Characterization of small-scale batch-fabricated carbon nanofiber probes

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Abstract. Linear-shaped single carbon nanofibers (CNFs) were batch-grown onto commercially available Si cantilevers for atomic force microscope by the Ar⁺-ion-irradiation method (9 cantilevers/batch). The force-curve measurements revealed that the long CNF probes (~ 1 μm in length) were as flexible as the carbon nanotubes probes, whereas the short CNF probes (~ 400 nm in length) were characterized by the rigid nature similar to the Si probes. Thus, the mechanical properties of CNF probes were controllable by the CNF length. The ion-induced CNF probes were metallic in electrical property, and the higher resolution images in scanning spreading resistance microscopy was attained by the CNF probes than by conventional conductive diamond probes, due to the small tip radius, high aspect ratio and the durability of the CNF probes. Because the small-scale batch-fabricated CNF probes showed good uniformity in the size, mechanical and electrical properties, it was concluded that they are promising as practical conductive SPM probes.

1 Introduction

One-dimensional nanomaterials, such as carbon nanotubes (CNTs) and carbon nanofibers (CNFs), are thought to be an ideal probe for scanning probe microscopy (SPM), due to their possible high spatial resolution and suitability in measurements of high-aspect-ratio trenches and semiconductor patterns of narrow line-and-space. Thus, much effort has been devoted to fabricate CNT- or CNF-based SPM probes [1-11]. Nevertheless, the batch fabrication of CNT- or CNF-tipped probes is still quite challenging because of several unsolved difficulties in conventional fabrication methods, such as the manual attachment of single CNTs or chemical vapor deposition growth of CNTs onto SPM chips.

In the previous papers, we demonstrated that Ar⁺ ion bombardment on bulk carbon and carbon-coated substrates induced the growth of conical protrusions and CNFs, 20 -50 nm in diameter, grew only on the tips even at room temperature [12-14]. In addition, the small-scale batch-growth of linear-shaped single CNFs onto commercially available Si cantilever tips (3 – 9 cantilevers / batch) was possible in this ion-irradiation method [15]. Needless to say, a larger number of CNF probes will be fabricatable in a batch-growth process by a larger ion source. In order to use these ion-induced CNFs as practical SPM probes, their mechanical and electrical properties, and the uniformity in those properties as well, should be investigated in detail. In the present work, we tackled this practically important subject.

2 Experimental Methods

The samples employed were commercially available Si cantilevers (Olympus OMCL-AC160TN, L x W x T=160 x 50 x 4.7 μm³; N-type; the bulk resistance of 4~6 Ω cm). The basic fabrication method of ion-induced CNF probes is described elsewhere in detail [14, 15]. In brief, arrays of carbon-coated cantilevers (9 chips/batch; see Fig. 1) were Ar⁺-ion irradiated using a Kaufman-type ion gun, 3 cm in ion-source diameter, in a nanofabrication system [16]. In this ion-irradiation method, CNFs grow due to the redeposition of sputter-ejected carbon atoms onto the sidewall of conical protrusions and the excess surface diffusion of the carbon atoms to the tips
during Ar+ ion irradiation [14]. The ion beam energy employed for the ion-induced CNF growth was 600 eV, and the growth duration was less than 10 min. The basal and working pressures were $1.5 \times 10^{-5}$ and $2 \times 10^{-2}$ Pa, respectively. After the CNF growth, the size and its uniformity were observed by field emission scanning electron microscope (FE-SEM; Hitachi S-4700).

The mechanical and electrical properties were measured using an atomic force microscopy (AFM) machine (SII-NT E-Sweep). For the force-curve measurements, during the levers were brought closer to the surface at a constant speed from a normal imaging position of the sample to a -200 nm-deeper position, the dependence of the amplitude voltage of the lever (i.e., the cantilever deflection) on the displacement of the lever was recorded. For the current-voltage (I-V) measurements, the probes were contacted with a gold sample surface gently (approximately 100 nN). The I-V measurements were carried out at different three points on the sample surface to confirm the reproducibility. The voltage was applied from negative to positive on the probe. The electrical property of CNF probes was further investigated by scanning spreading resistance microscopy (SSRM) methods, in which the resistance of the graphite surface was measured using AFM in the contact mode. For the SSRM measurements, the probes were contacted with the graphite surface strongly (approximately 2000 nN). The bias voltage applied was -0.5 V, and the scan area was set at $500 \times 125$ nm$^2$. The characteristics and the size of the cantilevers are shown in Table 1.

### Table 1. Characteristics, and sizes of cantilevers employed in this study.

| Cantilever | AC160TS | CNF-1 | CNF-2 | CNF-3 | CNT | DF3-A | CDT-NCHR |
|------------|---------|-------|-------|-------|-----|-------|----------|
| Resonant Frequency (kHz) | 270 ± 20 | 285 | 255 | 25 | 320 |
| CNF Tip Height (μm) | - | 1.0 | 0.4 | 0.7 | 0.3 | - |
| Radius (nm) | 7 | 15 | 11 | 22 | 150 |
| Resistivity (Ωcm) | 4-6 | $(1.375 \times 10^{-5})$ | $2.35 \times 10^{-5}$ | $4 \times 10^{-5}$ |

### 3 Results and Discussion

Figure 1 shows an SEM image of small-scale batch-fabricated CNF probes (9 chips/batch) at 50°C. Linear-shaped single CNFs, about 1 μm in length and 30 nm in diameter, pointing in the ion-beam direction, grew only on the respective cantilever tips. Ion-induced CNFs grown at room temperature are generally characterized by the amorphous nature and possess no hollow structure [13, 14, 16]. Since the growth temperature employed here was low enough, the CNFs grown on the Si tip were also thought to possess the similar crystallographic natures. The CNF length was controllable by the growth duration (ion-irradiation time).

The CNFs grown in the two batches showed excellent reproducibility and uniformity in size and the growth direction. The mean length measured 360 nm with a standard deviation (STDEV) of 50 nm. The minimum, maximum, mean radii and STDEV measured 8 nm, 14.5 nm, 11.1 nm and 2.0 nm, respectively.

**Fig. 1 SEM image of an array of commercially available Si SPM cantilevers. Inset: Enlarged SEM image of ion-induced CNF grown on the tip.**

One of the most important advantages of the ion-irradiation method is the controllability of the growth direction of CNFs; they grow in the ion-beam direction. In fact, STDEV of the growth angle of the batch-fabricated CNFs was 1.7 degree.
Figure 2 shows the results of dynamic mode force curve measurements for CNT, long CNF (~ 1 \(\mu\)m in length; referred to as CNF-1), short CNF (~ 400 nm in length, referred to as CNF-2) and Si without CNF (see also Fig. 3). Since the mechanical characteristics of the lever parts are almost identical for the probes employed, the inclination of the force-curve corresponds directly to the mechanical strength of the probe tip part that touches the surface of the sample. A small inclination of the force-curve implies that the change in amplitude voltage is small even for a large displacement of the lever. In other words, flexible probes yield a small inclination of the force-curve.

The CNT (curve a) and CNF-1 (curve b) showed the force-curve characteristics typical of flexible probes; the amplitude voltages decreased gradually with a decrease in the lever displacement at 0.06 and 0.1 mV/nm, respectively. By contrast, the CNF-2 (curve c) and the Si probe (curve d) showed a force-curve characteristic typical of rigid probes; the amplitude voltages decreased steeply with a decrease in the lever displacement at 10.2 and 8.5 mV/nm, respectively. It must be mentioned that the mechanical property is controllable from flexible to rigid simply by the CNF length.

Figure 3 shows SEM images of the probes after the force-curve measurements. No change in the probe shape was recognized for the CNT [Fig. 3(a)] and CNF-1, [Fig. 3(b)], proving that they possessed the elastic nature against the mechanical deflection. The gradual change in the amplitude voltage in the force-curve measurements would be due to this flexibility. Very interestingly, CNF-2 also showed no change in the probe shape [Fig. 3(c)] before and after the force-curve measurement, suggesting that the short CNF still possesses the enough elasticity. By contrast, the top part of the probe was broken and disappeared for the Si probe [Fig. 3(d)], that is typical for the rigid probes.

Next, the I-V measurement results of various probes and CNF probes were compared. CNF-3 and Au-coated Si probes show the typical metallic property, whereas the Si probe shows the typical diode characteristic. The probe resistances were evaluated to be 927 k\(\Omega\), 447 k\(\Omega\) and 11 G\(\Omega\) for the CNF-3, Au-coated Si and Si probes, respectively.
The electrical properties of CNF-3 probes were further investigated using the SSRM method. For comparison, the measurement was carried out also using electroconductive diamond probes, which are commonly used for SSRM analysis, and Si probes. Figures 4(a) - (c) show the topography of a graphite surface (500 ×150 nm$^2$) measured using diamond, Si and CNF-3 probes, respectively. The average resistance on the surface and the surface roughness (rms value) measured by the diamond probe were about 250 kΩ and 13.3 nm, respectively [Fig. 4(a)]. In the Si probe case, because of the high resistivity of the Si probe itself, the measured resistance was as high as 4 GΩ, and the measured rms value was 15.8 nm, which was smaller than that expected from the original probe-tip sharpness [Fig. 4(b)]. The small rms value implies the insensitiveness in the roughness measurement. Because the contact between the probe and the graphite surface was hard in the SSRM analyses, the tip shape of Si probe was thought to be round during the measurement. By contrast, the average resistance and rms values measured by CNF-3 probe were of about 3 MΩ and 50.4 nm, respectively [Fig. 4(c)]. The rms value was the largest for the CNF-3 probe. This may be due to the tip sharpness, high aspect ratio and durability of the CNF-3 probe.

FE-SEM taken after the SSRM measurements showed no difference in length or shape for the diamond and CNF-3 probes, whereas the Si tip was flattened after the SSRM measurements as was predicted above.

4 Conclusions

The mechanical and electrical properties of small-scale batch-fabricated CNF probes by the ion-irradiation method were investigated in detail. The long CNFs, ~ 1 μm in length, showed the flexible nature similar to the CNT probes, whereas the short CNFs, ~ 400 nm in length, showed rigid nature almost identical with Si probes. Thus, the mechanical property was controllable from flexible to rigid by the CNF length. The ion-induced CNF probes were metallic in electrical property, and possessed a sufficient tip sharpness, a high aspect ratio, and durability against a strong contact with the sample surface. Owing to these properties, highly resolved SSRM images, which are difficult to attain using conventional Si or conductive diamond probes, were obtained by CNF probes. Because the small-scale batch-fabricated CNF probes showed good uniformity in the size, mechanical and electrical properties, they are believed to be promising as practical conductive SPM probes.

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