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Nuclear Instruments and Methods in Physics Research B 228 (2005) 26–30
NIM B
Beam Interactions with Materials & Atoms
www.elsevier.com/locate/nimb

Irradiation-induced phase transformations in carbon nanostructures

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Abstract

Structural phase transformations from multi-walled carbon nanotubes to amorphous carbon nanowires by carbon ion irradiation are experimentally carried out. A volume expansion effect during the formation of amorphous carbon nanowires is observed by an in situ TEM measurement. Moreover, the transformation of carbon nanotubes to nanocrystalline diamond is performed by hydrogen plasma post-treatment of carbon nanotubes. More importantly, diamond nanorods can be obtained by prolonging the treatment time of hydrogen plasma. Different sputtering yields for different carbon allotropes under hydrogen plasma treatment are responsible for the formation of diamond nanorods.

PACS: 61.46.+w; 61.80.−x; 64.70.Hz
Keywords: Nanostructure; Particle beam irradiation; Phase transformation

1. Introduction

Carbon nanotubes (CNTs), the new member of carbon allotropes, are closed graphite structures produced by thermal chemical vapor deposition (CVD), plasma-enhanced chemical vapor deposition (PECVD), high temperature carbon arcs, laser ablation and so on. The phase transformations between carbon allotropes, especially between the new member-CNTs and other carbon allotropes are an exciting field of materials research. Energetic particle beams have been demonstrated to be a powerful tool for phase transformation, especially for metastable phase formations [1,2]. Recently the interactions between nanostructures and particle beams have brought about a variety of new physical phenomena and possible new applications. Particle beams are used to drive self-organisation of nanostructures [3,4] and to weld CNTs to form junctions of various shapes, which might be useful for nanoelectronics

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doi:10.1016/j.nimb.2004.10.017

[5]. Also a low-pressure phase transformation of graphite (planar as well as curved graphite) to nanocrystalline diamond under particle beam irradiation can be carried out [6–9]. Liu et al. [10,11] used ion beams to manipulate highly energetic solid-state microstructures in nano-sized metal–metal multi-layers. In our previous study, amorphous carbon nanowires and various junctions of amorphous carbon nanowires [12] were formed by carbon self-implantation onto MWCNTs, and hydrogen plasma induced structure transformations from MWCNTs to nanocrystalline diamond with ultrahigh equivalent diamond nucleation density above 10^{11} nuclei/cm^2 were realized [13]. In the present paper, a volume expansion effect of amorphous carbon nanowires by particle beam irradiation of CNTs (synthesized by thermal CVD) is presented, and the formation of single crystal diamond nanorods by hydrogen plasma treatment of CNTs (synthesized by PECVD) is introduced.

2. Experiment

The MWCNTs were synthesized by thermal CVD on catalyst iron particles, and purified ultrasonically. The MWCNTs were deposited on the holey carbon micro-grid for formation of amorphous carbon nanowires junctions, and bombarded by 40 keV carbon ions with 5×10^{16} C ions/cm^2 at the 100 kV Isotope Separator. The high-resolution transmission electron microscope (HRTEM) Philips CM 200-FEG-EM430 operating at 160 kV is adopted to examine nano-structures of samples at un-irradiated and irradiated, respectively. An in situ transmission electron microscopy (TEM) study was also carried out.

Highly oriented, multi-walled carbon nanotube arrays were grown on silicon wafer substrates by radio-frequency PECVD at temperature about 850 K. The frequency of AC electrical power supply for the plasma reactor was 13.65 MHz. The purified carbon nanotubes were dispersed onto Si(1 0 0) substrates and then were placed into a rf hydrogen plasma chamber to be treated for several hours at 1000 K. Scanning electron microscope (SEM) and TEM were used to characterize morphologies and microstructures of samples. Raman and X-ray diffraction were used to confirm the formation of diamond nanorods.

3. Results and discussions

HRTEM shows that the un-irradiated CNTs (20–40 nm in diameter) are well graphitized and typically consist of 20–30 concentric shells of carbon sheets. However, there are defective sites (vacancies or insertions) on both the outer and inner graphite sheets of CNTs. After carbon ion bombardment, the concentric shells and the hollow structures completely disappeared [12,13]. Crossed MWCNTs became the web-like nanowires with various shapes of X, T and Y types [12]. Analysis of TEM images show that the diameters of amorphous carbon nanowires increased. If increasing ion dose the surface of amorphous carbon nanowires will become rough. However, an in situ observation by TEM is difficult for ion beam irradiation. Ion bombardment causes the creation of vacancies and interstitials in MWCNTs by knock-on collisions if the carbon nuclei of MWCNTs receive the energy from the ion to be larger than the displacement energy. The mechanism of carbon atom displacement in MWCNTs under energetic electron beam irradiation is the same as that under ion irradiation. In order to observe evolution of carbon nanowire formation under particle beam bombardment in detail, in situ observation with high resolution is carried out during TEM measurement. Fig. 1 is a typical TEM image. The electron beam spot covers the MWCNTs at some point, shown by the arrows. Difference is easy to observe. Normally, 10–20% expansion of the diameter for irradiated tubes can be observed when the amorphous carbon nanowire keeps a smooth surface. If increasing bombardment time a rough surface of amorphous carbon nanowires will appear. The previous paper [12] indicated that the amorphous carbon nanowires have a circular solid cross section after irradiation. So 10–20% diameter expansion of amorphous carbon nanowires after irradiation brought about 20–40% volume expansion of amorphous carbon nanowires, which have a loose structure. For ion irradiation whole sample can be irradiated by ion

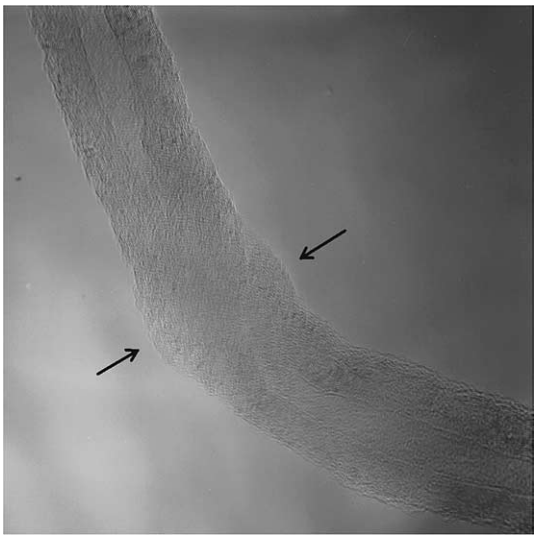

Fig. 1. TEM image of electron beam irradiated MWCNTs.

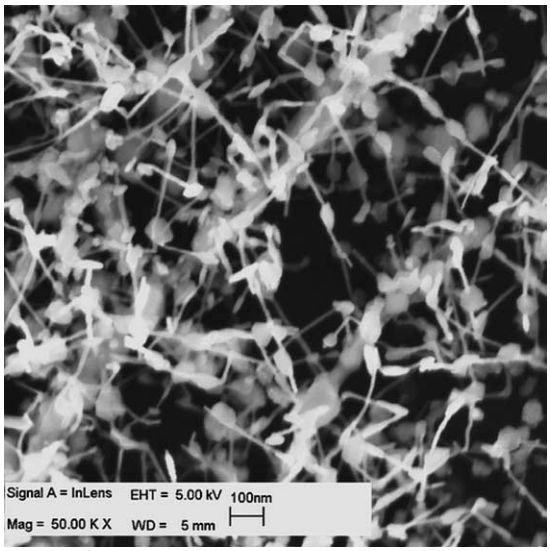

Fig. 2. SEM image of carbon nanorods after hydrogen plasma treatment of MWCNTs for 20 h.

beam because of ion sweeping. All MWCNTs on the grid evolve into amorphous carbon nanowires and their diameters are expanded if the ion dose is over the threshold dose for amorphization of MWCNTs. (In our experiments, the threshold dose for amorphization of MWCNTs is about 1–5×10^{16} C ions/cm^2 at room temperature which depends on the different types of MWCNTs.)

Phase transformation from MWCNTs to nanocrystalline diamond by hydrogen plasma treatment at high temperature was presented in [13]. As increasing treatment time of hydrogen plasma, the diamond nucleation density on the wall of MWCNTs increases. The equivalent diamond nucleation density could easily reach above 10^{11} nuclei/cm^2. When the treatment time of hydrogen plasma is about 20 h at 1000 K, many tiny nanorods grow on original MWCNTs, which are shown in Fig. 2. TEM is used to examine the structure of nanorods, which had 4–8 nm in diameter, and were 100–200 nm long rods with several nanometer cover layers. HRTEM image shows that the core is a single crystal diamond rod with plane spacing of 0.21 nm and the sheath is amorphous carbon material (Fig. 3). The selected area electron diffraction pattern and Raman spectra also confirmed the nanocrystalline diamond formation (not shown).

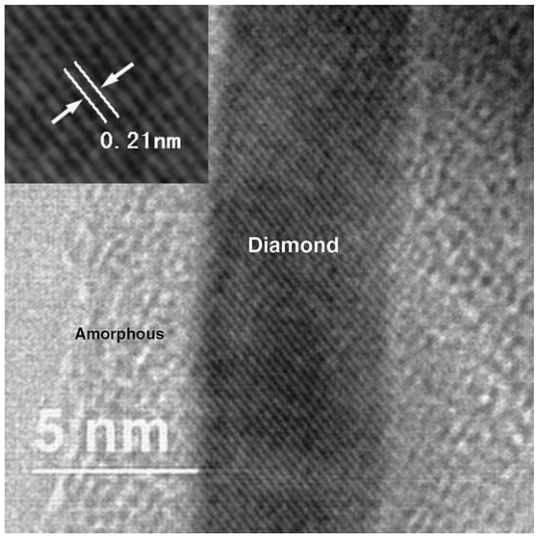

Fig. 3. HRTEM image of the crystalline diamond core and amorphous carbon sheath. The inset shows the (1 1 1) planes with a spacing of 0.21 nm.

Fig. 4 shows the proposed model for the formation of diamond nanoparticles and the growth of diamond nanorods. Diamond nanorods are considered to actually undergo a vapor–solid growth process although there have no additional hydrocarbon gas to be introduced into the reaction

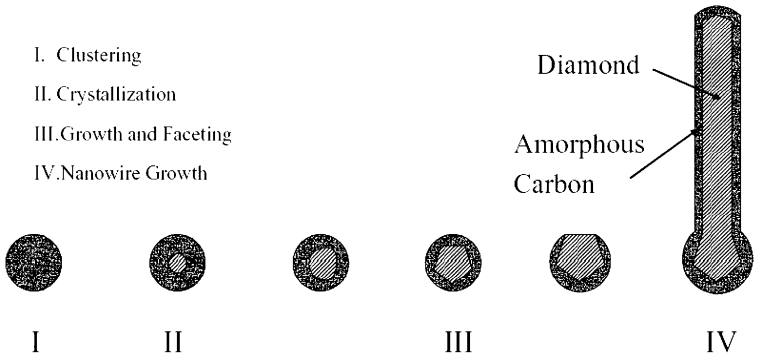

Fig. 4. The proposed model for the formation of nanodiamond and the growth of diamond nanorods under hydrogen plasma irradiation of MWCNTs at high temperature. Amorphous carbon clusters formed in the step I. The crystallization of diamond began in the core of carbon clusters (step II) followed by the diamond growth and faceting stage (step III). After the diamond nanocrystallites were faceted, diamond nanorods began to grow at the nanorod tips (step IV).

chamber. Under hydrogen plasma treatment at high temperature, carbon atoms sputtered from WMCNTs will react with hydrogen to form reactive hydrocarbons in the vicinity of surface of original carbon nanotube framework and deposited again to form sp^3 bonded amorphous carbon clusters. The crystallization subsequently occurred, which is mediated by the insertion of hydrogen atoms into the loosely bound amorphous carbon matrix or strained C–C bonds, as the hydrogen atoms diffuse through the amorphous carbon similar to the crystallization in amorphous silicon [14]. Under continue hydrogen treatment, hydrogen atoms in amorphous carbon clusters could be replaced by carbon atoms at treatment temperature of 1000 K, because the bonding energy of H–C is about half of that of C–C. Then diamond nuclei are formed. The impact of hydrogen on a crystalline structure could be characterized by the displacement threshold energy E_d. In diamond E_d of carbon atoms is about 35 eV, and in graphite the E_d is 10–20 eV depending on structure direction of graphite [9,15]. However, the displacement energy of amorphous carbon atoms is only about 10 eV. The sputtering yield of amorphous carbon atoms is one to two magnitude orders larger than that in diamond. In certain energy region diamond structure can be stabilized. The growth of single crystal diamond nanorods is the result of a balance of collision dynamics and hydrogen bonding-assisted thermally activated processes.

4. Conclusion

We have demonstrated the phase transformations from CNTs to amorphous carbon nanowires and diamond nanorods by employing particle beam irradiation. 20–40% volume expansion (or 10–20% diameter expansion) can be observed during the formation of amorphous carbon nanowires from MWCNTs (nanotubes having 20–40 nm in diameter consist of 20–30 concentric shells of graphite sheets) under particle beams irradiation by an in situ measurement of TEM. Single crystalline diamond nanorods with diameters of 4–8 nm and with lengths up to 200 nm have been successfully synthesized by hydrogen plasma post-treatment of MWCNTs. The diamond nanorods were identified to have a core-sheath structure with inner core being diamond crystal and outer shell being amorphous carbon. Different sputtering yields of carbon atoms in nanocrystal diamond, MWCNTs and amorphous carbon material under hydrogen plasma treatment are responsible for the formation of diamond nanorods.

Acknowledgements

The authors thank Professor S.S. Xie for his guide in the preparation of carbon nanotubes by CVD. This work was financially supported by the Key Project of Knowledge Innovation

Program of Chinese Academy of Sciences (Grant No. KJCX2-SW-N02), National Science Foundation of China (Grant No. 10375085, 10375086), National Basic Research Program of China (Grant No. 2003CB716901) and Shanghai Nanometer Special Foundation (Grant No. 0352nm050).

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