Vertically Aligned Carbon Nanotubes as the Sputter Resist in Space Propulsive Systems

Yoke Khin Yap, [1,*] Vijaya Kayastha, [1] Jitendra Menda, [1] Lakshman Kumar Vanga, [1] Jiesheng Wang, [1] Alex Kieckhafer, [2] Dean Massey, [2] Lyon B. King, [2,**]
[1]Department of Physics, Michigan Technological University, Houghton, MI 49931, USA.
[2]Department of Mechanical Engineering-Engineering Mechanics, Michigan Technological University, Houghton, MI 49931, USA.
[*]Email: ykyap@mtu.edu, [**]Email: lbking@mtu.edu

ABSTRACT

Two-types of vertically aligned multi-walled carbon nanotubes (VA-MWNTs) are evaluated as the protective coatings against ion erosion in electric propulsion systems. A series of experiments have been conducted to understand the erosion rate and erosion mechanism of these VA-MWNTs. These experiments were carried out with Xe propellant at an ion current density of 5 mA/cm^2. We found that the erosion rates of both types of VA-MWNTs were changing with time. Such a nonlinear erosion process is explained according to a possible erosion mechanism.

INTRODUCTION

The space exploration program faces enormous challenges as it seeks to achieve dramatic improvements in safety, cost, and speed of missions to the frontiers of space. Plasma propulsion systems have been recognized as far more efficient than chemical thrusters. This recognition has led to the development of highly efficient electric propulsion (EP) thrusters that are currently the only feasible technology for many deep space missions. However, these EP devices have in common electrode sputter erosion as a life-limiting process. To facilitate long thruster life, critical surfaces in EP thrusters are fabricated from sputter-resistant materials such as molybdenum (Mo). Carbon-based materials have shown nearly an order-of-magnitude improvement in sputter erosion resistance over Mo [1]. Among the tested carbon-based materials, diamond films prepared by chemical vapor deposition (CVD diamond) provide improvement by a factor of 1.5 in volumetric sputter erosion rate over others [2]. For thruster surfaces that are subject to sputter damage, yet must be electrical insulators, boron nitride ceramic has traditionally been used to increase the lifetime [3]. Recently, Meezan, et. al. found that polycrystalline diamond plates had 25% better resistance to sputtering than the traditional boron nitride ceramic [4].

On the other hand, unique mechanical properties of carbon nanotubes (CNTs) have triggered tremendous curiosities on their applications. CNTs are predicated to have extremely high Young's modulus values, similar to that of in-plane modulus of graphite (~1000GPa). This is much higher than the bulk modulus of diamond (~443 GPa). Furthermore, the chemical bonding strength of carbon atoms in CNTs is higher than that of diamond. Thus, it is interesting to find the resistance of CNTs to ion erosion.

Previously, we have compared two types of CNTs to CVD diamond, amorphous carbon and boron nitride films as exposed to the exhaust beam of a Hall-effect thruster [5]. We found that only CVD diamond films and vertically aligned multi-walled carbon nanotubes (VA-MWNTs) survived the erosion due to the 250 eV Kr propellant ions. VA-MWNTs were shown to have higher resistance against ion erosion as compared to horizontally laid MWNTs. This is consistent with the fact that CNTs are as stiff as diamond along the tubular axes and thus have higher sputter resistance when bombarded with ions along the tubular axes. Detailed analysis by scanning electron microscopy (SEM), backscattered electron (BSE) imaging, and Raman spectroscopy at the erosion boundary indicate that these VA-MWNTs were bundled at their tips before the erosion. Based on these results, a possible mechanism involved was proposed. In this paper, we provide the evidence that bundling occurred at the beginning stage of ion erosion. A series of experiments are conducted to understand the erosion rate of two types of VA-MWNTs. We found that both types of VA-MWNTs were eroded in a nonlinear rate.

EXPERIMENTAL DETAILS

Two types of VA-MWNTs are used. The first type is grown by a dual-RF-plasma enhanced chemical vapor deposition (dual-RF-PECVD) technique at 600 °C [5, 6]. These VA-MWNTs were grown in a tip-growth mode where the Ni catalyst particles required for the growth are remained at the tips of the nanotubes. The growth density of these VA-MWNTs is typically ~10^8 tubes/cm^2 as shown in Fig. 1a. The tips of these VA-MWNTs are brighter in contrast as compared to the remaining parts of MWNTs. This is due to the higher secondary electron current generated from the Ni tips as compared to the carbon nanotubes.

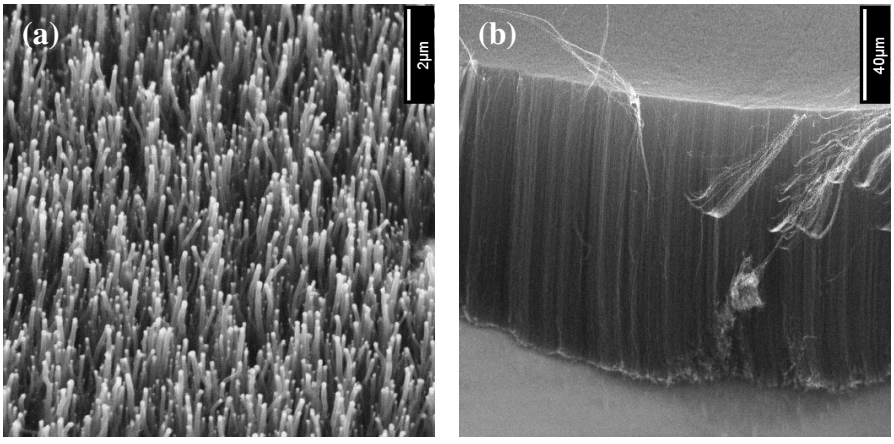

Figure 1. SEM images of VA-MWNTs grown by (a) plasma-enhanced CVD and (b) catalytic thermal CVD.

The second type of VA-MWNTs is grown by catalytic thermal CVD [7]. These nanotubes can be grown at a very high density > 10^{11} tubes/cm^2 as shown in Fig. 1b. In principle, these MWNTs are vertically aligned due to the van der Waals forces between adjacent MWNTs, which restrict the growth toward the free space (vertically upward). These MWNTs can be grown at a high growth rate ~1μm/minute [7]. Like the VA-MWNTs grown by the dual-RF-PECVD technique, the catalyst particles (Fe in this case) remained at the tips of these VA-MWNTs. Both the Ni and Fe catalysts are deposited on Si substrates that have a layer of SiO_2 film of 500 nm thick. This oxide film serves as the diffusion barrier that avoids interaction between the Si substrate and the catalysts. All these catalysts are first deposited as thin films at room temperature in a pulsed-laser deposition system by using a UV laser (λ=266 nm). Heat treatment of these catalyst films will transform them into nanoparticles that induce the growth of MWNTs. Pure CH_4 gas is used to grow VA-MWNTs by the dual-RF-PECVD while C_2H_2 is used for the growth of high-density VA-MWNTs in the thermal CVD system.

Erosion test was conducted in a 2-meter-diameter by 4-meter-long space simulation chamber [5]. All the samples were placed 0.5 m downstream on the plume centerline of the exhaust beam of a Hall-effect thruster. Graphite sheets are used to mask both the samples and the sample holders in such a way that only a portion of the nanotubes sample was exposed to ion erosion. In this way, the morphology of carbon nanotubes before and after ion erosion can be compared. The thruster is operated with Xenon propellant with a discharge voltage of 300 V producing nominally 250 Xe^+ ions. The ion current at the surface of the samples is measured as 5 mA/cm^2. Scanning electron microscopy (SEM) is used as the post-test characterization of the samples. All SEM images are taken at a tilted angle of 40 degree from the substrate surface.

DISCUSSION

First, we will discuss about the erosion of VA-MWNTs that are grown by our dual-RF-PECVD technique. Three samples have been tested for different durations of ion erosion. SEM images of these samples at the masked region are shown in Fig. 2a, b, and c. Under a high magnification, the initial diameters of nanotubes in the three samples are determined as ~100, 150 and 80 nm, respectively. All these MWNTs are ~ 2 micrometers long. The images of MWNTs after erosion are shown on the right of Fig. 2a, b, and c.

As shown in the image on the right of Fig. 2a, the morphology of VA-MWNTs has changed after 10 minutes of ion erosion. Individual MWNTs are not detected and have transformed into bundles of elongated clusters. According to our previous investigation, these structures are formed after the bundling of adjacent MWNTs [5]. Our results based on back-scattered electron (BSE) imaging, energy dispersive X-ray (EDX) analysis indicate that ion erosion will first cause the melting and the evaporation of Ni nanoparticles. These are possible because of sample heating due to the ion sputtering process and the low melting temperatures (T_m) of nanoparticles (T_m *~1/r, r is the diameter of the particles)*. The surface tension between the Ni vapor and the MWNTs will swing the melting tips, bring them in contact and cause them to fuse together. Next, the Ni will be flushed downward and overcoat the whole MWNTs.

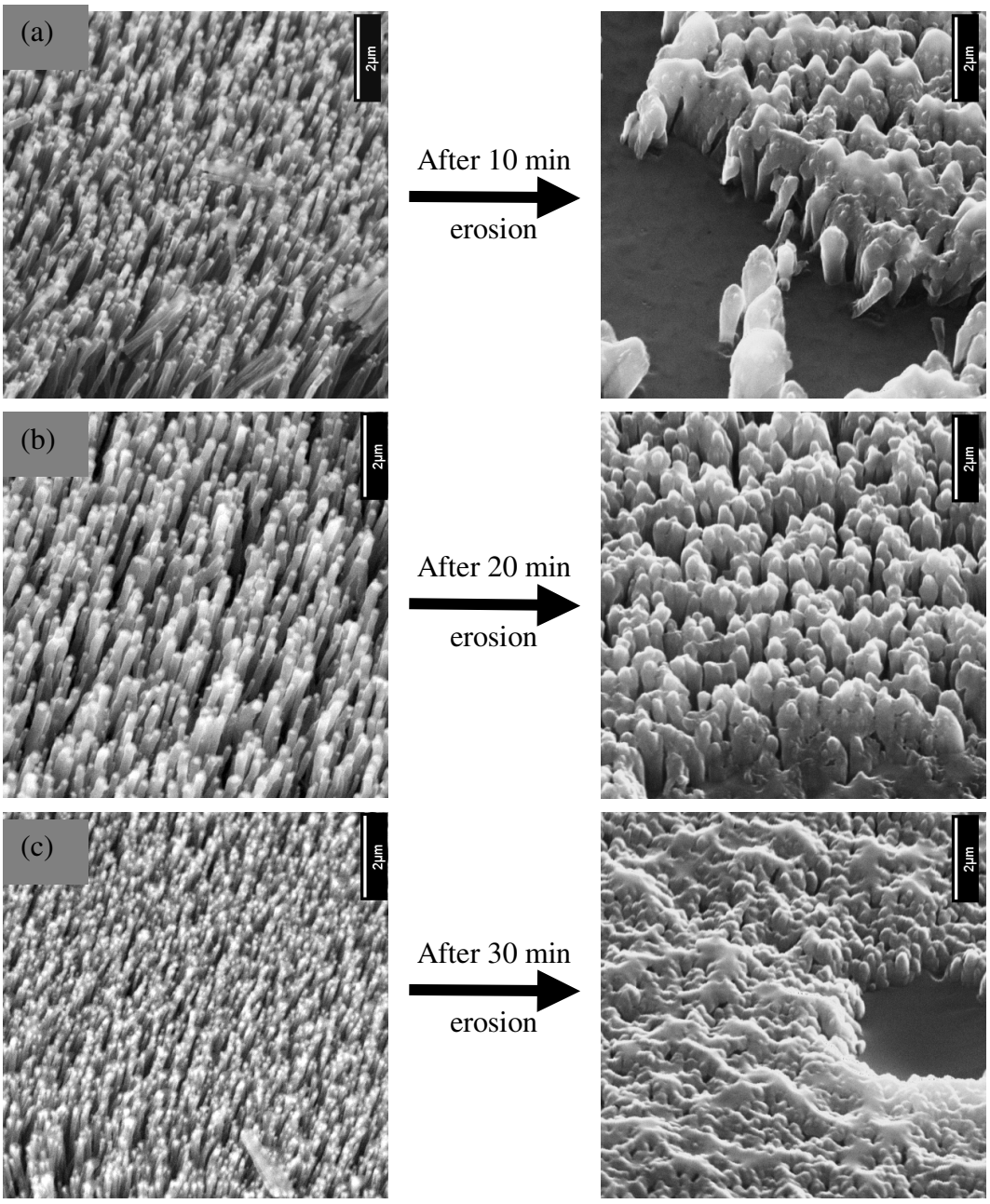

Figure 2. (a) to (c) Images of VA-MWNTs in the masked regions. The images of MWNTs after ion erosion are shown at the right.

High magnification SEM analysis is carried out to examine the erosion rate of the samples. We used a tweezer to scratch the samples in order to expose the surfaces of the substrates. This will enable the estimation of the length of MWNTs before and after erosion. We found that the lengths of these Ni/MWNTs clusters are ~1.8 micrometers after 10 minutes of erosion. Similar morphologies are observed from the second and third

samples after 20 and 30 minutes of ion erosion as shown in Fig. 2. The average lengths of these Ni/MWNTs clusters are estimated as ~1.6 and 0.7 micrometers, respectively.

Similar results occurred for VA-MWNTs samples that are prepared by catalytic thermal CVD technique (not shown here). Bundling of MWNTs start to occur after 10 minutes of erosion as those discussed earlier. We think that similar mechanism has occurred. The eroded lengths as a function of the duration of ion erosion are plotted in Fig. 3 for both types of VA-MWNTs. As shown, erosion rates are relatively low in the first 20 minutes (<0.9 μm/hour). However, the erosion rates (gradient of the curves in Fig. 3) increase significantly after 20 minutes of ion erosion. The erosion rates after 30 minutes of ion erosion are 2.6 μm/hour and 5 μm/hour, for VA-MWNTs grown by plasma enhanced CVD and thermal CVD, respectively.

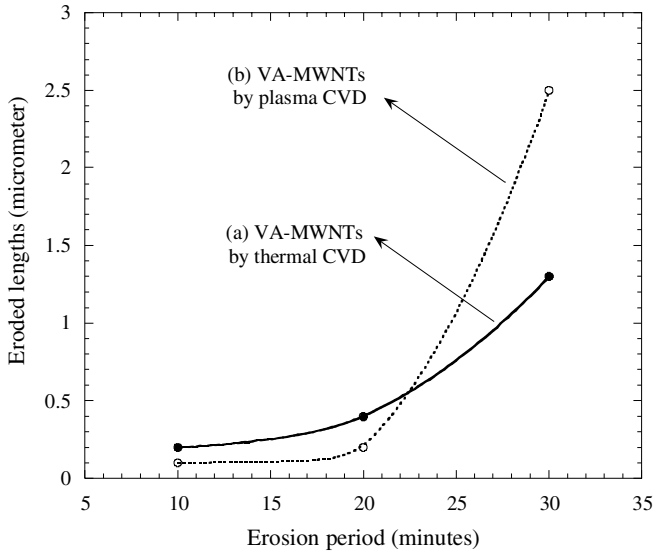

Figure 3. (a) to (c) Images of VA-MWNTs in the masked regions. The images of MWNTs after ion erosion are shown at the right.

We interpret the increase of erosion rates after 20 minutes of ion erosion as follows:

1) In the first 10 minutes, ion erosion causes the melting of both Ni and Fe nanoparticles on the tips of the VA-MWNTs. This is possible because of sample heating due to the ion sputtering process and the low melting temperatures of nanoparticles.
2) During the first 20 minutes, the melted Ni and Fe are flushed downward and overcoat the VA-MWNTs.
3) After about 20 minutes, both Fe and Ni might start to dissolve MWNTs. This is possible because of the high diffusion of carbon in both Fe and Ni. This is one of the reasons for Fe and Ni to function as the catalyst for the growth of MWNTs according to the vapor-liquid-solid growth models [7]. This process is responsible for the fast erosion rate detected.

CONCLUSIONS

We found that VA-MWNTs are not as resistant as diamond against ion erosion. Erosion rate can be higher than 2.5 μm/hour under the irradiation of 250 eV Xe ions. We think that the melting of the catalyst particles (Fe and Ni) at the tips of MWNTs is one of the reasons for such a high erosion rate. Removal of these nanoparticles after the growth process could improve the performance of MWNTs as the protective coating in electric propulsion thruster. The fast growth rate of MWNTs (~1μm/minute) and their conducting nature could be their advantage as the protective coatings.

ACKNOWLEDGEMENTS

Y.K.Y. acknowledges supports from the Michigan Tech Research Excellence Fund and the Army Research Office (W911NF-04-1-0029, through the City College of New York).

REFERENCES

[1]. T. Haag, M. Patterson, V. Rawlin and G. Soulas, 2001 International Electric Propulsion Conference, Paper No. IEPC-01-94.
[2]. J. J. Blandino, D. G. Goodwin and C. E. Garner, Diamond & Relat. Mater. **9**, 1992 (2000).
[3]. V. Kim, V. Kozlov, A. Semenov, and I. Shkarban, 2001 International Electric Propulsion Conference, Paper No. IEPC-01-073.
[4]. N. B. Meezan, N. Gascon, and M. Capelli, 2001 International Electric Propulsion Conference, Paper No. IEPC-01-39.
[5]. Y. K. Yap, J. Menda, L. K. Vanga, V. Kayastha, J. Wang, L. B. King, S. Dimovski, and Y. Gogotsi, Mat. Res. Soc. Symp. Proc. Vol. 821 (2004 Materials Research Society), paper 3.7 (2004).
[6]. T. Hirao, K. Ito, H. Furuta, Y. K. Yap, T. Ikuno, S. Honda, Y. Mori, T. Sasaki, and K. Oura, Jpn. J. Appl. Phys. **40**, L631 (2001).
[7]. V. Kayastha, Y. K.Yap, S. Dimovski, and Y. Gogotsi, Appl. Phys. Lett. **85**, 3265 (2004).

Changes on the revised manuscript:
The reviewer has suggested three minor changes. We have made all these changes according to the suggestions:

1. Page 3, last paragraph, line 5th from below: These are possible because...

2. Conclusions,
Line 3, …..MWNTs is one of the reasons….
Line 4, ...for such a high erosion rate.

3. Page 5, second paragraph, line 5th , Fig. 3, line 7, Fig. 3
All figures in the text are now referred as: Fig. 1, Fig. 2 etc.