Nanowear Characteristics of Carbon Nanotube Film Made by Surface Decomposition of SiC*

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Abstract

This paper shows the wear characteristics of carbon nanotube films made by surface decomposition of SiC. By this method, one can obtain remarkably high density of CNTs with well vertical alignment. For the purpose of measuring the wear characteristics of CNT films with submicrometer thickness, we carried out nanoscratch and nanoindentation tests by using an atomic force microscope (AFM). And we used 2 kinds of AFM cantilever tips with tip radii of about 20 nm and 150 nm. The experimental results showed wear behaviors of CNT films dependent on CNT length and normal load. And CNT films were worn gradually as the number of wear cycles increased. The effect of CNT length on wear of CNT films appeared as different behaviors of CNT films under normal load. That was originated from bending stiffness of each CNTs with different length as measured by nanoindentation. Shorter-CNT films had less wear because of higher deformation resistance than longer ones. Under the normal load, the SCD tip penetrated to several tens of nanometers in depth, but the CNT films showed only wear depth on the order of angstrom for each scratch cycle. Thus we confirmed that CNT films have both strength and flexibility, which reflects remarkable mechanical properties of CNTs. These results are important for machine designs using CNT films as friction materials.

Key words: Nanowear, CNT Film, AFM, Scratch

1. Introduction

Carbon nanotubes (CNTs) were first discovered by Iijima in 1991¹⁾. And they have interesting structures as rolled graphene sheets and are capped by hemispheres of fullerene, which cause their very high aspect ratios. There are single-walled carbon nanotubes (SWNT) and multi-walled nanotubes (MWNT) and their diameters and lengths are generally in the order of nanometer and micrometer respectively. For the synthesis of large amount of CNTs, chemical vapor deposition (CVD)²⁻⁴⁾ and surface decomposition of carbides^{5, 6)} are known. CNTs originally have both stiffness and flexibility. The uniaxial tensile strengths of CNTs have been shown experimentally to be 200 GPa for SWNTs⁷⁾ and 11- 63 GPa for MWNTs⁸⁾. These experimental values are smaller than analytical values⁹⁾, which may be caused by presence of defects and interactions between adjacent tubes such as friction and adhesion.

CNTs with high stiffness and flexibility are expected to be good material for mechanical

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use. But few studies have been done to clarify the wear of CNTs although it is necessary for the design guide. Therefore the aim of this paper is to clarify the nanowear characteristics of CNTs. For the purpose of overcoming the difficulty of measuring wear properties of CNTs, the specimen should be aligned CNTs rather than a single CNT or random CNTs. And usually, aligned CNTs made by CVD have weak interface strength because they are not densely packed enough and not bonded to the substrate directly with, for example, covalent bonds. In addition, the CNTs will be deformed dynamically and randomly by a counter body during wear tests so that it is still difficult to measure the wear characteristics of CNTs even if we use well-alignment and densely packed CNT films with strong adhesion to a substrate. Therefore we employed surface decomposition of Silicon carbide as a synthesis method which makes densely-packed and highly-aligned CNT films with high interface strength. And we also employed AFM for the measurement of wear of CNT films. We could measure wear progress of CNTs by area scratching using AFM cantilever tips which contacted only with ends of CNTs under low load and penetrated into the CNT films under high load. The wear of cantilever tips was confirmed to be negligibly small by using FESEM.

Fig. 1 Schematic of AFM nanoscratch test

2. Experiments

Wear tests (nanoscratch tests) were carried out in room temperature and relative humidity of 30 to 40 %RH by using commercial AFM (SII, SPA-400). We used 2 kinds of cantilevers with different tip radii of 150 nm and 20 nm (or less) as shown in table 1. The cantilevers are made of poly crystalline diamond (PCD tip) and single crystalline diamond (SCD tip) respectively and tip wear was not observed for both of them by using FESEM. During nanoscratch tests, the trajectories of the tips were programmed to be the same through all tests. As schematically described in Fig. 1, the tip was first at top-left corner of inner square area (scratch area) and then translated by 500 nm along x axis with loading and translated for the same distance along -x direction with unloading. After the round trip motion, the tip was translated by 10 nm along -y direction. These trajectories were repeated for 50 times to

scratch over the area of $500 \times 500 \text{ nm}^2$. This cycle were repeated to progress the wear of the CNT films and followed by scanning over the area of $2000 \times 2000 \text{ nm}^2$ (scan area) to obtain the surface profiles after each cycles. To repeat scratching over the same area after scanning, we used the same tip for both scratching and scanning through all cycles. Additionally, we carried out nanoindentation tests by using AFM with the same tips as used in nanoscratch tests. And we clarified the relationship between normal loads and displacement (penetration depths) into the films. Based on obtained force-displacement curves, we determined the appropriate normal load for nanoscratch tests. And we found that if the load is too high for the interface between the substrate and CNT films, CNTs were removed from the interface before CNTs themselves were broken. Therefore the normal load was chosen to be less than the critical load under which CNT films were not removed. The stage speeds of AFM were $1 \text{ }\mu\text{m/s}$ and 10 nm/s for scratch tests and indentation tests respectively.

The CNT films were made by surface decomposition of Silicon carbide. Well polished c face of 6H-SiC substrates (CREE Inc.) were heated to 1500°C or 1700°C for 0.5h at a rate of 15°C/min and held at each temperature in a vacuum ($1 \times 10^{-4} \text{ Torr}$) chamber with an electric resistance carbon heater. During the treatment, the surface was oxidized by residual CO gas in the furnace and Si was removed from the substrate as SiO gas, and remaining C atoms formed CNTs with well alignment and high density. The mean diameter of CNTs is 5 nm and length is 50 and 210 nm. The density was estimated to be $3 \times 10^{10} / \text{mm}^2$.

Table 1 Data of cantilevers

	Spring constant	Tip radius
Poly-crystal diamond AFM tip (Nanoworld AG)	42 N/m	150 nm
Single-crystal diamond AFM tip (Olympus)	42 N/m	20 nm

Fig. 2 Wear progress of CNT films with CNT length of 210 nm under normal load of 500 and 1000 nN by a PCD tip

3. Results

Figure 2 shows the wear progress of CNT films with CNT length of 210 nm (210-nm CNT) as a function of wear cycles with a PCD tip. As shown, the wear depth was proportional to both wear cycle and normal load. Based on this, the wear mechanism of CNT films is assumed to be adhesive wear or abrasive wear. In the graph, we used wear depth instead of wear volume. Here, the wear depth is essentially identical to the wear volume because wear amount in this experiment is expressed by multiplying the wear depth and the scratch area ($500 \times 500 \text{ nm}^2$). And Fig. 3 shows the normal load as a function of penetration depth of PCD tip by AFM nanoindentation tests. The loading curve shows that the depth of indentation is proportional to normal load. And shorter CNT showed higher deformation resistance against the PCD tip. The unloading curve shows the recovery without plastic deformation. The cause and its mechanism of hysteresis loop were explained in elsewhere¹⁰.

Fig. 3 Force displacement curve of 50 nm and 210 nm CNT film by using a PCD tip

And Fig. 4 shows wear depths per cycle of 50-nm CNT, 210-nm CNT, and Cu under the normal load of 500 nN wear depth per cycle of 210-nm CNT under 1000 nN. Under the same load of 500 nN, longer CNT film (210 nm) showed deeper wear depth than shorter CNT film (50 nm) and Cu showed similar depth as 210-nm CNT. And under higher value of 1000 nN, 210 nm CNT films showed higher value.

Next, Fig. 5 shows wear progress of 50-nm and 210-nm CNT as a function of wear cycles with a SCD tip which is sharper than a PCD tip. This result showed that wear depth is proportional to wear cycles as scratched by a SCD tip. The sudden increase at the initial stage may be caused by cap removals, but the cantilevers which we used were so stiff (42 N/m) that we could not confirm the change in surface morphology caused by cap disappearances of each CNTs in this experiment. Figure 6 shows the force displacement curve of 50-nm and 210-nm CNT. Comparing with Fig. 3, CNTs showed larger displacement by a SCD tip. And both 50-nm and 210-nm CNT showed perfect elastic recovery after the penetration of about 40 and 70 nm respectively and hysteresis was more clearly shown.

Fig. 4 Wear depths per cycle of 50-nm CNT, 210-nm CNT, and Cu under the normal load of 500 nN and 210-nm CNT under the normal load of 1000 nN by a PCD tip

Fig. 5 Wear progress of CNT films with CNT length of 50 and 210 nm under normal load of 500 nN by a SCD tip

Figure 7 shows the wear depths per cycles for 50-nm CNT, 210 nm-CNT, and Cu by a SCD tip under the normal load of 500 nN and those by a PCD tip for comparison. Cu showed much higher value by a SCD tip than by a PCD tip. CNT films showed the similar values by both tips. And for both tips, shorter CNT film (50-nm CNT) showed lower values of wear depth.

Table 2 shows the specific wear rate of 50-nm CNT, 210-nm CNT, and Cu specimens scratched by a PCD tip and a SCD tip. This infers that the tip behaved as a single abrasive asperity against copper specimens. CNT films showed relatively low specific wear rate compared with Cu specimens. These values measured by AFM nanoscratch tests showed agreement with ones of macro scale.

Table 2 Specific wear rate

	50 nm	210 nm	Cu
PCD tip	1.0×10^{-6}	2.5×10^{-6}	3.1×10^{-6}
SCD tip	7.9×10^{-7}	2.8×10^{-6}	2.0×10^{-4} (mm ² /N)

Fig. 6 Force displacement curve of 50 nm and 210 nm CNT film by using a SCD tip

Fig. 7 Comparison of wear depths per cycles of 50 nm CNT film, 210 nm CNT film, and Copper specimen by using PCD and SCD tips.

Figure 8 shows the topographic images of AFM at 0, 1, 2, 4, 10, 20, 30, 40, and 50 cycles. The surface was gradually worn by repeated scratches as a function of wear cycles without material flow. And these images also showed that the scratch tests were successfully done on exactly the same area through all scratch cycles. Because each CNT has very small average tip radius of about 5 nm, the AFM tips could not detect any caps or tubes of each CNT. But unlike other CNT films made by CVD, a CNT film made by surface decomposition of SiC behaved as a solid film against AFM tips due to both the high density and relatively short length of CNTs. The reproducibility of surface topographies of not-scratched area is also infers this. A tip was observed after 50 cycles of wear cycles on 210 nm CNT as shown in Fig. 10. The broken line is an original tip shape before scratches. The wear of the tip was not confirmed but some debris adhered on the tip. The debris could be the carbon particles generated after scratches on CNT film surfaces.

Fig. 8 AFM images of scratch area of 50 nm CNT

Fig. 9 Cross sections of scratch area of 50 nm CNT

Fig. 10 SEM image of a PCD tip after 50 cycles of area scratches on 210 nm CNT film

4. Discussions

We carried out nanoscratch tests with PCD and SCD tips. Obviously, in the case of Cu in Fig. 7, the tip diameters are attributed to the remarkable difference between values of PCD and SCD tip. And we should note that the value of wear depth per cycle can be easily estimated by concerning the indentation depth of the tip based on an abrasive wear model as shown in Fig. 11(a). Based on this model, the specific wear rate is derived by means of hardness H of the material and the tip radius r . Because wear depth is identical to the wear amount as written above, we focus on the wear depth by a single scratch instead of wear amount. As shown in Fig. 11(b), the projected contact area A is expressed by dividing normal load N by hardness of softer material H ($A=N/H$). And one can express the depth h as a function of tip radius r by applying Pythagorean theorem to the right triangle in the figure.

$$h = r - \sqrt{r^2 - r'^2} \quad (1)$$

And noting that contact area A is a quarter of $\pi r'^2$, Eq(1) is rewritten like this.

$$h = r - \sqrt{r^2 - 4N / \pi H} \quad (2)$$

The hardness H of Cu specimen was 2.2 GPa measured by a commercial nanoindenter using a diamond verkovic stylus with tip radius of about 20 nm. Then this equation is plotted with experimental results as shown in Fig. 12 and it shows great agreement between the experimental values of Cu and a curve of abrasive-modeled Eq. 2. And this also infers that estimation of wear amount based on abrasive model is well applicable to AFM scratching tests in the same load range. Contrary to Cu, CNT films did not show abrasive behavior. Furthermore, we could confirm that high stiffness and flexibility of CNTs because CNTs did not deformed plastically despite of large penetration depth of about 50 nm under 800 nN by a sharp SCD tip as shown in Fig. 6. The values of wear depth per cycle of CNT films are on the order of angstrom as shown in Fig. 7. Therefore we consider that the wear of CNTs was caused by sliding and adhesion with AFM diamond tips in atomic scale and the wear mechanism of CNTs was thought to be adhesive wear. Lower values of wear depth per cycle of 50-nm CNT than that of 210-nm CNT can be explained by smaller depths of 50-nm CNT (Fig. 3 and 6) which corresponds to contact areas. Under dry contact condition, this atomic-scale wear caused by adhesion is very difficult to prevent. Considering the high affinity of CNTs with diamond, however, it is possible to reduce the wear by using counter bodies of other materials than carbon. And because under higher load than which employed in this experiment, the CNTs were removed from the interface at once, thus, it was impossible to measure the wear behavior of CNTs under higher load in this experiment.

(a) Perspective view

(b) Magnified front view on the tip

Fig. 11 Schematic of contact between the tip and the specimen

Fig. 12 Experimental wear depths per cycle of 50-nm CNT, 210 nm-CNT and Cu specimens as a function of AFM tip radius plotted with theoretical line of abrasive model of Cu

5. Conclusions

We carried out nanoscratch tests by using AFM with diamond tips and nanoindentation tests with the same AFM tips. The wear characteristics of CNTs were discussed with 50 nm and 210 nm CNT films and Cu specimen as reference specimen. These are the conclusions below.

1. The wear mechanism of CNT films scratched by AFM tips was mainly adhesive wear.
2. The wear of CNT films progressed as a function of wear cycles and normal load.
3. We confirmed that CNT films have both stiffness and flexibility. Because the wear depth per scratch cycle was on the order of angstrom for CNT films and penetration depth under the same load was measured to be several tens of nanometers by AFM nanoindentation tests with same tips as used in nanoscratch tests.
4. By using Cu specimen, we confirmed that wear amount is able to be estimated based on abrasive wear model in nanoscale AFM scratch tests under sufficiently high load to cause plastic deformation.

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