The Effects of Surface Treatments on the Growth of CNTs on 3-Dimensional Carbon Foam Structures.

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ABSTRACT

Carbon nanotubes (CNTs) have been the focus of significant research since Iijma's 1991 *Nature* article. CNTs have primarily been grown on flat substrates for a range of potential applications due to their superior mechanical, electrical and thermal properties. However, limited research has been accomplished on open cell foam structures. Initial attempts to grow CNTs onto as-received foam samples resulted in low CNTs growth. This then prompted surface treatment research to enhance CNTs growth onto the foam surface. For this study, the surface modification methods of interest included: nitric acid treatment, oxidation, coating with hexamethyldisilazane (HMDS), and atomic layer deposition (ALD) of oxides.

Dense, aligned CNTs were grown on all surfaces of 3-dimensional open cell reticulated carbon foam. The best results were achieved when a thin layer of Al_2O_3 was deposited on the foam via ALD prior to CNT growth. The foam samples were 1cm x 1 cm x 0.5cm, with CNTs found throughout the volume of the sample and not just the outer layers of the foam. Highly aligned CNTs were realized using floating catalyst chemical vapor deposition (FCT-CVD) with xylene and ferrocene as the carbon and catalyst sources, respectively.

Growing CNTs on a 3-dimensional foam structure will dramatically increase the surface area available for heat dissipation, thus enhancing the thermal properties of the foam, as suggested by initial thermal testing. Preliminary results include scanning electron microscope images and thermal conductivity results.

Keywords: surface treatments, atomic layer deposition, carbon nanotubes growth, thermal testing.

1 INTRODUCTION

Carbon nanotubes (CNTs) are known to have superior thermal, mechanical and electrical properties[1]. Due to these properties as well as a high aspect ratio, CNTs are thought to be ideal for use as a heat sink material in high power electronic packages. In this study, 3-dimensional carbon foam was chosen to grow CNTs on because it has a far greater surface area than a flat surface substrate. Growing CNTs onto carbon foam surfaces increases the available surface areas by orders of magnitude without adding noticeable amount of weight to the system. According to Zhang et al., at elevated temperatures carbon surfaces can become reactive to the metal catalysis needed for CNT growth and thus hinder the process. This reactive surface property of the carbon foam is one of the challenges to overcome in order to grow CNTs onto the surface of carbon foam[2]. It is therefore necessary to study different surface treatments and determine which result in enhanced CNT growth. Since the foam is a complex geometry with multiple depths and layers, the types of treatments being performed will need to deliver uniform surface treatments throughout the depth of the foam. It would be ideal to grow CNTs directly onto the carbon foam surface without any additional layers because each added layer would reduce the overall thermal conductivity of the composite. Thus, surface treatments such as nitric acid and oxygenation were first used to modify the surface morphology of the carbon foam. Both treatment types add functional layers to the carbon foam. It has been reported by literature that CNTs grow well on oxide supported substrates such as alumina and silica[3]. Thus, Hexamethyldisilazane (HMDS) and atomic layer deposition (ALD) alumina were also used to modify the surface of the carbon foam.

2 EXPERIAMENTAL METHODS

2.1 General growth

Fourty-five pore per inch (PPI) reticulated vitreous carbon foam was purchased from Ultramet, Inc. The foam was then cut down to the experimental size of 10 mm x 10 mm x 5mm for growth analysis and 10 mm x 10 mm x 3 mm for thermal testing analysis. CNTs were grown using the floating catalyst thermal chemical vapor deposition (FCT-CVD) method. The

FCT-CVD system is equipped with both pure hydrogen and argon gas sources. During growth, the hydrogen to argon flow ratio was set to 1:2 standard cubic centimeters per second (sccm). Ferrocene was dissolved into xylene solvent in a 0.008M ratio. The xylene/ferrocene liquid mixture serves as carbon feed stock as well as an iron catalytic particle source carrier. During growth, xylene/ferrocene was introduced at a flow rate of 3 ml/hr via a digital syringe pump. The CNT growth time was set for 20 minutes at 750 °C.

The initial growth on as-received carbon foam yields a low CNT growth on the surface. To solve this challenge, we attempted to modify the surface of the carbon foam to see if there is an improvement in terms of density of CNTs growth. Types of surface modification include nitric acid, HMDS, thermal oxidation, and ALD of alumina. Details of surface treatments are in the following sections.

2.2 As received Carbon Foam

After cutting and cleaning, the as-received carbon foam was first put through the CNT growth parameter, described earlier. The growth results are used as a baseline to be compared with other growths.

2.3 Nitric Acid Treatment:

The nitric acid treatment method provided by Yuzun Fan, et al. [4] is said to provide better surface adhesion for carbon surfaces. The clean carbon foam samples was first soaked in acetone for 2 hours and rinsed with DI water. Following this step, the samples were dried at 120 °C for 4 hours before being soaked for either 4 hours or 8 hours in 70% nitric acid solution. The resulting foam was then placed into the FCT-CVD for CTNs growth.

2.4 HMDS Treatment

It has been reported that CNTs grows well on silica surfaces[5]. MP-P20, a commercially available product containing HMDS, is commonly used in semiconductor processing to coat the surface of a substrate with a layer of organic silica. This process is usually done using a spin coater. For this study, the foam was simply dropped into a beaker of MP-P20 solution and allowed to soak for 30 seconds. The foam was then removed from solution and baked on a hot plate to cure the silica layer. The sample was left on the plate for 5 minutes at 112 °C.

2.5 Thermal Oxidation Treatment

According to Ultramet, the reticulated carbon foam is stable up to 350 °C in air and 3500 °C in an inert environment. That is, the carbon foam will start to decompose in oxygen above 350 °C. Hence one way to functionalize the surface of carbon foam is to treat it in an elevated temperature environment filled with oxygen[6]. The reticulated carbon foam in this study was treated at temperatures of 350 – 500 °C for one hour in a pure oxygen filled environment. The oxygen was introduced at a flow rate of 2 sccm.

2.6 ALD alumina Treatment

ALD uses trimethylaluminium as the alumina precursor source to deposit 2 nm and 10 nm of alumina onto the carbon foam. The ALD deposits a uniform self-limiting monolayer of alumina on the surface of the carbon foam with each pulsed cycle[7]. The thickness of monolayer is estimated to be 1 Å per cycle. This method was repeated until the desired thin film thickness was achieved.

3 RESULTS AND DISCUSSION

Figure 1 shows the surface morphology of the as-received carbon foam from Ultramet, Inc. The pore size is estimated to be 300 μm in diameter. There is a higher magnification image on the top right corner. The image shows that the surface of the carbon foam is smooth and glassy-like.

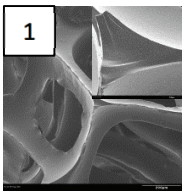


Figure 1: SEM mage of as-received carbon foam from Ultramet, Inc.

Figure 2 shows sparse CNT growth on the surface of the untreated carbon foam. Areas with CNTs seem to cluster together. This pattern was seen throughout the sample. According to Zhang, it is challenging to grow CNTs directly onto carbon surfaces as the surface carbon reacts with metal catalysis as they come in contact with each other at elevated temperature via FCT-CVD growth method. The low CNT growth may be resulted from this type of reaction described by Zhang[2].

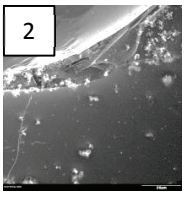


Figure 2: SEM image of the surface of grown sample, showing sparse CNTs growth on the surface of untreated carbon foam.

Figure 3a, and 3b shows CNT growth after 4 hours and 8 hours carbon foam treatment with nitric acid, respectively. The purpose of the nitric acid treatment is to functionalize the

surface of the carbon foam for better CNT growth. However the image shows that there was no noticeable difference in the amount of CNTs that grew on either the 4 hour treatment or from the 8 hour treatment batch of foam samples. The overall growth is also very sparse, and similar to what is seen in the untreated sample. Carbon based materials are chemically inert, therefore the nitric acid treatment may not be adequate enough to provide the surface functionalization or modification needed for better CNT growth.

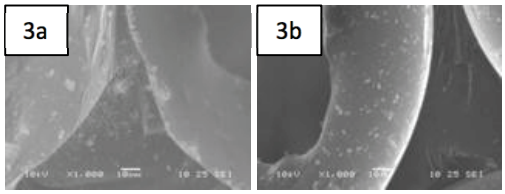


Figure 3a and 3b: SEM image of CNTs growth on 4hours and 8 hours nitric acid treatments. The images show low CNTs growth on the treated samples.

Figure 4 shows CNT growth on the oxygen treated carbon foam at temperatures of 350 °C (Figure 4a), 400 °C (Figure 4b), 450 °C (Figure 4c), and 500 °C (Figure 4d). Results show that there could be a correlation between the amounts of CNTs grown versus the temperature at which the carbon foam is being treated. Figure 4 shows the samples treated at 450 and 500 °C have higher CNT growth concentrations than the samples grown at 350 and 400 °C. However, these are preliminary results; systematic testing needs to be performed in order to verify these results. The foam samples were not treated above 500 °C, due to severe deterioration of the foam sample if treated above this temperature. It has been reported in [2] that at elevated temperatures, carbon based materials will create defects that weaken the mechanical properties. Although the images show better yield of CNT growth on samples treated at a higher temperature, the grown sample may not be used for power electronic device due to its severe deterioration observed during high temperature heat treatment. This deterioration may have weakened its mechanical properties. To verify this, a mechanical test will need to be done.

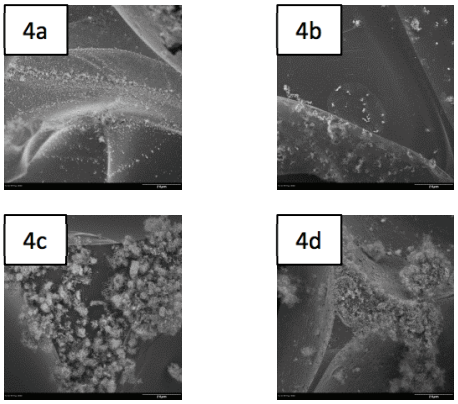


Figure 4: SEM images showing CNTs growth on oxygenated samples at (a) 350 °C, (b) 400 °C, (c) 450 °C and (d) 500 °C. The samples that were treated with higher temperatures show more CNTs growth on the surface than ones being treated at a lower temperature.

Figure 5 show the CNT growth on HMDS treated carbon foam. The HMDS test resulted CNT growth. The amount of silica coated on the surface of carbon foam may not have been thick enough for iron particles to nucleate and promote CNT growth.

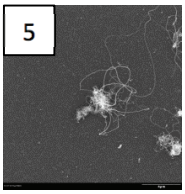


Figure 5: SEM images of CNTs growth on HMDS treated carbon foam. Image shows a low CNTs growth on the surface of the foam.

Figure 6 highlight the CNT growth on ALD treated carbon foam. The samples were coated with 2 nm (Figure 6a), and 10 nm (Figure 6b) alumina. Compared to 2 nm alumina, with 10 nm, the growth of CNTs was so dense that it covered the carbon foam in its entirety. Also, with the 10 nm samples, we can see that highly dense aligned CNTs are grown. This was not seen with any other surface treatments discussed above. One possible reason for this dense growth may be that the 10 nm alumina thin film provides a thick enough barrier layer between the reactive carbon surface and the metal catalyst. Thus the catalyst was able to nucleate on the surface of the alumina and provide dense CNT growth as seen in Figure 6b.

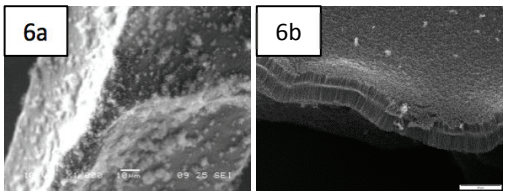
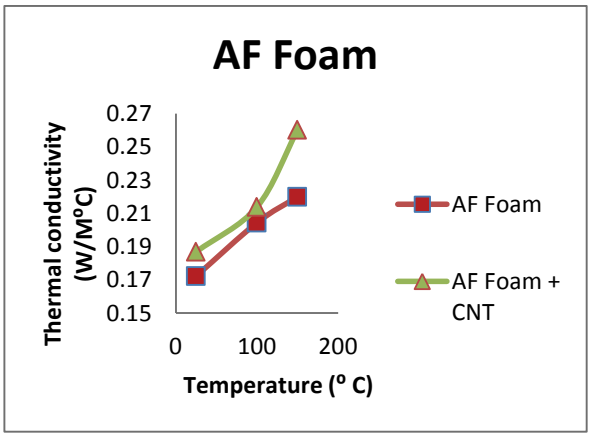


Figure 6a: SEM image of CNTs growth on 2 nm ALD alumina treated carbon foam. Image shows that CNTs growth was improved and covered all surfaces of the foam. Figure 6b: SEM image of CNTs growth on 10 nm ALD alumina treated carbon foam. Dense, aligned growth was seen here, the growth was far better than any other type of surface treated samples.

Figure 7 shows the initial thermal testing results of carbon foam with CNTs resulting from the 10 nm ALD coated alumina. The thermal testing uses laser flash analysis by Netzsch. The figure shows that the sample with CNTs had higher thermal conductivity value than the samples without. This is just an initial result; to make a firm conclusion, further tests are needed.



Fiigure 7: Graph showing the improvement in thermal conductivity by samples containing CNTs over the samples without CNTs.

4 CONCLUSIONS

Growing CNTs onto carbon surfaces still remains as a challenge due to the reactivity of carbon surfaces with the metal catalysts. In order to grow dense CNTs, the carbon surface needs to be either functionalized or buffered from the catalysts. Of the various surface treatments performed through this study, the ALD alumina process resulting in the most promising CNTs growth. Furthermore, with an increase in alumina thickness, highly dense, aligned CNTs are achievable. Preliminary thermal testing results revealed that samples with CNTs provided higher thermal conductivity values than ones without CNTs.

5 ACKNOWLEDGEMENTS

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6 REFERENCES

[1] C. Varanasi, J. Petry, L. Brunke, B. T. Yang, W. Lanter, J. Burke, H. Wang, J. S. Bulmer, J. Scofield, and P. N. Barnes, "Growth of high-quality carbon nanotubes on free-standing diamond substrates," *Carbon*, vol. 48, no. 9, pp. 2442–2446, Aug. 2010.

[2] Q. Zhang, J. Liu, R. Sager, L. Dai, and J. Baur, "Hierarchical composites of carbon nanotubes on carbon fiber: Influence of growth condition on fiber tensile properties," *Composites Science and Technology*, vol. 69, no. 5, pp. 594–601, Apr. 2009.

[3] H. Chen, A. Roy, J. Baek, L. Zhu, J. Qu, and L. Dai, "Controlled growth and modification of vertically-aligned carbon nanotubes for multifunctional applications," *Materials Science & Engineering R*, vol. 70, no. 3–6, pp. 63–91, 2010.

[4] Y. Fan, H. Yang, H. Zhu, X. Liu, M. Li, Y. Qu, N. Yang, and G. Zou, "Metallization of Carbon Fibers with Nickel by electroless Plating Technique," *Metallurgical and Materials Transactions A*, vol. 38 A, p. 2148, 2007.

[5] S. Mukhopadhyay, P. Joshi, and R. Pulikollu, "Thin Films for Coating Nanomaterials," *Tsinghua Science & Technology*, vol. 10, no. 6, pp. 709–717, Dec. 2005.

[6] Z. Konya, P. M. Vilarinho, A. Mahajan, and A. Kingon, "Studies on the thermal decomposition of multiwall carbon nanotubes under different atmospheres," vol. 90, pp. 165–168, 2013.

[7] R. L. Puurunen, "Surface chemistry of atomic layer deposition : A case study for the trimethylaluminum / water process," *Journal of Applied Physics*, vol. 97, pp. 1–53, 2005.