Signatures of irradiation-induced defects in scanning-tunneling microscopy images of carbon nanotubes

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Using empirical-potential and tight-binding models, we study the structure and stability of atomic-scale irradiation-induced defects on walls of carbon nanotubes. We model the temporal evolution of the defects and calculate their lifetimes at various temperatures. We further simulate scanning-tunneling microscopy (STM) images of irradiated nanotubes with the defects. Our simulations indicate that at low temperatures, the defects live long enough to be detected by STM and that different defects manifest themselves in STM images in different ways, which allows to distinguish the defects experimentally.

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Recently, numerous experimental and theoretical studies on carbon nanotubes (NTs) have demonstrated possibilities for developing carbon-based electronics [1,2]. However, implementation of even the simplest electronic devices demands a thorough understanding of the structural and electronic properties, not only of perfect NTs, but also of NTs with various defects. Moreover, recent experiments [3] indicate that defects in NTs can be used to fabricate an intratube quantum dot device. Thus, the methodological development of such electronic NT-based devices requires knowing what the defects involved are, and how they can be produced.

Inasmuch as irradiation of NTs potentially makes it possible to create defects in a controllable way, the effects of electron [4,5] and ion [6–8] irradiation on structural and electronic properties of NTs are of particular interest. However, the behavior of irradiation-induced defects as well as their experimental detection are still open questions.

In this paper, we study the stability and temporal evolution of irradiation-induced defects in single-walled NTs and simulate scanning-tunneling microscopy (STM) images of irradiated NTs with the defects.

1. The Simulation method

The method used in this study has been described in detail in other publications [7,9–11]; so only a brief description is given here.

We considered individual $(10, 10)$ armchair NTs. Using molecular dynamics [12], we simulated impact events of Ar ions with energies of from 50 up to 3000 eV on NTs. The Brenner potential [13] without bond conjugation terms was used for modeling the carbon atom interaction. To examine the stability of the irradiation-induced defects, we simulated the time evolution of a 100-Å-long NT with the defects over timescales up to ten nanoseconds at temperatures of 1000−3000 K. For every temperature considered, we carried out at least 40 independent runs and averaged the results.

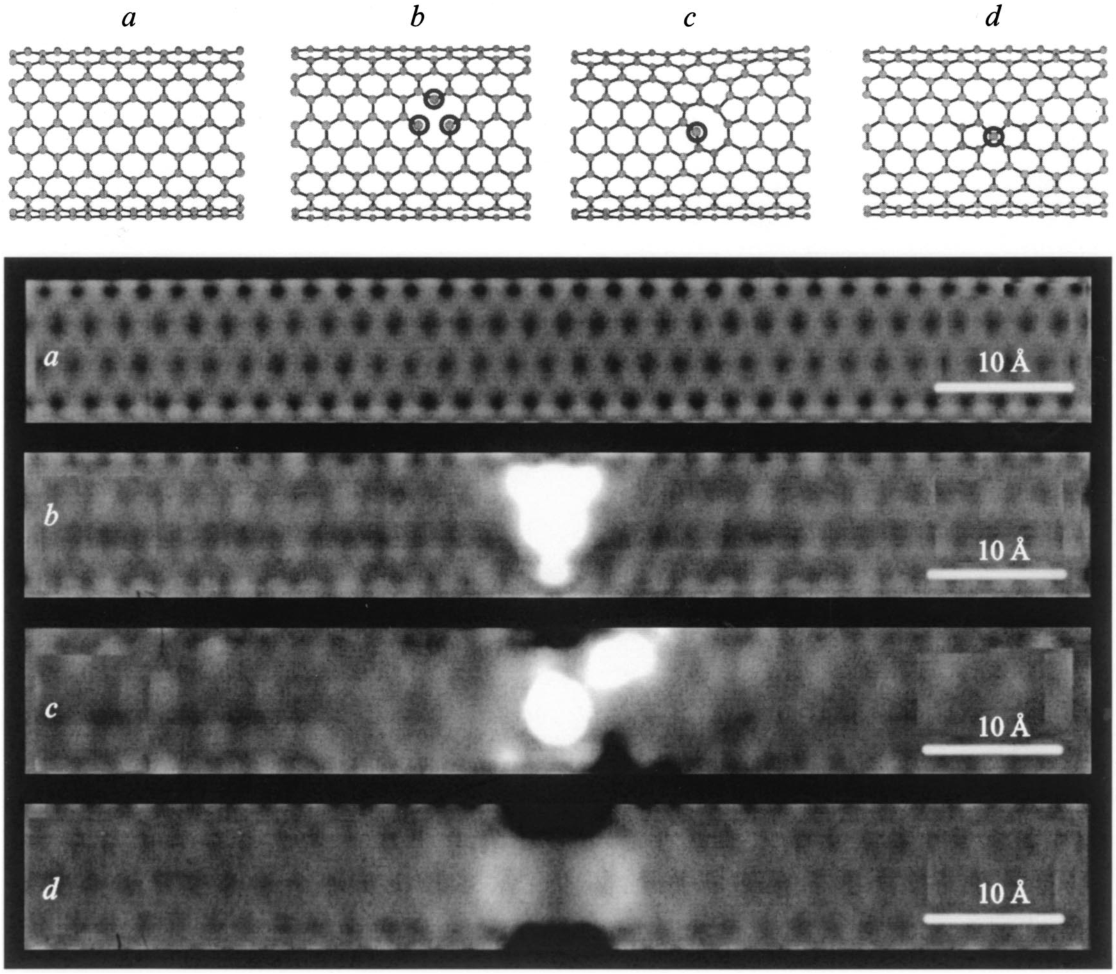
Having calculated the geometry of the defects within the framework of the classical model by minimizing the total energy of the carbon network after defect creation, we computed the STM images of the irradiated NTs near the defects within the framework of the tight-binding approximation [14].

2. Results and discussion

As follows from our simulations, the most common defects produced under ion irradiation are vacancies which, at low temperatures, are metastable but long-lived defects. At high temperatures, the vacancies (which have three dangling bonds, see Figure, *b*) can transform to two other defects. These are a single pentagon–one dangling bond atomic configuration and a four-fold coordinated atom in the center of two pentagons and two hexagons, c. f. Figure, *c, d*. For brevity, we label the former defect "5–1 db" and the latter "5−6" defect. Formations of such defects under high-dose electron irradiation have also been reported [5].

Since the 5–1 db defect has the lowest energy [5,7], although all three defects may appear as a result of ion impact, the long quenching of the NT should eventually lead to the transformations of single vacancies and 5−6 defects to 5–1 db defects. However, since single vacancies and 5−6 defects are metastable (i. e., there is an energy barrier separating these two configurations from the configuration with the minimum energy), such defects may survive at low temperatures for finite times, which may be long enough for detecting the defects experimentally.

We extimated the lifetimes of the metastable defects as described in the previous section. For single vacancies, with simulations between temperatures of 1500 and 2200 K, the avarage vacancy lifetime can be well described with activated behavior with a single activation energy, i. e. by the formula $\tau_{\text{vac}} = a \exp(b/k_B T)$, where τ_{vac} is the time before the vacancy transforms into the 5–1 db defect, k_B is Boltzmann's constant, T is the temperature, and a and b are the fitting constants. Determining the constants at high temperatures,



Ball-and-stich representation of the carbon network of a pristine $(10, 10)$ single-walled nanotube and the nanotube with defects and their STM images. Pristine nanotube (a); nanotube with an irradiation-induced vacancy (b), "5–1 db" (c) and "5−6" (d) defects. Only the front walls of the nanotubes are sketched. Atoms with unusual numbers of bonds are circled. The defects are at the centers of the STM images.

we estimated the lifetime at room temperature which proved to be of at least the order of a hundred hours. Thus, the vacancies might be experimentally detected by, e. g., STM.

We also carried out similar simulations for 5–6 defects in a temperature range of 1200–1800 K. The lifetime of 5–6 defects was found to be about five hours at room temperature. Thus, 5–6 defects may also survive long enough to be found.

To facilitate experimental identification of the defects, in Figure we present the grey-scale STM images of the NTs with the defects calculated for positive $V_{\text{bias}} = 0.2\,\text{V}$. Defects are always at the origin. To establish a correspondence with the already published results, we also show a grey-scale STM image of a perfect NT.

The main feature of the STM image with the vacancy is a dramatic protrusion above the defect. Depending on the sign of V_{bias}, the height of the hillock is $\approx 0.7{-}0.8\,\text{Å}$, while its linear size is independent of V_{bias} and constitutes $\approx 5\,\text{Å}$. The enhancement in the tunneling current is due to vacancy-induced states near the Fermi energy (which may be interpreted as "dangling bonds"), and these states are spatially localized on the atoms surrounding the vacancies. Since it is specifically these states which STM probes at small bias voltages, a vacancy is imaged as a protrusion.

Figure, *c* shows an STM image of the NT with a 5–1 db defect. Again, similar to the case of a vacancy, a hillock-like feature above the defect is evident, which also has electronic origin. However, the shape of the feature is quite different from that in the case of the single vacancy.

The 5–6 defect, if it exists long enough to be measured by STM, also gives rise to a small bump in the STM image of the NT, see Figure, *d*. The shape of the hillock reflects the symmetry of the underlying atomic structure of the defect, cf. Figure, *d*. Additional information may be also obtained from the current-to-voltage characteristics, which are different for the defects.

Thus, it is possible to experimentally detect and distinguish the irradiation-induced defects in NTs. It is also noteworthy that the experiments on irradiating NTs with inert gas ions and subsequent STM probing, if carried out, may enable one to observe the temporal evolution of irradiation-induced defects at various temperatures and compare experimental lifetimes to those predicted theoretically. Such experiments may not only contribute to understanding the mechanisms of defect formation, but may also serve as a test for the validity of tight-binding and empirical potential molecular dynamics models.

In summary, we studied the behavior of atomic-scale defects produced by low-dose irradiation of nanotubes with Ar ions and computed their lifetimes at various temperatures. We demonstrated that at low temperatures the defects are likely to be stable on macroscopically long timescales, and appear as hillock-like features in STM images due to the growth in the local electron density of states on atoms surrounding the defects. Since the shape of the hillocks are different for different defects, they might be experimentally distinguished using STM.

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