNT is shown with lighter and the (5,0) SWNT with darker grey. The (5–10,0) DWNT contains both of these within each other.

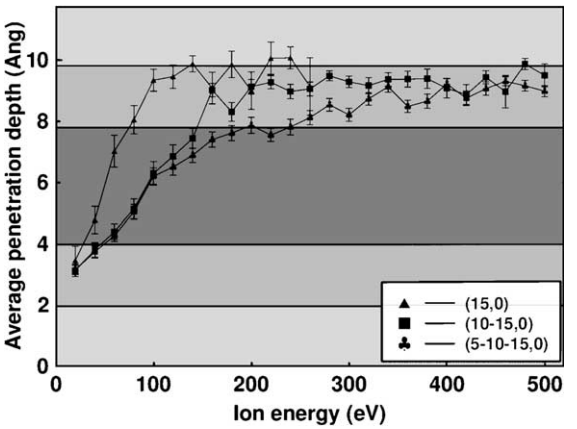

Fig. 3. Averaged penetration depth of K as a function of the ion energy. The (15,0) SWNT is shown with the lightest, the (10,0) SWNT with darker and the (5,0) SWNT with the darkest grey. The (10–15,0) DWNT contains both SWNTs (10,0) and (15,0) within each other and the (5–10–15) TWNT contains all of them.

We used the obtained energies in CNT simulations to study the depth profile of K atoms after irradiation as a function of the irradiation energy. 50 simulation runs were again performed for each irradiation energy. The average depths are presented in Figs. 2 and 3 for CNTs with the outermost tube (10,0) and (15,0), respectively.

We also studied the probability of the K atom to stay within the atomic network of the CNT after the irradiation as a function of the irradiation

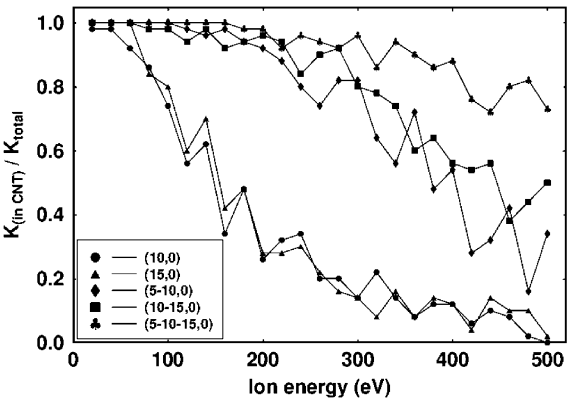

Fig. 4. Probability of K atom to penetrate the outermost wall of CNT and to stay within the CNT volume as a function of the initial ion energy for all simulated CNTs.

energy. Probabilities for all CNTs are presented in Fig. 4, from which it can be seen that the probabilities depend clearly on the number of coaxial tubes but much less on the diameter of the CNTs.

3.3. Higher dose K irradiation of TWNT

3.3.1. Stochastic method

To study the clustering of K atoms inside the CNT, we used the obtained depth profiles for K ion penetration into (5–10–15, 0) TWNT. We inserted artificially K atoms inside the volume of the TWNT by generating random numbers according to the known profile using the von Neuman rejection method [30]. In this way we obtained coordinates for K atoms which have not interacted with each other, but with the correct depth distribution. From this stochastic data set we then analysed the average size of the clusters and also the number of clusters as functions of the number of K atoms inside the TWNT.

Because this method does not involve any force calculations or estimation of the dynamics of the system, it is very computationally effective. However, this method only gives us a point of comparison to use with MD simulation results described below. This comparison allows us to deduce how much the clustering is enhanced by the K–K interaction and thus by the mobility of K ions in the CNT.

3.3.2. MD simulations

We also performed MD simulations with multiple K ion impact events. In addition to the number of clusters and average cluster sizes we analysed the damage produced to the TWNT during the irradiation. Because long time scales can still not be simulated with MD, the simulation time we used between impacts was far shorter than any realistic experimental time would be. However, we assume that our simulations give reasonable understanding of the clustering of implanted potassium ions in CNTs at low temperatures.

We used similar techniques as for the single K irradiation simulations. The main difference was that now we simulated the system for 30 ps per ion and in the end of each irradiation event we quenched the system to a temperature of 100 K, to prevent temperature rise during prolonged irradiation. The simulated system was the largest CNT studied, specifically the (5–10–15, 0) TWNT. We ran higher-dose-simulations with irradiation energies from 60 eV to 1 keV to ensure that the whole reasonable energy range was covered. One higher-dose-simulation was performed for each energy.

We first studied the probability for a K ion to get into the TWNT (cf. Fig. 5). To study the clus-

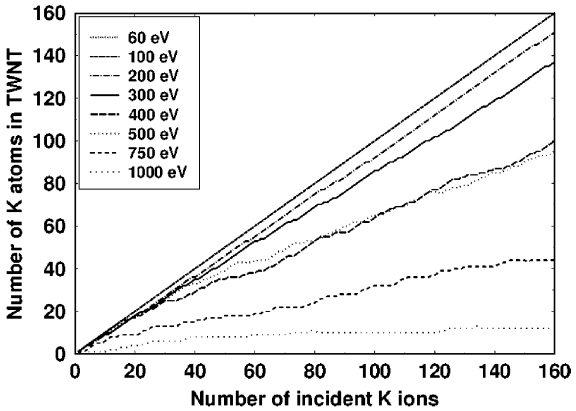

Fig. 5. Number of K atoms in a (5–10–15, 0) TWNT as a function of the number of incident K ions. The data for 60 eV and 100 eV are identical and thus only the data for 100 eV can be seen from the figure.

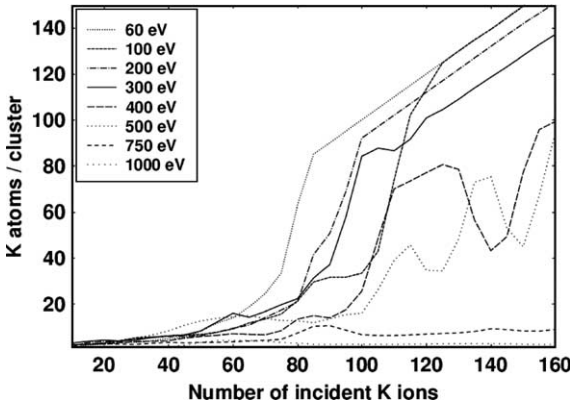

Fig. 6. Average cluster size in a (5–10–15, 0) TWNT as a function of the number of incident K ions. To clarify the data, we calculated the average of nine surrounding data points for the same energy into a single point in the graph. The large jumps in the graphs are due to large clusters first joining and then parting again.

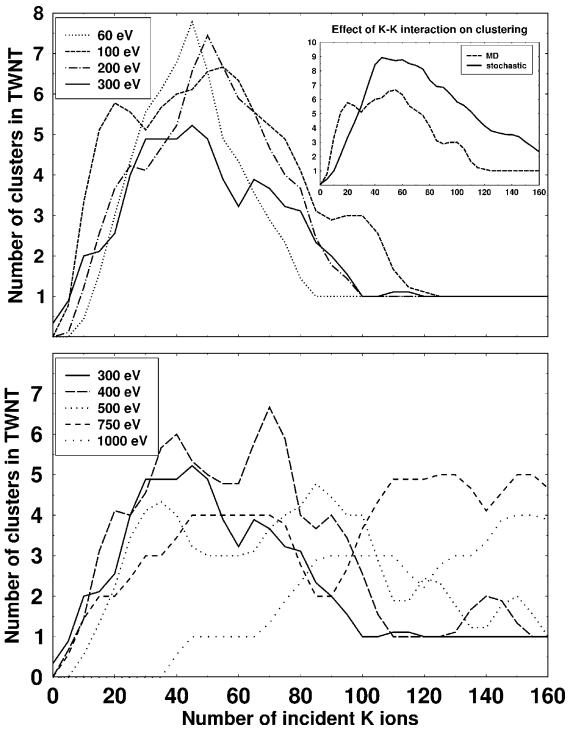

Fig. 7. Number of clusters in a (5–10–15,0) TWNT as a function of the number of incident K ions. Data for lower energies are presented in the upper and for higher energies in the lower graph. The solid line presenting the data for the irradiation energy of 300 eV is included in both graphs to ease the comparison. Every data point in the figure is averaged from nine surrounding data points for the same energy to clarify the data. The inset in the upper part of the figure presents the averaged results from stochastic data for 100 eV and from the corresponding MD simulation.

tering of K atoms in a (5–10–15,0) TWNT we analysed the positions of atoms after every irradiation event. We defined a K cluster to be a group of K atoms in which the distance between two K atoms i and j, $d_{K_{i,j}} < 5.0$ Å, and then calculated the average size of clusters and the number of clusters as functions of the number of incident K ions. The results are presented in Figs. 6 and 7.

We also analysed the damage produced to the system by the incident K ions. The results are presented in Fig. 8 and a picture series of three simulations is shown in Fig. 10. To at least partially estimate the effect of defect annealing at low temperatures but with macroscopic time scales [21], we also simulated multiple impacts with a 30 ps annealing phase at 2000 K in between the impacts and analysed the produced damage. The results with annealing were within the statistical fluctuations with those obtained without the annealing.

From comparison of Figs. 5 and 8 it can be seen that irradiating with energies higher than 100 eV will produce significant amount of damage into the CNT before a sufficient K dose is reached. On the other hand, with energies less than 100 eV the K atoms will mostly be in that part of the CNT from which the ions have arrived. Thus less clusters are produced and they are not uniformly distributed into the CNT. Because (K-atom)–(zigzag CNT) structures with stoichiometry KC_{48} have been found to be clearly metallic [10], it might not be needed to achieve the stoichiometry of the superconducting K_3C_{60} [5]. These stoichiometries correspond in the current structure of the 3000-atom TWNT to 62.5 and 150 K atoms inside the tube, respectively.

To emphasise the clustering effect and at the same time the damage caused to the system, we also studied the ratio *(K clusters)/damage* as a function of the number of incident ions. Ideally this ratio should be as large as possible, which would correspond to high K concentration in the CNT with as low damage as possible. We also found the corresponding values for stoichiometries KC_{48} and K_3C_{60} for different irradiation energies. The results are presented in Fig. 9. From this fig-

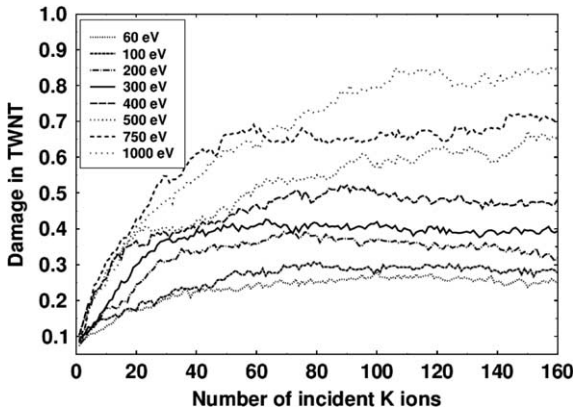

Fig. 8. Damage produced in a (5–10–15,0) TWNT as a function of the number of incident K ions.

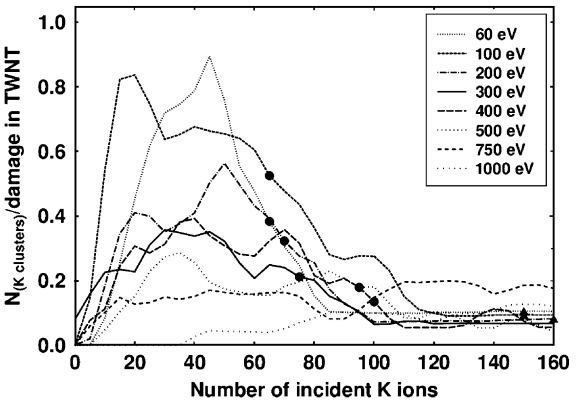

Fig. 9. Clusters/damage ratio of a (5–10–15,0) TWNT as a function of the number of incident K ions. Every data point in the figure is averaged from nine surrounding data points for the same energy to clarify the data. Points where the structures have a stoichiometry KC_{48}/K_3C_{60} are marked with a circle/triangle for each simulation energy. Some of the values did not fit in the x-axis range chosen for the figure.

ure it can be concluded that the best irradiation energy is about 100 eV when the clustering of K atoms is considered. Note that because some K atoms do not enter or stay in the tube, the circles and triangles marking the specific KC_{48} and K_3C_{60} stoichiometries are not in the same x axis positions for all energies. If very high dose of K atoms is wanted, severe damage will be caused to the system even with lower energies (Fig. 10).

4. Discussion

By looking at Figs. 1–3 it can be concluded that before a certain threshold energy needed to penetrate the next CNT wall has been reached, the K atoms will on average be a bit off the nearest CNT wall. Thus K atoms typically lie intercalated in the hollow parts of the CNT and can easily form

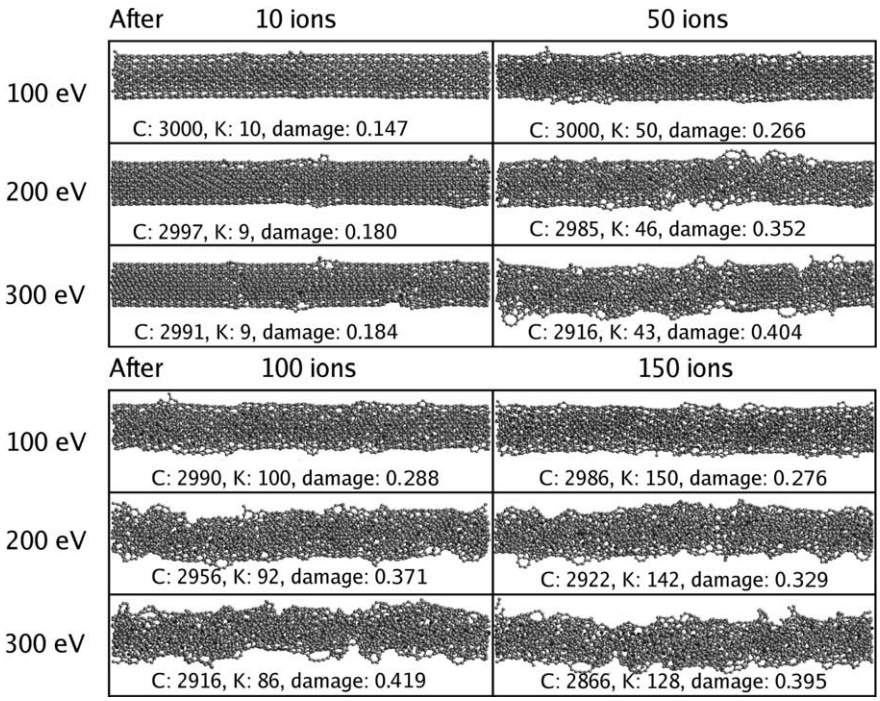

Fig. 10. A ball-and-stick picture series of a (5–10–15,0) TWNT irradiated with K using energies 100 eV, 200 eV and 300 eV. Shown pictures are after 10, 50, 100 and 150 K ions. Nearly all visible atoms are carbon. K atoms are a bit darker, but they can barely be seen. Below each picture the number of C and K atoms in the structure are written along with the damage ratio.

clusters. Interestingly, this result is similar to the recent experimental study of K doping of fullerene peapods using a vapour-phase method, in which the K atoms were found inside the CNTs at inter-fullerene sites [13].

By comparing the results of the stochastic method and the MD simulations of high-dose K irradiation, it can be seen that the clustering is significantly more probable than would be statistically assumed neglecting the interactions between K atoms. This means that the K ions are mobile in the CNT right after the irradiation event and thus cluster together. This effect can be seen from the inset in the upper part of the Fig. 7 for the irradiation energy of 100 eV. The effect is similar for all energies.

On longer time scales than those studied in this work, one can reasonably assume that the clustering of K atoms would at least not decrease. It might well increase if the temperature is such that the K atoms can diffuse in the tubes. Also the damage of the CNTs would be much reduced if the irradiation were carried out at temperatures of 600 K or higher, where irradiation damage in carbon structures is known to be much reduced compared to room temperature [31].

The simulated CNTs were quite small, and even the largest one was only three-walled. With larger and hollower CNTs the clustering effect might well be even greater. It can also be assumed that the amount of produced damage decreases while the diameter of the CNTs increases because the K–C interaction is much longer ranged than the C–C interaction, and thus the most favourable position of the K atoms is either between the CNT layers or inside the innermost tube.

It is interesting to note that the K atoms almost never (at most 2% of the time for all energies) stay in the 'plane' of a nanotube wall. This is in sharp contrast to recent results on B/N doping of nanotubes, which show that about half of these dopant atoms can enter a substitutional site in the nanotube wall during ion beam doping [19,20]. This is related to the much larger size of the K atom compared to B or N; a K atom (which has a covalent radius about twice as large as B, C or N) can not fit into the site of a single C atom without inducing excessive strain. While a K atoms of course could replace 2 or more C atoms, our present results show that this is quite unlikely to occur.

5. Conclusions

In this study we have found that ion irradiation can be used to introduce K ions into different types of CNTs. The irradiation energy leading to the best results varies depending on the number of coaxial tubes forming the specific MWNT, but not on the diameter. For CNTs with 1–3 coaxial tubes, this energy proved to be about 100 eV. Ions with energies lower than this can presumably not penetrate deep enough into the CNT, but on the other hand, ions with more energy will cause severe damage and eventually destroy the CNT. Irradiation of CNTs with higher doses of K ions was found to definitely introduce clusters of K atoms inside the CNT.

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