Synthesis and Characterization of RF - Magnetron Sputtered Carbon Nanostructures

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We present a new method for graphitic nanostructure growth using thermal annealing of a precursor carbon thin film deposited by RF-magnetron sputtering. The morphology and microstructure of the as-deposited and post-annealed films were investigated by high resolution transmission electron microscopy. It was found that the precursors transform to locally well-graphitised polyhedral nanoparticles, including some carbon nanotubes.

1. Introduction

Carbon nanostructures are an intriguing field for fundamental and practical research due to their low dimensionality and their interesting chemical, mechanical and electrical properties [1], which generate many potential applications. Methods which have been used to synthesize carbon nanotubes and related structures are arc discharge [2], laser ablation [3], ion beam radiation [4] and chemical vapour deposition [5], etc. However, there are only few reports of their synthesis using sputtering [6,7]. This has the advantage of growing an excellent film uniformity over a large area and is a widely used technique in industry.

2. Experimental Procedure

The carbon nanostructures were synthesized using a two-step method, involving RF-magnetron sputtering of carbon onto heated substrates, followed by thermal annealing at an elevated temperature. The molybdenum substrates were heated at a range of temperature from 130 ^{o}C (ambient temperature heating from magnetron) to 450 ^{o}C for 3 h. The target was high-purity (99.99%) graphite with a 76.20 mm diameter. The base pressure of the vacuum chamber was about 1.33 x 10^{-3} Pa (10^{-5} torr). Argon was introduced into the chamber to create plasma by applying an RF-power of 200 W at a relatively low pressure of 4 Pa. A clamping ring was used to hold the substrate firmly onto the heater block to ensure good thermal contact between the heater block and the substrate. In order to activate nanostructure growth, the as-deposited films were then annealed in situ at 850 ^{o}C for 2 h under argon pressures of 101 kPa. The morphology and microstructure of the as-deposited and post-annealed films were investigated by high resolution transmission electron microscopy (HRTEM, JEOL JEM 2011), combined with energy dispersive x-ray spectroscopy (EDXS). TEM samples were prepared by scraping specks off the deposited film and placing them onto a holey carbon film supported by a copper mesh.

3. Results and Discussion

Figure 1 shows typical HRTEM images taken from an as-deposited carbon thin film sample when the substrate temperature is 130 ^{o}C. At low magnification, layered columnar structures are generally observed (Fig. 1a). At high magnification, regions of a disordered, porous and turbostratic graphitic structure [8] are observed (Fig. 1b). This implies that the precursor structures can be formed at a relatively low substrate temperature. The HRTEM micrograph shown in Fig. 2 reveals that the precursor structures transformed to various

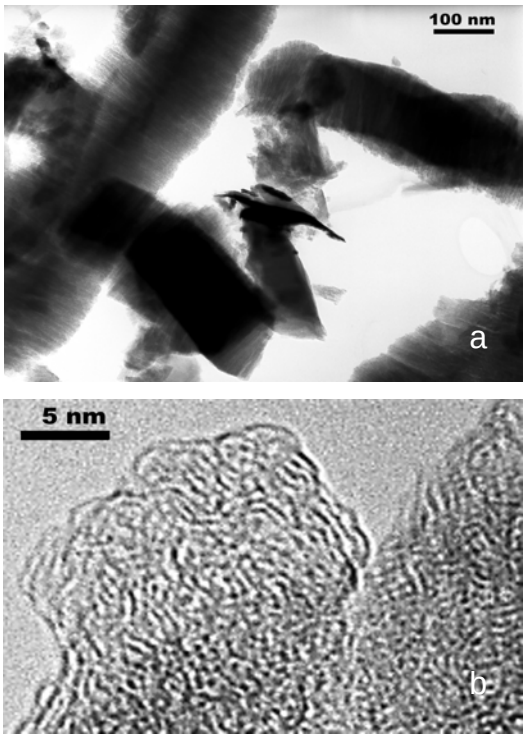

Fig. 1 TEM images of precursor thin film as-deposited at 130 ^{o}C for 2h. (a) Layered columnar structures at low magnification, (b) Porous and turbostratic graphitic structures at high magnification.

locally well-graphitised polyhedral nanoparticles, including multi-walled nanotubes (MWNTs), nanoboxes and fullerenes [8]. Regions of untransformed nanoporous particles are also visible.

It is worth pointing out the presence of particles fully encapsulated by graphene sheets, as shown in Fig. 3. Figs. 3(a) and (b) show the EDX spectrum obtained using a nano-beam (15 nm in diameter) focused on an encapsulated particle (white dot **a** in TEM image) and on a graphitic particle (white dot **b** in TEM image), respectively. EDXS from a number of such encapsulates indicates that they were mainly iron with minor nickel and chromium contents. The graphitic particle had an average carbon content up to approximately 98.00 at%, as determined by EDXS. Experiments without a clamping ring have confirmed that the iron particles come from the clamping ring (stainless steel). Previous studies have emphasised the positive catalytic role on nanotube formation [9]. However, in our case the same nanostructured morphology without the presence of iron was observed.

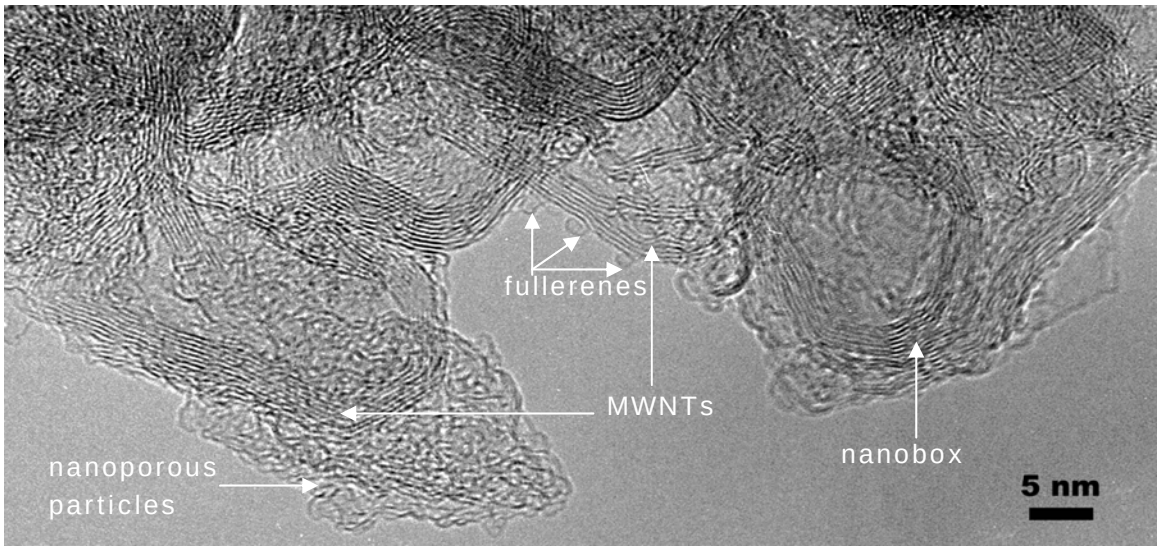

Fig.2 TEM image of various well-graphitised polyhedral nanoparticles found in a graphite sample after sputtering at 130 ^{o}C for 3h and annealing at 850 ^{o}C for 2h.

The above-mentioned variety of nanostructures suggests that multiple mechanisms of formation exist in our two-step method. It is well accepted that metal catalysts are essential for single-wall nanotube formation, but are not necessary for the MWNT formation [10]. MWNTs can be formed in a fullerene-type nucleation [11]. It was reported that MWNTs which contained fullerene molecules with a nanoporous structure were produced by heating carbon soot materials using the arc-discharge process [12]. The structure of our as-deposited graphite is very similar to the soot materials. Therefore, we speculate that the formation of

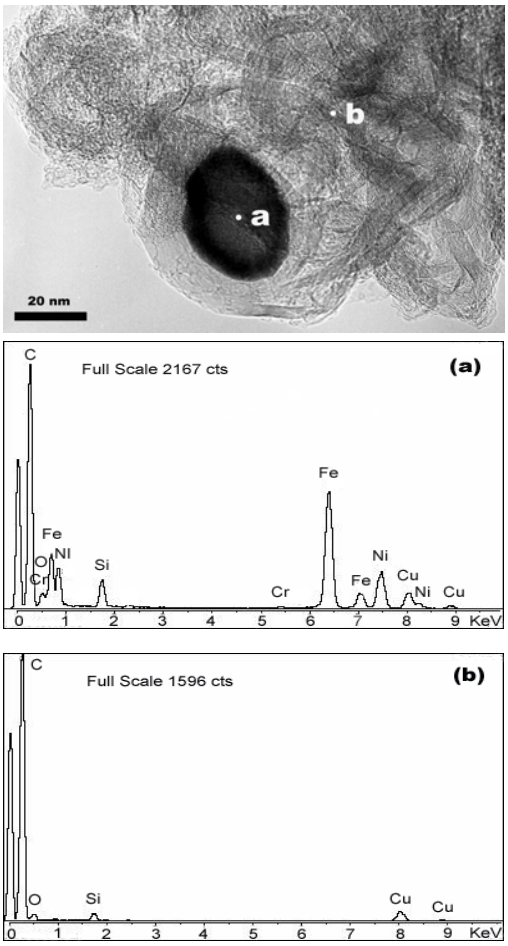

Fig. 3 TEM image showing a contaminant particle encapsulated by graphite layers. (a) EDX spectrum for the contaminant particle (white dot **a** in TEM image), (b) EDX spectrum for the graphitic particle (white dot **b** in TEM image).

MWNTs in Fig. 2 is determined by the initial nanoporous carbon structure and little influenced by the metal contaminants.

At this stage it is difficult to determine the growth mechanisms. However, it is likely that due to the relatively low annealing temperature, which is much lower than the sublimation point of any type of carbon, the dominant atomic transport is surface diffusion [13].

Further work at higher annealing temperature and longer duration is underway to improve the abundance and aspect ratio of the nanotubes.

4. Conclusions

Locally well-graphitised polyhedral nanoparticles, including multi-walled nanotubes, nanoboxes and fullerenes, were produced by magnetron sputtering deposition at ambient temperature and subsequent thermal annealing up to 850 ^{o}C. This study suggests a straightforward and cost-effective method to grow high-purity and high-quality carbon nanostructures.

Acknowledgments

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