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Graphite-to-amorphous structural transformation of multiwalled carbon nanotubes under proton beam irradiation

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ABSTRACT

The graphite-to-amorphous structural transformation of multiwalled carbon nanotubes (MWCNTs) was investigated under 70 keV proton beam irradiation at room temperature. It was found that under proton irradiation some amorphous structure homogeneously covers the inner tube walls with graphite structure in irradiated MWCNTs. Moreover, the amorphous structure continuously proceeds and the graphite structure is reduced during the proton irradiation until the irradiated MWCNTs become amorphous nanowires with a hollow structure. The proton irradiation induced structural transformation of MWCNTs was a unique graphite-to-amorphous structural transition from the outer walls to the inner walls of the irradiated MWCNTs. The structural evolutionary mechanism of proton-beam-irradiated MWCNTs has been discussed.

1. Introduction

Carbon nanotubes (CNTs) exhibit fascinating properties arising from their unique one-dimensional geometrical hollow graphitic structure [1–4]. The excellent properties of CNTs have attracted considerable research regarding their potential applications [4]. However, it is important to control and modify the structures of CNTs because the properties of CNTs are strongly affected by their structures [5,6].

Energetic particle beam irradiation is a useful technique for the production of defects in CNTs, which can alter their structural properties in a highly controllable manner [7,8]. Interest in the effects of irradiation on CNTs has been triggered by recent observations of fascinating irradiation-induced phenomena, including the coalescence and welding of CNTs, the creation of links between nanotubes, etc. [9–12].

The mechanisms of irradiation-induced structural change in CNTs are substantially different from those in bulk carbon systems. At present, a great number of experimental and theoretical data on irradiation effects on CNTs have accumulated and some novel phenomena have been induced in CNTs by particle beam irradiation. For example, the inner layers of multiwalled CNTs (MWCNTs) can be reorganized into nanocompartments with pillbox-like and bamboo-like structures with heavy ion irradiation, respectively [13,14]. CNTs under bombardment with MeV protons and heavy keV ion beam can be degraded into an amorphous material [15,16]. The irradiation-induced amorphous structures of MWCNTs are considered to be caused by defect concentrations in/between the tube walls resulting from the collision cascades caused by doses of heavy ion irradiation. However, the evolution of the structural transformation of MWCNTs under ion irradiation is still unclear. Here, we chose proton beams to irradiate MWCNTs and studied the structural evolution of irradiated MWCNTs because the effects of proton beam irradiation differ from those of both electron and heavy ion beam irradiation. Electron beam irradiation creates point defects in CNTs, whereas heavy ion beam irradiation induces a strong collision cascade effect. Proton irradiation of MWCNTs may be expected to provide some detailed information on the irradiation-induced structural evolution of MWCNTs. Moreover, protons are the most abundant particles in deep space. Therefore, this research may be helpful in future applications of CNTs as components of various space structures, such as coating layers, radiation shields and electronic devices in space shuttles and space stations.

2. Experimental

The MWCNTs used were synthesized by thermal chemical vapor deposition. The MWCNTs were dispersed on holey carbon microgrids. The prepared specimens were then irradiated at room temperature (RT) in a 100 kV electromagnetic isotope separator (EMIS). The irradiation energy was fixed at 70 keV. The irradiation dose ranged from 1×10^{15} to 1×10^{18} protons/cm^2. The dose rate ranged from 1×10^{14} to 1×10^{15} protons/cm^2 s. The vacuum pressure in the chamber was maintained at 10^{-4} Pa during the proton irradiation. Transmission electron microscopy (TEM) was used to examine the structural changes in the proton irradiated MWCNTs.

3. Results and discussion

High-resolution TEM (HRTEM) shows that the as-grown MWCNT is well graphitized (inset of Fig. 1a). And some amorphous carbon contamination is occasionally adsorbed to the outer walls of the

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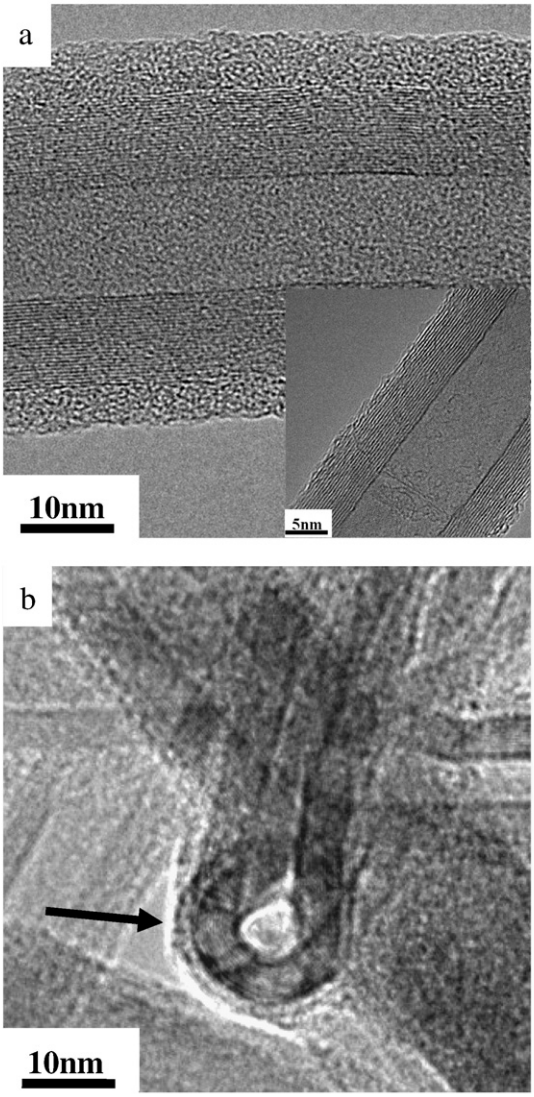

Fig. 1. (a) HRTEM image of a MWCNT irradiated with a 70 keV proton beam at a dose of 5×10^{16} protons/cm^2. The inset shows the HRTEM image of an as-grown MWCNT. (b) Cross-sectional TEM image at a slightly tilted angle. The amorphous structure of the MWCNT is denoted by the arrow.

MWCNT. After proton beam bombardment with a dose of 5×10^{16} protons/cm^2, the typical HRTEM shows that some outer graphite layers of the MWCNTs have lost their initial ordering and have become amorphous structures (Fig. 1a). However, it should be noted that the inner walls are not yet damaged. When we observe the cross-sectional TEM image at a slightly tilted angle (Fig. 1b), it can be seen that the amorphous structure of the MWCNT, denoted by the arrow, encapsulates the inner tube walls with the graphite structure. The boundary between the amorphous structure and the graphite structure is clear and sharp. From the HRTEM images of irradiated MWCNTs in Fig. 1, we can conclude that the proton beams can traverse the MWCNTs and the irradiation effect of the proton beam is isotropic for the MWCNTs, i.e., independent of the irradiation direction. This can be easily understood by ion beam irradiation theory. According to the calculation of the program SRIM-2003 [17], the traverse depth of 70 keV protons in carbon materials with a density of 2.25 g/cm^3 is over 400 nm, which is much greater than the diameter of the MWCNTs. The MWCNTs irradiated by electron or ion beams have been widely studied. However, to our knowledge, the formation of an amorphous structure in the outer shells and the inner graphitic layer structure in irradiated MWCNTs is first reported.

The sharp boundary between the amorphous structure and graphitic structure in the irradiated MWCNTs should be explained by the interaction of proton beam with MWCNTs. Under ion beam irradiation, one important mechanism is knock-on atom displacement resulting from kinetic energy transfer [7]. This mechanism leads to the generation of interstitial-vacancy pairs and the cascade collision effect. A 70 keV proton beam irradiated onto MWCNTs has sufficiently low displacement cross sections. Thus, the proton beam may induce mostly isolated defects (Frenkel pairs, or vacancy and an interstitial) and very few defect clusters (e.g., di- or tri-interstitials and their vacancy counterparts). Moreover, the migration energy of single interstitials in the open spaces between the adjacent shells in the MWCNTs, E_{pm}, is ~0.1 eV. Therefore, the defect recombination rate is relatively high, even at RT. Apart from the generation of defects induced by proton irradiation, there are no obvious structural changes in most of the graphitic layers of the MWCNTs because the energy of the protons is high enough to penetrate the MWCNTs. Therefore, only the irradiation-induced defect mechanism cannot explain the graphite-to-amorphous structural transformation of the irradiated MWCNTs, i.e., the existence of the sharp boundary between the amorphous structure and graphitic structure in the irradiated MWCNTs. Irradiation induced sputtering is another important mechanism that cannot be ignored, especially in the outer walls of the tubes. Sputtered carbon atoms can be deposited

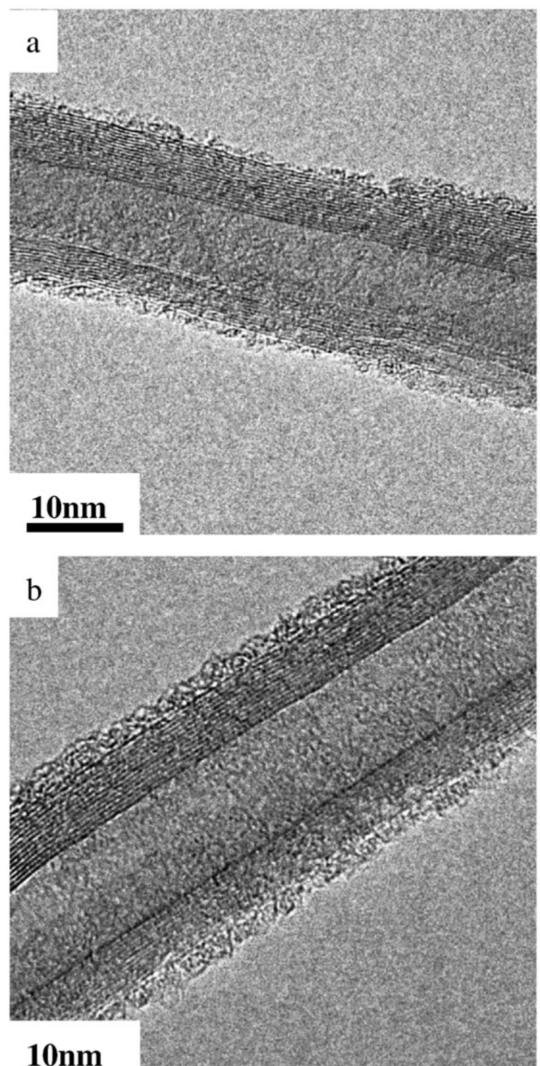

Fig. 2. HRTEM images of MWCNTs irradiated with 70 keV proton beams at doses of (a) 1×10^{15} and (b) 5×10^{15} protons/cm^2.

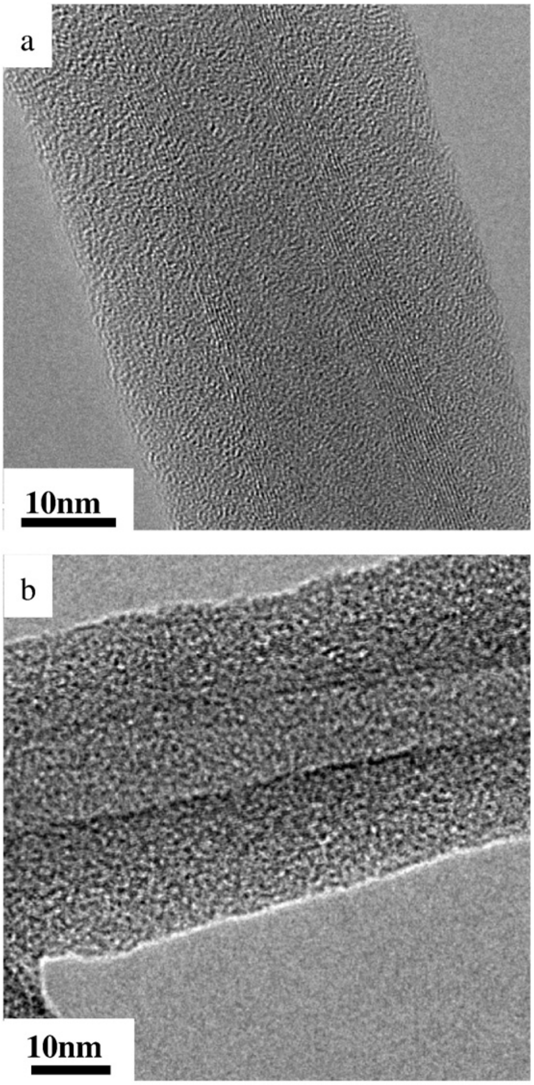

Fig. 3. HRTEM images of MWCNTs irradiated with 70 keV proton beams at doses of (a) 1×10^{17} and (b) 1×10^{18} protons/cm^2.

on the outer walls of the MWCNTs [7,18] and consequently form some amorphous carbon structures on the outer walls of the MWCNTs. Under proton irradiation, the irradiation-induced interstitial defects in the outer walls of the tubes preferentially agglomerate with some amorphous carbon.

Here, we display the results of some MWCNTs irradiated at low proton doses (see Fig. 2) in order to observe the sputtering effect of irradiated MWCNTs. At an irradiation dose of 1×10^{15} protons/cm^2, some amorphous carbon structures agglomerated and adsorbed to the outer walls of a MWCNT (Fig. 2a). At an irradiation dose of 5×10^{15} protons/cm^2, it can be seen that the amorphous carbon covered the outer wall of a MWCNT, leading to the formation of an amorphous structure surrounding the graphite structure of the MWCNTs (Fig. 2b). Obviously, the amorphous carbon structures should be caused by the deposition of sputtering carbon atoms.

The amorphous carbon structures around the irradiated MWCNTs are stable during proton irradiation. This is because the migration energy of the carbon cluster is very large. For example, even the migration energy of di-interstitials can reach 0.86 eV [19]. The sputtering induced amorphous structures are like nucleus in a phase transformation system. When sputtering induced amorphous carbon structure covers the irradiated MWCNTs, the amorphous carbon structure can continuously grow in MWCNTs under proton irradiation. Thus, the boundary between the amorphous structure and the graphite structure in MWCNTs is formed. At the boundary, ballistic displacement leads to preferential damage to the graphite layers. And the amorphous structure continuously proceeds and the graphite structure is reduced during the proton irradiation. Therefore, the irradiation induced sputtering deposition effect, the starting point of the structural transformation, is very important in the structural transfomation.

Fig. 3a indeed shows that the amorphous structure of the irradiated MWCNTs continuously increased and the graphitic structure decreased under high irradiation doses. Therefore, the proton irradiation induced graphite-to-amorphous structural transformation is considered to be the motion of the boundary, and the irradiation-induced structural transformation is a typical far-from-equilibrium process, where a thermodynamically stable structure under equilibrium conditions can continuously transform into a metastable structure along the boundary between the two structures [19,20]. Finally, it should also be noted that the morphology of irradiated MWCNTs is not greatly changed even at a high irradiation dose. Fig. 3b shows that at a dose of 1×10^{18} protons/cm^2, the graphitic layers of a MWCNT were completely transformed into an amorphous structure. Nevertheless, the hollow structure is still maintained.

4. Conclusions

In conclusion, we have studied structural transformation of MWCNTs irradiated with 70 keV proton beams. Under proton irradiation, the amorphous structure homogeneously encapsulates the inner tube walls with graphite structure in irradiated MWCNTs. The amorphous structure of the MWCNTs grows continuously during the irradiation until the irradiated MWCNTs become amorphous nanowires with a hollow structure. The structural evolutionary mechanism of proton-beam-irradiated MWCNTs has been discussed.

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