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Synthesis and characterization of diamond nanowires from carbon nanotubes

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Abstract

Chain-like diamond nanowires have been prepared by hydrogen plasma post-treatment of mutiwalled carbon nanotubes. Diamond nano-particles embedded in an amorphous matrix are formed on the original carbon nanotube framework. Ultrahigh equivalent diamond nucleation density above 10^{11} nuclei/cm^2 can be easily obtained. More importantly, many tiny single-crystal diamond nanowires with diameters of 4~8 nm and with lengths up to 200 nm grow from the diamond nano-particles of chain-like diamond nanowires by prolonging the treatment time of hydrogen plasma. The possible mechanism of nucleation and growth of diamond nanowires are discussed.

Keywords: Synthesis; Characterization; Diamond nanowires; Carbon nanotubes

1. Introduction

One-dimensional structures with nanometer diameters, such as nanotubes and nanowires, have attracted extensive interest in recent years because of their unusual quantum properties and potential applications as nanoconnectors and nanoscale devices. Since the discovery of carbon nanotubes in 1991 [1], various one-dimensional materials [2–4] have been fabricated. Although a number of studies have reported on the structures and properties of semiconductor nanowires including carbon [5], the development of diamond nanowires (DNWs) has been slow. The growth of carbon nanowires has been achieved using a number of techniques [6–9]. Aligned diamond nanowhiskers have been successfully formed using air plasma etching of polycrystalline diamond films [10]. Dry etching of the diamond films with molybdenum deposits created well-aligned uniformly dispersed nanowhiskers up to 60 nm in diameter with a density of 50/μm^2 [11]. Diamond nanocylinders with a diameter of ~300 nm have been synthesized on anodic alumina template by microwave plasma-assisted chemical vapor deposition and by nucleating with 50 nm diamond particles at the bottom of membrane holes [12]. More recently, nanorods of single crystalline diamond with a diameter of 50–200 nm were fabricated by a microfabrication method combining a microwave plasma treatment with a reactive ion etching method [13]. Although there have been some theoretical predictions on the crystalline orientations [14], stabilities [15,16] and electronic structures [17] of DNWs, until now there is no report on the synthesis of DNWs with diameters less than 10 nm and with a single crystalline structure. Here we report the preparation of single-crystal and chain-like DNWs by hydrogen plasma post-treatment of mutiwalled carbon nanotubes (MWCNTs).

2. Experimental

The purified MWCNTs were dispersed onto silicon substrates and then were placed into the radio-frequency plasma-enhanced chemical vapor deposition reaction chamber. After the samples were heated to a temperature of about 1000 K, hydrogen was fed into the chamber at a gas flow rate of 50 sccm to maintain the reactant pressure at 150 Pa and plasma with a power density of 0.5 W/cm^2 was initiated simultaneously. After reaction for several to several tens of hours, the specimens were cooled down in vacuum.

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Scanning electron microscope (SEM, LEO-1530VP), high-resolution transmission electron microscope (HRTEM, JEOL JEM-2011 operated at 200 kV) were used to examine the formation of diamond nanocrystallites and nanowires.

3. Results and discussion

Fig. 1a shows the TEM image of the chain-like DNWs (similar to silicon chain-like nanowires [18]) from the carbon nanotube specimens after treatment in hydrogen plasma at temperature of 1000 K for 10 h. Instead of ordered concentric graphite sheets of MWCNTs, many nanoparticles are formed on the original carbon nanotube walls after hydrogen plasma treatment. The nanotube hollow structure is reserved to some extent, indicated by two rows of nanoparticle arrays formed along the carbon nanotube precursor [19]. The inset of Fig. 1a shows the electron diffraction pattern that corresponds to the diamond spacings. The microstructure of chain-like DNWs was further confirmed by HRTEM observation. Fig. 1b gives a lattice image of a chain-like nanowire, in which the core-shell structure is clearly visible. The spacing between the parallel fringes of the crystalline core was measured to be about 0.21 nm, which is equal to the spacing of (111) planes of crystalline diamond. If the chain-like nanowires form a closely aligned network on a substrate, we can simply estimate that a nucleation density above 10^{11} nuclei/cm^2 is achievable. To the best of our knowledge, current nucleation density achieved is about 10^{10} nuclei/cm^2 [20], which is one order of magnitude lower than our current nucleation density.

Fig. 2 shows the SEM image of the hydrogen plasma treatment of MWCNTs at a temperature of 1000 K for different treatment times. At the initial stage (Fig. 2a) of hydrogen plasma treatment, many spherical clusters are formed on the surface of original carbon nanotube framework. With the treatment time prolonged, the number and the diameters of the clusters increase. When the treatment time approaches 10 h, the chain-like DNWs (Fig. 2b) can be obtained. More interestingly, numerous wirelike structures (Fig. 2c) with a uniform diameter attached the side of the treated CNTs can be observed when the treatment time is up to 20 h. The diameters of these nanowires are in the range of 10–15 nm, and their lengths are up to 200 nm. Energy dispersive X-ray spectra (EDX) demonstrate the presence of carbon alone without the contamination of metal catalysts introduced in the process of carbon nanotube preparation, which indicates that the catalyst particles were effectively removed from the CNTs after ultrasonic purification. Fig. 3a is the TEM image of the single-crystal DNWs. The high density nanowires on the original carbon nanotube framework can be clearly seen. The high-magnification TEM image (Fig. 3b) shows that the nanowires form a core-sheath structure. The inner diamond nanowire core with a diameter of 4–8 nm and the outer amorphous carbon sheath with a thickness of 2–4 nm are separated by an atomically sharp

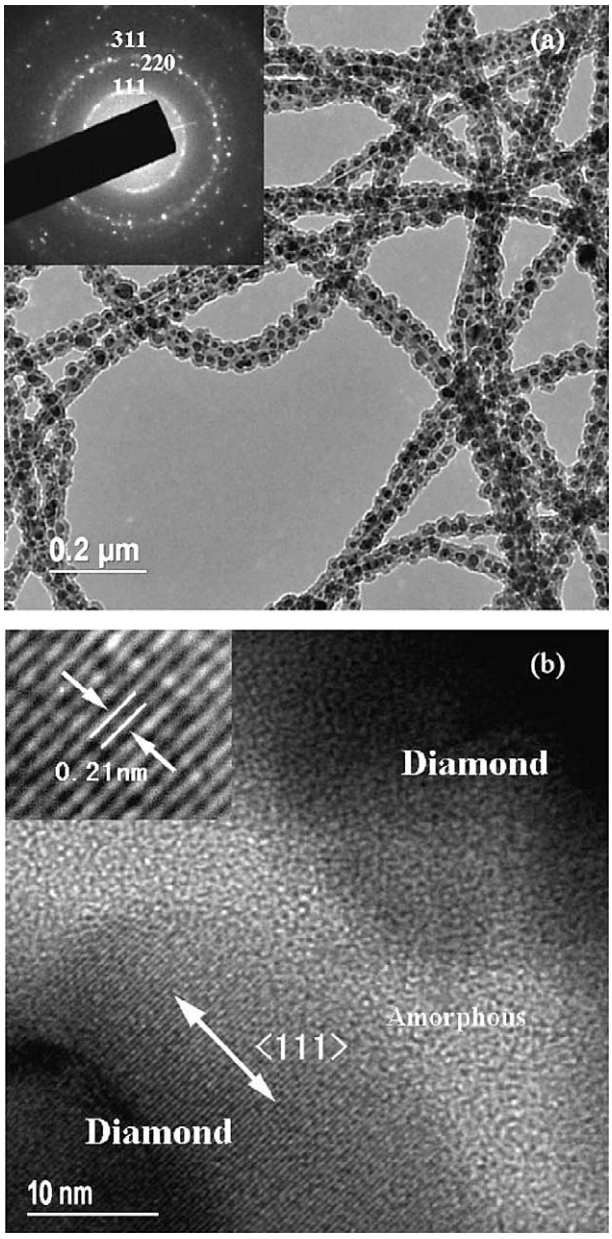

Fig. 1. (a) Low magnification TEM image of chain-like DNWs from the MWCNTs after hydrogen plasma treatment at temperature of 1000 K for 10 h. The ring pattern in the inset from electron diffraction confirmed the diamond structure of nanocrystallines. (b) HRTEM image shows the diamond (111) lattice planes with a d-spacing of 0.21 nm. The inset is the simulated image of the nanocrystals after image filter processing by Fourier transform.

interface, which is similar to silicon nanowires wrapped in an amorphous silicon oxide sheath [21]. The spacing between the parallel fringes of the crystalline core was measured to be about 0.21 nm, which is equal to the lattice spacing of (111) planes of crystalline diamond.

Considering the nucleation of nanodiamond and the growth of DNWs under hydrogen plasma irradiation of MWCNTs at high temperatures, we investigated the initial stage (Fig. 2a) of hydrogen plasma treatment. It is shown that amorphous carbon clusters with nearly spherical shape

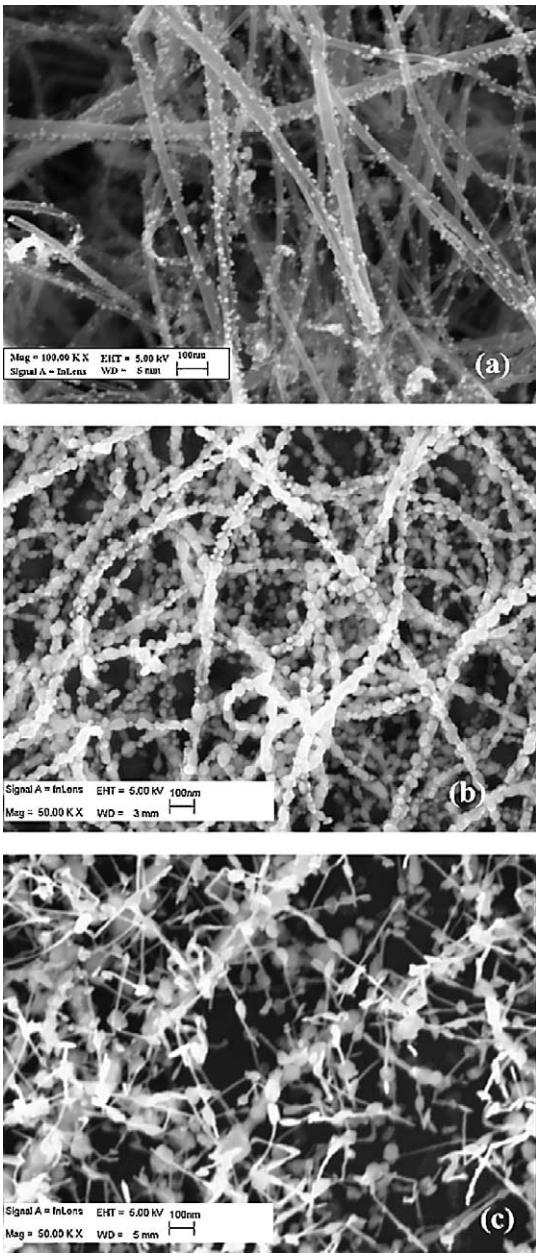

Fig. 2. SEM image of hydrogen plasma treatment of MWCNTs at temperature of 1000 K for 4 h (a), 10 h (b) to form chain-like DNWs and 20 h (c) to form single-crystal DNWs.

were formed at this stage. The area density of these clusters is much lower than that in samples with prolonged treatment. The defects on CNT walls are expected to be the origin of these clusters. With the increase in treatment time, diamond crystallites can be seen by TEM and the density of carbon clusters increases rapidly. Based on these observations, we propose a four-step process for the nucleation of nanodiamond and the growth of single-crystal DNWs under hydrogen plasma treatment of MWCNTs—clustering, crystallization, growth and faceting, and nanowires growth, which is similar to that proposed by J. Singh for the diamond nucleation, crystallization and growth from amorphous carbon precursor [22].

Under hydrogen plasma treatment at high temperature, carbon atoms sputtered out or etched by hydrogen plasma from WMCNTs will be reacted with hydrogen to form reactive hydrocarbons in the vicinity of the surface of the original carbon nanotube framework and deposited again to form 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

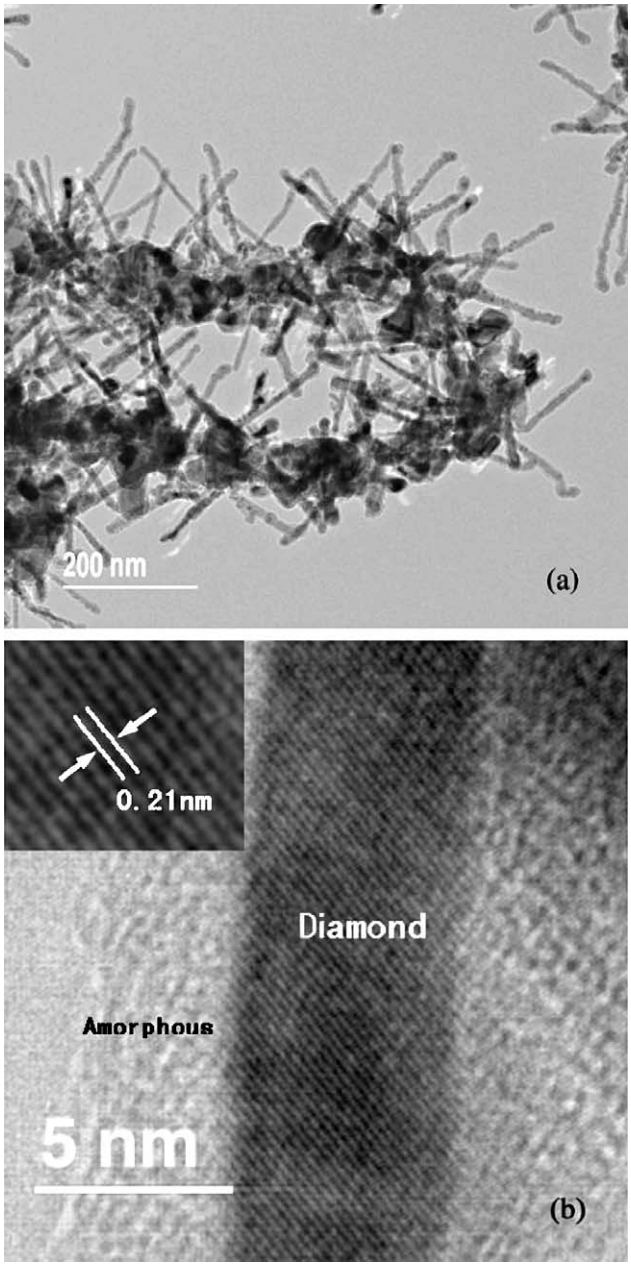

Fig. 3. (a) TEM image of the single-crystal DNWs from the MWCNTs after treatment in hydrogen plasma at temperature of 1000 K for 20 h. (b) High-resolution TEM image shows the structure of single-crystal DNWs with crystalline core and amorphous carbon sheath. The inset is the simulated image of the nanocrystals after image filter processing by Fourier transform.

in amorphous silicon [23]. The hydrogen termination plays an important role in the diamond crystallization and growth [20]. Once the diamond nucleus is present in a sp^3 bonded environment, the growth and faceting of diamond may take place through thermally activated processes. (If stopping the hydrogen plasma treatment in this stage, we will only obtain the chain-like DNWs that diamond nanocrystalline particles embedded in a wire-like amorphous network.) Single-crystal DNWs began to grow after diamond nanocrystallites were faceted. The carbon nanotubes and nanowires growth from spherical carbon nano-particles without any metal catalyst were reported by S. Botti et al. [6]. Their results showed that, instead of a metal catalyst, the amorphous largely hydrogenated carbon nano-particles were the special and effective catalysts for nanotubes and nanowires growth. This implies that it is possible to form a sp^2 hybridized stable structure from a highly hydrogenated amorphous carbon nanoparticle. The transformation of nanodiamond to carbon onions [24,25] or bucky-diamonds [26] by high temperature annealing was observed both experimentally and theoretically. These results indicate the existence of a competition between transformation from graphite structure to diamond and its reverse in our case. The nanodiamond particles formed by the hydrogen plasma treatment could be responsible for the formation of single-crystal DNWs, while the amorphous carbon matrix which sheathes the nanodiamond particles would favor the formation of a layer of a stable graphite sp^2 structure in one dimensional growth. However, the competition between the formation of sp^2 structure and diamond nucleation under hydrogen plasma irradiation forms and stabilizes the precipitation-induced outer amorphous carbon sheath ultimately to prevent further lateral growth of diamond. At the same time, the size effect at the tip of nanorod makes the tip more reactive and enhances the atomic absorption, diffusion, deposition and reconstruction [27], thus favoring the growth of DNWs along one dimension and in a favorable crystalline orientation.

4. Conclusion

Chain-like DNWs with ultrahigh equivalent diamond nucleation density ($>10^{11}/cm^2$) and single-crystal DNWs with diameters of 4~8 nm and with lengths up to 200 nm have been successfully synthesized by hydrogen plasma post-treatment of mutiwalled carbon nanotubes. The diamond nanowires were identified to have a core-sheath structure with the inner core being diamond crystal and outer shell being amorphous carbon. The amorphous carbon layers which sheathe both diamond nanoparticles and nanowires are important for one dimensional growth of diamond nanowires by preventing the lateral growth of diamond and providing the carbon source for diamond nanowire growth at the nanowire tips.

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