Testing Multiwall Carbon Nanotubes on Ion Erosion for Advanced Space Propulsion

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ABSTRACT

Are carbon nanotubes more resistant than diamonds against ion erosion? Here, we report an evaluation of multiwall carbon nanotubes (MWNTs) as the protective coating against plasma erosion in advanced space propulsion systems. We have compared polycrystalline diamond films with MWNTs, amorphous carbon (a-C) and boron nitride (BN) films. Two types of MWNTs were investigated including vertically aligned (VA) MWNTs, and those horizontally laid on the substrate surfaces. Only diamond films and VA-MWNTs survived erosion by 250 eV krypton ions of a flight-quality Hall-effect thruster. VA-MWNTs are found to bundle at their tips after ion erosion.

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 that 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 modules of diamond (~443 GPa). Thus, it is interesting to find out the resistance of CNTs to ion erosion. In this paper, we discuss our preliminary observation on ion erosion of MWNTs by Kr ions generated by a Hall effect thruster. Similar erosion is also tested for CVD diamond films, boron nitride (BN), and amorphous-carbon (a-C) films. MWNTs are tested because they can be grown in high density with their axes either horizontally or vertically oriented to the substrate surface. The effect of tubes orientation can thus be examined.

EXPERIMENTAL DETAILS

Two types of MWNTs were used. First, MWNTs were grown vertically aligned to the substrate surface by a dual-RF-plasma enhanced CVD system [5]. Secondly, MWNTs were grown by thermal CVD so that their tube axes were aligned parallel to the substrate surface. All BN and a-C films were grown using a pulsed-laser deposition (PLD) system [6, 7]. The tested BN film was sp^2- bonded with typical IR absorption band at ~780 cm^{-1} and 1380 cm^{-1}. The a-C films were deposited at room temperature in vacuum by using a UV laser (λ=266 nm) at an intensity of ~5 GW/cm^2. Both BN and a-C films were thinner than 200 nm. The CVD diamond films are standard products of Sumitomo Electric Industries, Ltd (Japan). They are randomly oriented polycrystalline films, 800 μm thick on Si substrate. These films are mechanically polished to have a surface roughness ~ 1 nm rms.

Erosion test was conducted in a 2-meter-diameter by 4-meter-long space simulation chamber, as shown in figure 1. All the samples were placed 0.5 m downstream on the plume centerline of the exhaust beam of a 1.35-kW Hall-effect thruster. Each sample was partially masked in such a way that a portion of the material was exposed to ion erosion for 80 min, while another portion was protected. The thruster was operated on krypton propellant with a discharge voltage of 300 V producing nominally 250 Kr^+ ions at a total beam current of 1.8 A. Post-test analyses of the samples included: scanning electron microscopy (SEM) images taken at the masked and the exposed areas, profilometry across the masking boundary in an attempt to determine the eroded depth, Raman spectroscopy, Fourier transformed infrared (FTIR) spectroscopy, back-scattered electron (BSE) imaging, energy dispersive X-ray (EDX) analysis. In this paper, we focus our discussion based on the SEM images, profilometry, Raman, and FTIR spectroscopies. Our results indicate that only CVD diamond films and vertically aligned MWNTs survived the ion erosion. Furthermore, formation of vertically aligned MWNT bundles was discovered in these experiments.

Figure 1. Space simulation chamber at Michigan Tech used for the erosion test.

DISCUSSION

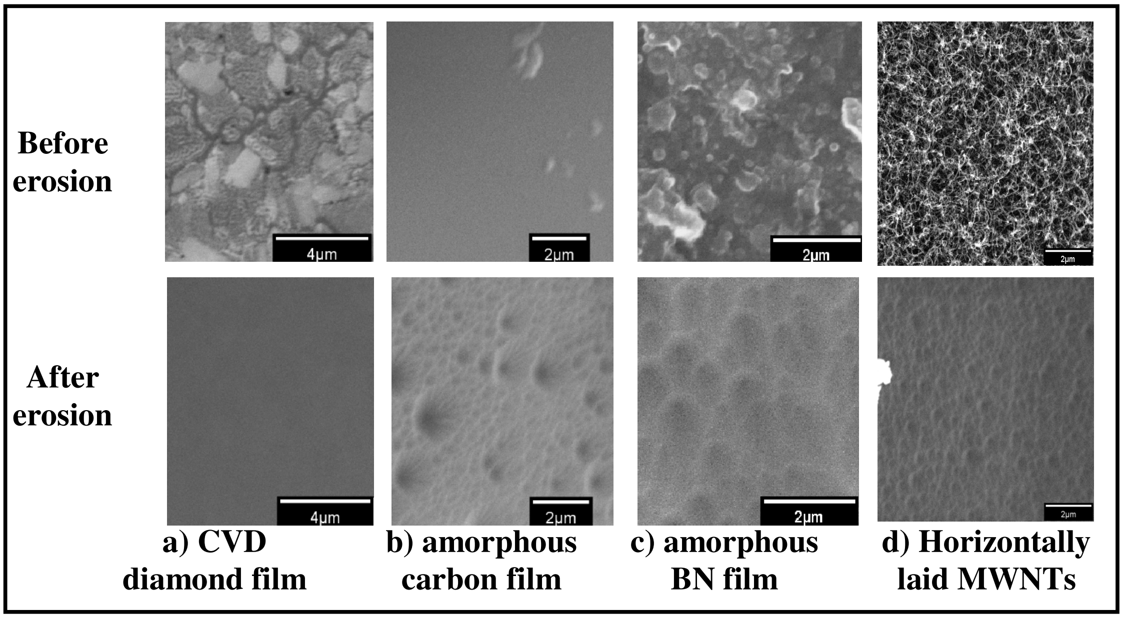

Figure 2. SEM images of CVD diamond films, amorphous carbon (a-C) films, amorphous boron nitride (BN) films, and horizontally laid multiwall carbon nanotubes (MWNTs) before and after ion erosion.

As shown by the SEM images in figure 2, all samples are eroded by the krypton ions from the Hall effect thruster. The grains of CVD diamond films are visible before erosion, but they disappear after. The surface of the diamond films could have been polished by the ions as observed in optical materials [8]. There is no significant change in Raman spectra from the masked and eroded regions. Thus, diamond film remained on the substrate after ion erosion. Profilometry analysis by a non-contact inteferometer shows that the CVD diamond film is eroded at a depth of 45 nm.

The SEM images of BN and a-C films after erosion indicate etch pits on the surface. Such morphologies do not appear by etching of amorphous materials. Thus, we conclude that this is the etched Si surface of the samples' substrate and both the BN and a-C films are totally sputtered away by the Kr ions. Complete sputtering also happened on the horizontally laid MWNTs as shown in figure 2d. As shown, no MWNTs are found on the substrate surface.

On the other hand, VA-MWNTs remained on the substrate after ion erosion. The typical image of "as-grown" VA-MWNTs is shown in figure 3a. These VA-MWNTs are about one micrometer long with an average diameter of ~70 nm, and density of ~5 x 10^{9} per square centimeter. The Ni nanoparticles used for the growth of MWNTs remained on the tips of nanotubes as indicated in a brighter image contrast (figure 3a) and in backscattered electron (BSE) images (inset). Figure 3b shows both the masked and eroded regions of the VA-MWNTs sample are shown. Clearly, MWNTs survived sputtering. The boundary of the mask is seen as a bright stripe.

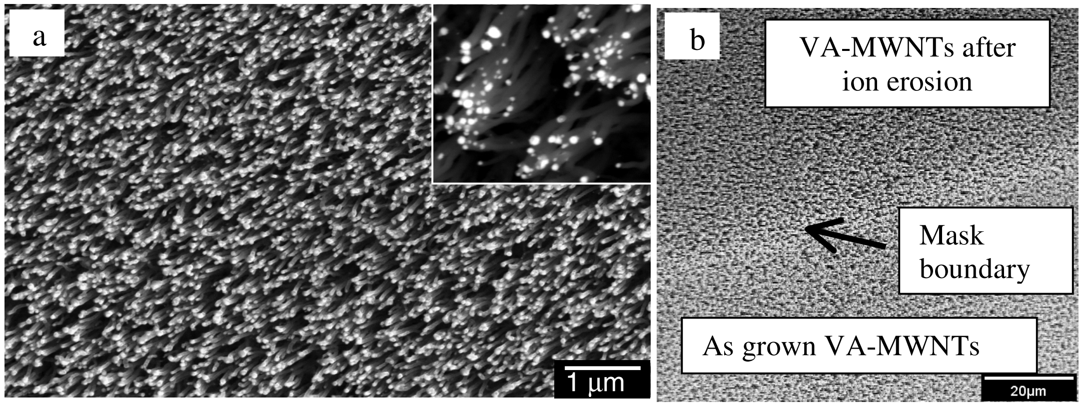

Figure 3. Image of (a) VA-MWNTs in the masked region. (b) VA-MWNTs are clearly seen in the masked and eroded regions.

High-resolution SEM images, however, suggest that VA-MWNTs were eroded by ~0.5 micron. According to Raman spectroscopy, the intensity of both the G- and D-bands at ~1580 and ~1360 cm^{-1} are reduced and broaden. These results coincide with observation by SEM that the MWNTs are shortened as shown in figure 4a. As shown, the appearance of these MWNTs has changed from a regular cylindrical tube (diameter ~70nm) to a flat-top irregular cones. Some of these cones are formed by merging and welding of several adjacent nanotubes. The change of morphology is related to the broadening of the Raman bands.

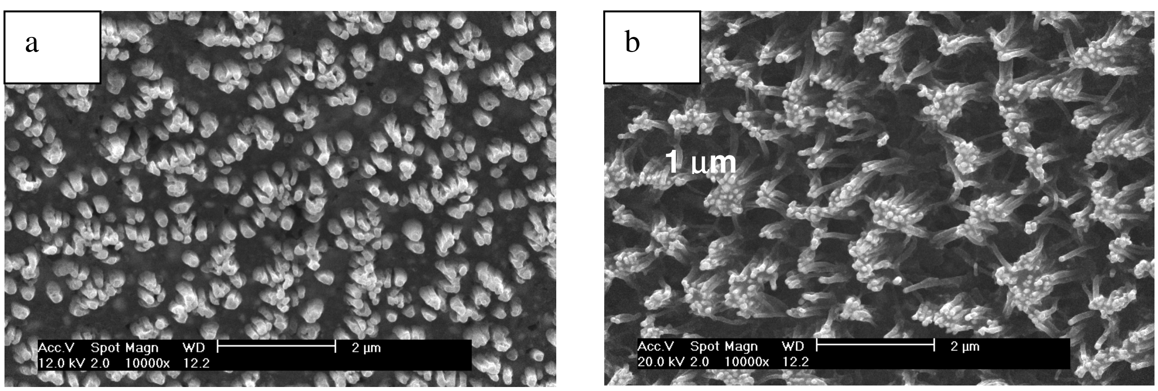

Figure 4. (a) Images of VA-MWNTs after ion erosion. The MWNTs appear as flat-top cone-like structures. (b) At the mask boundary, VA-MWNTs are found to bundle-up at their nickel tips.

In order to understand the formation of these flat-top nanostructures, we carefully mapped the transition of morphology across the mask boundary by a high-resolution field emission SEM. From this mapping, we found that individual VA-MWNTs merged with the surrounding nanotubes and formed MWNT bundles as shown in figure 4b. The only reason of bundling is the swinging of the tips of VA-MWNTs so that they can get close to each other. Under the ion sputtering, both erosion and heat are generated and caused surface melting of the tips. When these nickel tips are swinging, there are chances that the tips will stick to the adjacent tips and form the bundle. At present, the reason of swinging tips is not clear.

At the unmasked region, similar mechanism should have occurred at a faster rate. Due to a higher sputter yield at higher ionic energy and density, at one point these bundles will start to erode. We speculate that the removal of the nickel tips will avoid bundling of the VA-MWNTs and enhance the resistance of VA-MWNTs against ion erosion. This speculation will be tested by future experiments.

CONCLUSIONS

CVD diamond films have higher resistance than VA-MWNTs against ion erosion. However, VA-MWNTs are more resistant than horizontally laid MWNTs. We found that VA-MWNTs bundled at their tips as irradiated by krypton ions. The removal of nickel particles from the tips could lead to higher resistance of VA-MWNTs against ion erosion. Beside CVD diamond films, VA-MWNTs are another prospective protective coating for advanced propulsive engines.

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). S.D. and Y.G. were supported by DOE grant BSE- DE-FJ02-01ER45932.

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