Disordering of carbon nanotubes by ion bombardment

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Abstract. In this work, the formation of defects during the ionic modification of carbon nanotubes was studied. It was shown that during the ionic modification of multiwalled carbon nanotubes, the defect formation mechanism is reduced not only to the formation of recoil atoms by ions, but also due to the thermal peak. It can be seen that the radial distribution function for the irradiated nanotube is significantly different from the radial distribution function of a heated 4000 K nanotube. In addition, disorder has a special character: in the case of ion irradiation, in contrast to heating.

1. Introduction
Carbon nanotubes are a unique carbon material [1]. Carbon nanotubes have unique physical [2-5], chemical [6] and biological [7-12] properties. However, the synthesis of nanotubes and their subsequent modification are associated with defect formation, which affects their properties. The carbon nanotube consists of graphene layers. Defect formation in graphene during ion bombardment into heated substrates occurs less intensively [13]. However, in our case, due to the isolation of the tubes from each other, defect formation occurs more intensively. Modifications of carbon nanotubes and graphene are the subject of many works; [14-15]. The materials ion modification is widely used method [16]. Carbon nanotubes ion modification is presented in the works of the groups Chechenin [17], Lee [18], Shemukhin [19]. There are many studies on the ion modification produced by Krasheninnikov and Nordlund [20-22]. Currently existing models of carbon nanotubes ion modification cannot always predict how given energy irradiation with ions particular dose will allow modifying the carbon nanotubes properties.

The aim of this work is to study defect formation during the multi-walled carbon nanotubes ion modification. The main contributions are defect analysis and discovering the mechanism of amorphization [23, 24].

2. Methods
The current work main method is molecular dynamics simulation. Classical molecular dynamics simulation is performed using the LAMMPS code [25]. Periodic boundary conditions for the simulation cell are used. The AIREBO [26] manybody interatomic potential is used to describe the C – C interaction in a multi-walled carbon nanotube. A multi-walled carbon nanotube consists of 14 layers. The inner layer is a (10, 10) single-walled carbon nanotube with a diameter of 1.4 nm. The outer (75, 75) tube has a diameter of 10 nm. The MWCNT length is 29.2 nm with a total number of carbon atoms of 285600. The simulation cell has a
size of $12 \times 12 \times 30$ nm. The layers are rotated one after another to form a stack of ABAB-graphene. The MWCNT simulation begins at 300 K.

Ar$^+$ ion irradiation was chosen to reduce the calculation time. The Ar$^+$–C interaction is described by the Ziegler-Birsak-Littmark potential [27]. The initial position of the Ar$^+$ ion is on the plane $\pi$ at 5.5 nm from the axis of the tube, the incidence angle ($\alpha$) is randomized in the range of 3-5º, azimuthal angle ($\varphi$) is randomized in range 0-360º, the initial energy is 80±0.3 keV (Figure 1). The electron stopping power was not taken into account, but for the Ar$^+$ ion with an energy of tens keV, the nuclear stopping power still exceeds the electronic stopping power [28].

They are presented in Figure 1.

![Figure 1](image)

**Figure 1.** Initial conditions and the multi-walled carbon nanotube ion irradiation problem geometry. Here $D$ – external and $d$ – internal diameters of MWCNT, $\alpha$ and $\varphi$ – initial incidence and azimuthal impact angles, $\pi$ – ion start plane.

### 3. Results and discussion

After the Ar$^+$ ion passes across the nanotube along the trajectory (typical view is shown in Fig. 2), a cascade of collisions arises; recoil atoms can be resputtered onto neighboring tubes. During the ion passage, the nanotube’s temperature increases up to 800 K, while the ion energy losses is about 15–20 keV.
Figure 2. The trajectory of the Ar$^+$ ion in the cross section of MWCNTs. Atoms are shown in blue as atoms at room temperature, and warmer shades to red indicate recoil atoms when the Ar$^+$ ion passes.

Figure 3 shows the defects in the nanotube sector that arise after the passage of 14 ions. As one can see, there are: vacancies, interstitials, adatoms between layers, non-hexagonal rings and interlayer crosslinks.

Defects such as vacancies and interstitials are the most common types of defects during the ion irradiation of nanotubes. The remaining defects, such as adatoms, non-hexagonal rings, interlayer bridges are obtained during the development of cascades of collisions and further annealing of the formed defects due to a local short-term temperature increase – a thermal peak after the passage of the Ar$^+$ ion.

The ratio of sp$^3$-bonds with respect to sp$^2$-bonds increasing during accumulation of defects is observed. If we compare the experimental data obtained by x-ray phase spectroscopy (XPS, Table 1) with the results of a numerical experiment (Table 2), good agreement can be noted. In Table 2, the radiation doses correspond to the span of the 1st, 7th and 14th ions are given.

### Table 1. The results of measuring the concentration of sp$^2$ and sp$^3$ bonds by the XPS method in the samples obtained in [19].

| Type       | Binding energy, eV | Concentration, at.% |                  |                  |                  |
|------------|-------------------|---------------------|------------------|------------------|------------------|
|            |                   | Unirr. | 5×10$^{15}$ ions/cm$^2$ | 10$^{16}$ ions/cm$^2$ | 2×10$^{16}$ ions/cm$^2$ |
| C–C (sp$^2$) | 284.2–284.3     |         | 99.71           | 81.09            | 77.43            | 70.01            |
| C–C (sp$^3$) | 285              |         | 0.29             | 18.91            | 22.57            | 29.99            |

### Table 2. The concentration sp$^2$- and sp$^3$-bonds measuring results by the Winger-Seitz method obtained by numerical calculation.

| Type       | Concentration, at.% |                  |                  |                  |
|------------|---------------------|------------------|------------------|------------------|
|            |                     | Unirr. | 3.33×10$^{11}$ ions/cm$^2$ | 2.33×10$^{12}$ ions/cm$^2$ | 4.67×10$^{12}$ ions/cm$^2$ |
| C–C (sp$^2$) | 100                |         | 99.99           | 75.66            | 73.17            |
| C–C (sp$^3$) | 0                  |         | 0.39×10$^{-2}$  | 24.34            | 26.83            |

Carbon is a unique element thanks to a variety of allotropic modifications. A diamond in sp$^3$ hybridization state is an excellent dielectric, graphite (sp$^2$) and carbon (sp$^1$) are conductors, and graphite in the direction
perpendicular to graphene planes is a semiconductor. Accordingly, controlling only the type of hybridization, we can try to control the conductivity. In most electronic devices, the conductivity changes due to doping with impurity atoms, in CNTs we can change hybridization, that is, in essence creating structural defects in carbon nanotubes. Our calculation shows that using the formation of defects during irradiation, it is possible to create the required number of defects. Our further work will be aimed at studying the influence of the formed defects on the electrophysical properties.

According to our assumption, the main mechanism of amorphization is the development of a cascade, and then the formation of a thermal peak with subsequent annealing. For comparison, we simulated the heating of a multi-walled nanotube at 4000 K, the radial distribution function is shown in Figure 4. It can be seen that the radial distribution function for the irradiated nanotube is significantly different from the radial distribution function of a heated 4000 K nanotube. In addition, disorder has a special character: in the case of ion irradiation, in contrast to heating.

![Radial Distribution Function](image)

**Figure. 4.** The radial distribution function of carbon atoms at different temperatures of a multi-walled carbon nanotube.

### 4. Conclusions

One of the possible mechanisms for the amorphization of carbon nanotubes during the ion bombardment of Ar⁺ is thermal heating. In the existing model, such heating leads to significant defect formation in a carbon nanotube even at low radiation doses. In general, such defects as vacancies and interstitial atoms form during ion irradiation, and with further development of the collision cascade, resputtering of recoil atoms and annealing, defects such as adatoms, non-hexagonal rings, and interlayer bridges appear.

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