Aerosynthesis: Growth of Vertically-aligned Carbon Nanofibres with Air DC Plasma

Regular Paper

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Abstract Vertically-aligned carbon nanofibres (VACNFs) have been synthesized in a mixture of acetone and air using catalytic DC plasma-enhanced chemical vapour deposition. Typically, ammonia or hydrogen is used as an etchant gas in the mixture to remove carbon that otherwise passivates the catalyst surface and impedes growth. Our demonstration of the use of air as the etchant gas opens up the possibility that ion etching could be sufficient to maintain the catalytic activity state during synthesis. It also demonstrates a path toward growing VACNFs in the open atmosphere.

Keywords Carbon Nanofibres, Plasma Processing, Scalable Manufacturing

1. Introduction

Plasma-aided nanofabrication is one of the most actively studied approaches for the synthesis of nanostructured materials [1]. Plasmas are commonly used to control the synthesis of vertically-aligned carbon nanofibres (VACNFs). VACNFs are cylinders composed of graphitic carbon with typical lengths > 1 μm and diameters of several nm and are usually grown perpendicularly (vertically) to the substrate [2]. VACNFs are grown on a variety of conductive substrates in a DC plasma-enhanced chemical vapour deposition (PECVD) process. One such substrate is Si coated with metal (e.g., Ni, Fe, Co) catalyst particles, which serve to remove carbon from a carbonaceous source gas and precipitate it beneath the catalyst in the form of a VACNF. Plasma is used to guide the direction of nanofibre growth [3, 4].

VACNFs have been demonstrated as functional nanoscale elements in a variety of devices prototypes, including electron field emission sources [5], scanning probe tips [6], electrochemical probes [7], neuronal interfaces [8] and gene delivery arrays [9, 10]. Some of these applications require precise placement and the controlled growth of individual nanostructures, including their location, exact position, length, diameter and number of nanofibres at

each site. Many applications, however, would benefit simply from the high surface area of nanofibre coatings. Such examples include battery materials [11], photo-electrochemical cells [12], superhydrophobic coatings [13, 14] and cellular scaffolds [15]. For such applications, synthesis in an ambient atmosphere would be highly desirable for scaling up manufacturing. Thus, we have investigated VACNF synthesis in a mixture of air and acetone.

Most of the results on the synthesis of VACNFs that have been reported to date have been obtained using NH_3 as the 'etchant' gas with C_2H_2 as a carbon source gas, though in a few studies H_2 was used as an 'etchant' gas [16], [17]. For both NH_3 and H_2, atomic hydrogen is generated and is known to serve as an etchant by removing excess carbon from the surface of a catalyst nanoparticle. Excess carbon would otherwise hinder access of C_2H_2 to the nanoparticle surface, thus preventing VACNF growth. Indeed, many studies have shown that copious amounts of atomic hydrogen are present when using plasma to synthesize carbon nanofibres or nanotubes in the presence of NH_3 or H_2 [18-20]. Furthermore, the interplay between the plasma current and the C_2H_2 to NH_3 ratio has proven that carbon removal is caused by reactive ion etching (RIE). RIE consists of both anisotropic ion sputtering of carbon and isotropic carbon removal via the formation of volatile species by reacting monatomic hydrogen.[21, 22] At present, it is largely believed that monatomic hydrogen and other such reactive species serve the crucial role in maintaining accessibility to the catalyst nanoparticle surface and preventing the build-up of a passivating film. Because air contains significantly less hydrogen than previously-used etchants, we had not anticipated that VACNFs could be grown in an acetone/air mixture. For instance, synthesis in a C_2H_2/N_2 mixture produced no nanofibres due to the lack of hydrogen in N_2 [23].

Here, we report the use of a gaseous acetone/air mixture to synthesize VACNFs by PECVD. Moreover, our structural and compositional analyses show that the aerosynthesized (synthesized using air) nanofibres on silicon, incidentally, do not contain silicon nitride, unlike nanofibres grown using C_2H_2/NH_3 mixtures; rather, they contain a silicon oxide compound. Furthermore, high-resolution transmission electron microscopy revealed a stacked-cone structure of the carbon core of the nanofibres.

2. Materials & Methods

The substrate for these experiments was n-type Si, 100 mm in diameter. An array of Ni circles, called "dots", each 2 μm in diameter and 50 nm thick, was defined using photolithography and physical vapour deposition.

The entire array consisted of four different sections, each having different spacing (5, 10, 25 and 50 μm, respectively) between the Ni dots. This Si wafer was cleaved into square silicon chips, each 1 cm by 1 cm. After the Si chips were loaded onto a hot plate, its the temperature was brought to 700 °C under vacuum at a residual pressure of 0.1 Torr in about 15 minutes. During this heating procedure, the Ni film was transformed into a collection of nanoparticles (resulting in tens of nanoparticles per dot), in a process known as 'dewetting'.

Acetone was loaded into a cylindrical vessel with an inner diameter of 38 mm. Limited by this surface area available for evaporation, we empirically determined that a maximum possible flow rate of 28 sccm acetone could be maintained at room temperature. Air was introduced through a tube opened directly to the laboratory, with no additional filtering.

After the substrate reached 700 °C, air flow was initiated to bring the internal pressure to 4 Torr. Acetone was then introduced into the chamber and voltage was simultaneously applied between the substrate (cathode) and the showerhead (anode). The plasma was maintained in a constant current mode.

Growth was sustained for a period of 30 minutes after starting the acetone flow. At the end of the 30 minutes, the plasma current, hot plate, and air and acetone flows were turned off. The chamber was evacuated for the duration of cool-down, which lasted approximately 15 minutes. The chamber was then vented and opened, and the substrate with VACNFs was removed for analysis.

After each synthesis, the substrate was analysed using a scanning electron microscope (Zeiss Merlin). Further analysis was conducted using a Bruker QUANTAX energy dispersive X-ray spectroscopy (EDS) system. Transmission electron microscopy (TEM) images were acquired with a JEOL 2010F field emission transmission electron microscope.

3. Results & Discussion

Figure 1a shows VACNFs synthesized under flows of 24 sccm of acetone and of 115 sccm of air and a 0.2 A plasma current. The most remarkable observation is that VACNFs have been produced (observed in the middle part of the image). Analysis of the material surrounding the VACNFs by EDS-mapping further shows why the growth of the VACNFs is surprising. This material contains substantial amounts of carbon (Figure 1c), some oxygen (Figure 1e), and even less nitrogen (Figure 1b). No conclusions could be made regarding Si (Figure 1d), except that there is less Si than in the underlying Si substrate.
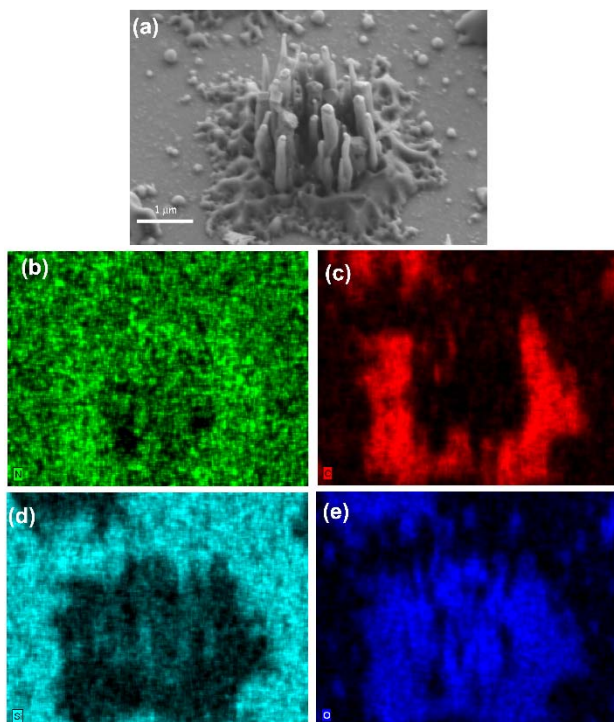
Figure 1. (a) Scanning electron micrograph of VACNFs. The image was acquired at 30° tilt angle, at which the nanofibres appear half as tall as their actual height. The nanofibres are surrounded by materials deposited non-catalytically. Energy dispersive X-ray spectroscopy maps of VACNFs in (a) for (b) N, (c) C, (d) Si and (e) O.

We would generally expect non-catalytic deposition of carbon film due to the decreased amount of hydrogen, which is necessary for carbon removal.

Without spectroscopic measurements of the plasma, we cannot determine the actual amounts of available atomic hydrogen (or other reactive species) in the plasma. Here, we present simple estimates of the ratio of hydrogen to carbon based on the stoichiometric relationships in the acetone/air and C_2H_2/NH_3 systems. In acetone, C_3H_6O, the H:C ratio is 2:1, and the contribution of air is negligible [16]. In 'conventional' synthesis of VACNFs, C_2H_2 and NH_3 are mixed in a 1:2 ratio (45 sccm/90 sccm), giving roughly a 4:1 H:C ratio.

Figure 2 shows VACNFs grown at 25 sccm/115 sccm of acetone/air ratio and at a plasma current of 0.4 A, which are roughly three times longer than the VACNFs in Figure 1a (6 μm vs. 2 μm tall). Thus, the non-catalytically deposited carbon film which appears as a residue in Figure 1a could have been expected to expand. This difference is likely due to the increase of the plasma current (from 0.2 A for Figure 1a to 0.4 A for Figure 2), thus effectively increasing the ion bombardment component of reactive-ion etching. The surface around the nanofibres in Figure 2 appears completely clean, without a non-catalytically deposited carbon film, which

is further confirmed by EDS mapping. There is virtually no carbon outside of the nanofibre-covered regions on the substrate (Figure 3a). There is slightly elevated contrast between the substrate and the nanofibre region in Figure 3b, suggesting the presence of some nitrogen in the coatings on the nanofibres. Figure 3c indicates that the nanofibre regions are enriched in oxygen. Figure 3d shows that there is some silicon on the nanofibres, which is most apparent in the slightly lighter regions near the base of the fibres.
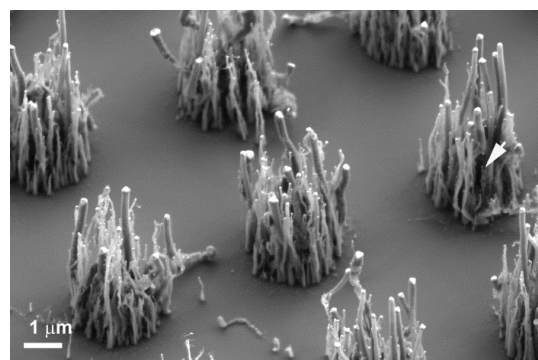

Figure 2. Scanning electron micrograph of VACNFs. The image was taken at a 30° tilt angle, at which the nanofibres appear half as tall as their actual height. The arrow points to where the EDX spectrum of Figure 4 was acquired.

The EDS spectrum presented in Figure 4 was acquired at a point near the mid-height on a nanofibre. The carbon peak is attributed mostly to the carbon nanofibre core. Ni is from the catalyst nanoparticles; Ni is present not only on top of the nanofibres but is also typically found sporadically internally along their length [24]. The Si peak is attributed mostly to the substrate, but a conclusive determination could only be made with the nanofibres removed. All these observations are somewhat common for C_2H_2/NH_3-grown VACNFs. It was surprising, however, that the nitrogen peak was relatively insignificant and that instead there is a prominent oxygen peak. In our prior experience with C_2H_2/NH_3 grown VACNF, we have observed that silicon nitride has formed under similar conditions [25]. Thus, we suspect that triple-bonded N_2 in the air is not conducive to the formation of silicon nitride. The large oxygen peak could only come from surface oxide, and suggests SiO_2.

Figure 5 provides further insight into the EDS mapping results. TEM images distinctly show the graphitic core of carbon nanofibres, appearing similar to that of nanofibres grown with C_2H_2/NH_3, which is coated with a thin film. Figure 5a shows that thickness of this thin film coating is non-uniform along the length. Figure 5b shows distinct contrast between the graphitic core and this outer coating, which is ~10-20 nm thick.

Further insight into the coating chemistry was obtained by subjecting the nanofibres to 3 minutes of concentrated

HF etch. This procedure has been used to remove SiO₂ from nanofibre surfaces [26]. Figure 6 shows the resultant nanofibre surface after such treatment. While the graphitic carbon core is largely preserved, the distinct surface coating is no longer observed, which further supports assignment of the coating as SiO_2.
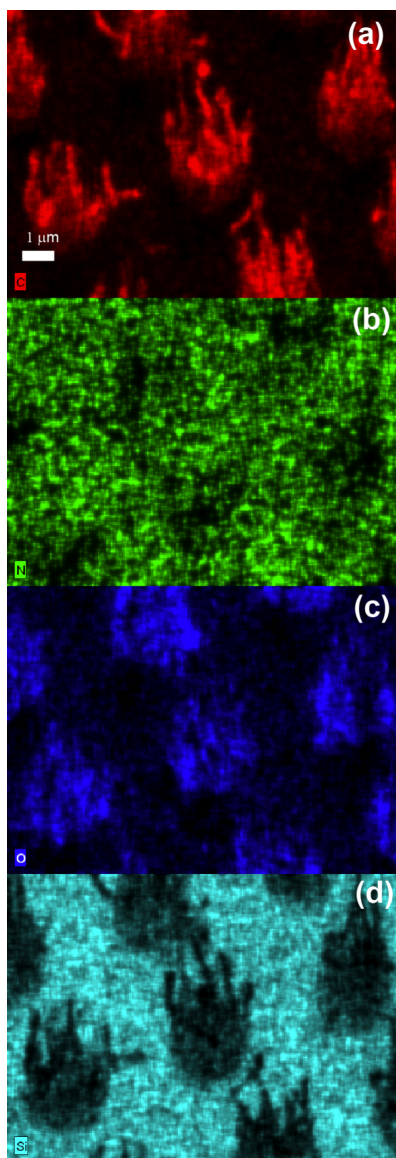

Figure 3. Energy dispersive X-ray spectroscopy maps of VACNFs in Figure 2 for (a) C, (b) N, (c) O and (d) Si.

Subsequent EDS analysis was conducted with VACNFs removed from the substrate and placed onto TEM copper grids (with carbon film). The observed composition was as follows (in atomic percent): 88.82 at C.%, 10.61 at.% O, 0.53 at.% Ni, 0.04 at.% F, and < 0.01 at.% Si. Disappearance of the Si peak confirms removal of Si. If Si is unoxidized, then HF treatment would not normally remove it. Surprisingly, however, the oxygen peak remained fairly strong. This suggests that the carbon core of the nanofibre was oxidized in the process of VACNF synthesis or subsequent treatment.
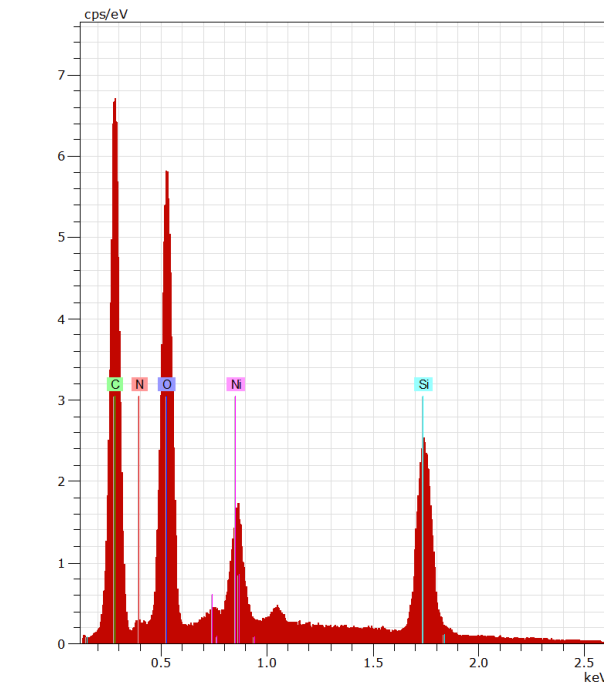

Figure 4. Energy dispersive X-ray spectrum taken at mid-height of the nanofibres in Figure 2.

The surface of the underlying carbon core appears to be rough, for reasons which are unknown and yet to be understood.
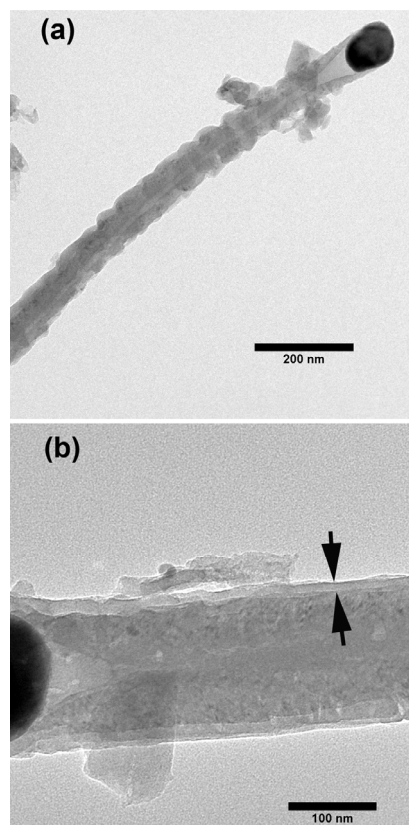

Figure 5. TEM images of VACNFs after growth. The nanofibre in (a) exhibits an undulated outer coating. The two black arrows indicate the outer nanofibre coating in (b).
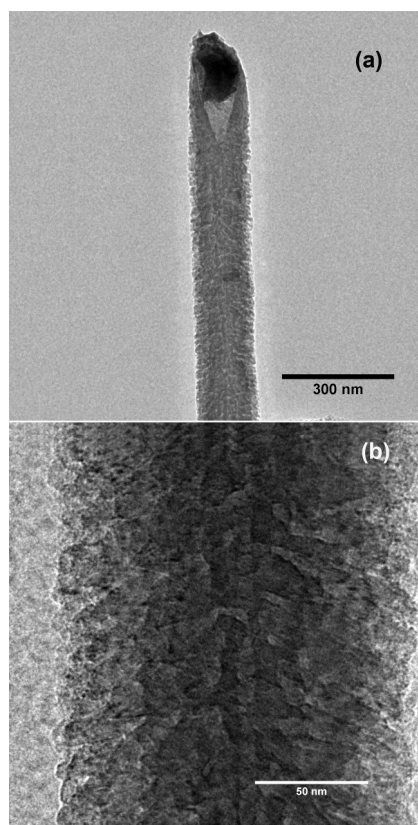
Figure 6. TEM images at different magnifications of a VACNF synthesized in an air/acetone gas mixture and emancipated from the outer shell with hydrofluoric acid.

It has been speculated in the past that plasma synthesis yields carbon nanofibres – bamboo- or stacked cone-type structures instead of the concentric pattern of true carbon nanotubes – because of the presence of copious amounts of atomic hydrogen. The idea behind this hypothesis is that atomic hydrogen terminates graphene layers at the catalyst nanoparticle, thus effectively preventing nanotube formation. Atomic hydrogen is likely diminished in the acetone/air mixture, as compared with the conventional C_2H_2/NH_3 synthesis, and may thus result in less termination in this new growth mixture. To verify this hypothesis, we investigated the internal graphitic structure of the nanofibre cores. The TEM image in Figure 7 shows the sidewall of a nanofibre after the HF treatment to remove the outer coating. The graphene edges are clearly visible and the cone angle of a stacked-cone nanofibre is about 20°. Therefore, acetone is a sufficient source of atomic hydrogen to prevent carbon nanotube-formation. Alternatively, there could be another explanation, if the hypothesis of hydrogen-controlled nanofibre growth in plasma is not valid. While verifying this hypothesis is beyond the scope of this study, the possibility of using an essentially hydrogen-free 'etchant' gas opens up the possibility of plasma synthesis in a much more hydrogen-deficient environment – close to thermal CVD environments – in which nanotubes are typically grown.
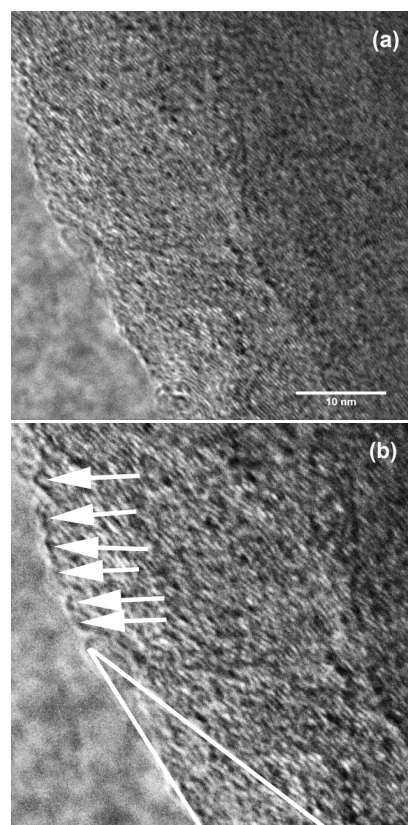

Figure 7. (a) High-resolution TEM image of the sidewall of a VACNF after HF treatment; (b) a magnified view of the top left portion of (a). The arrows indicate the edges of the graphene layers. The angle between the sidewall and the graphene cones is indicated by two intersecting lines.

4. Conclusions

After over a decade of experience in growing VACNFs using an C_2H_2/NH_3 mixture, switching to acetone/air instead of C_2H_2/NH_3 would resolve many of the problems that we experienced in the integration of vertically-aligned nanofibres into various devices [27].

The central finding of these experiments is proof of the feasibility of growing VACNFs in air plasma. This result is quite surprising and has great significance for the field of carbon nanofibre synthesis. It is surprising in several ways. Air is 20% oxygen, and intuition suggests that carbon should be consumed in reactions with oxygen rather than in forming carbon nanostructures. Air is also an insignificant source of hydrogen. In non-catalytic solid carbon synthesis (diamond), hydrogen is used to balance feeding the catalyst particles with carbon, and it prevents carbon from piling up on the catalyst surface and impeding nanofibre growth. Apparently, no hydrogen is necessary, except perhaps that which is supplied in the carbonaceous source gas.

We suspect that in DC plasma, ion bombardment can also cause etching without requiring atomic hydrogen,

however this hypothesis requires further study. N_2 can suffice in the role of such an ion cleaner. Finally, this result is significant because it shows that it may be possible to grow carbon nanofibres in the open air. Future work is needed to demonstrate the process in atmospheric pressure plasma. If this is achieved, then nanofibre coatings could be realized in open air, allowing for massive scale-up in the production process.

5. Acknowledgments

6. References

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