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Decrease in reflectance of vertically-aligned carbon nanotubes after oxygen plasma treatment

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ABSTRACT

Oxygen plasma treatment was used to lower the reflectance of multiwall vertically-aligned carbon nanotubes (VACNT). Specular reflectance measurements at an incident angle of 65° from normal show a decrease in reflectance over the wavelength range of 250-2500 nm, with up to 5 times lower reflectance at long wavelengths. Total hemispherical reflectance measurements show a decrease in reflectance from 300-2400 nm, with up to 8 times lower reflectance at short wavelengths. Etch rate measurements and helium ion microscopy reveal that the oxygen plasma reduces the reflectance of VACNT by modifying the surface morphology, characterized by etching away the top layer and inducing agglomeration of nanotube tips.

1. Introduction

Vertically-aligned carbon nanotubes (VACNT) have been measured to be the blackest known substance [1–4]. However, typical VACNT samples are not perfect absorbers and often tend to increase in reflectance at short wavelengths [1,5,6] and appear specular at large viewing angles. The reflectance of VACNT depends on many variables – including density, height, uniformity, and alignment [5,7–9]. Each of these variables is determined by a complicated interplay between the sample substrate, catalyst, and the specific growth conditions. Plasma treatment of VACNT is a promising post-growth modification that has been shown to remove carbon impurities, randomly shorten and kink individual nanotubes, and cause tip agglomeration, all of which should decrease reflectance by making the surface less uniform [10–16]. While numerous groups have reported oxygen plasma treatment (ashing) of VACNT [13–19], to our knowledge, no measurement of the change in reflectance has been reported. We have performed careful reflectance measurements on VACNT samples, with and without oxygen plasma treatment.

2. Experimental

Multiwall VACNT were grown on 100 mm silicon wafers by a commercial company. The fabrication steps consist of a growth of 500 nm SiO2, deposition of 10 nm Al2O3 and 1 nm Fe catalyst layers, and growth of VACNT using water-assisted chemical vapor deposition. Each wafer was introduced into a 15 cm quartz tube furnace and ramped to a temperature of 780 °C while flowing Ar gas at 3250 sccm and H2 gas at 580 sccm through the tube. Nanotube growth was carried out at atmospheric pressure by adding C2H4 gas at 300 sccm to the flow. The resulting VACNT are ≈ 2 mm tall, and by eye appear very black except when viewed nearly edge-on, where they appear shiny.

Each wafer was divided into 4 pie-shaped samples using a diamond scribe. One sample from each wafer was left...
unexposed to serve as the control and the other samples were exposed to an oxygen plasma using a commercial plasma system. The settings used for the oxygen plasma treatment were a flow rate of 50 sccm O₂, pressure of 32 Pa (0.24 T), RF power of 50–200 W at 30 kHz, and duration of 15–300 s.

2.1. Specular reflectance

To measure the specular reflectance of the samples, we used a commercial spectrophotometer with an accessory for measuring absolute specular reflectance. The incident light spot size on the sample was 4 mm by 4 mm and an integration time of 1 s was used for each data point. A reference scan that did not reflect off the sample was used to convert the raw detector data to absolute reflectance. Since the specular reflectance of the samples is so small, the signal is very small and noisy, and only becomes appreciable at large incidence angles. We have not fully evaluated the uncertainty of the measurements, but believe it is roughly 0.005 (k = 2) due to instrument drift and uncertainties in gains. Specular reflectance at an incident angle of 65° from normal is shown in Fig. 1. The plasma-treated samples all show lower specular reflectance over the whole measured wavelength range, with up to 5 times lower reflectance at long wavelengths.

2.2. Total hemispherical reflectance

To measure the total hemispherical reflectance of the samples, we used the same commercial spectrophotometer with a 150 mm diameter integrating sphere accessory. Samples were held at the back of the sphere against a 18 mm diameter port, tilted at 8° from normal incidence. The incident light spot size on the samples was 7.5 mm by 15 mm, the slit width was 5 mm, each data point was integrated for 1 s, and three separate scans were averaged together. Background scans were used to account for any stray light in the sphere and a calibrated standard black reference material1 was used to convert the raw detector data to absolute reflectance. The total hemispherical reflectance is shown in Fig. 2. The plasma-treated samples show lower total reflectance over the whole measured wavelength range, with up to 8 times lower reflectance at short wavelengths.

2.3. Etch rate

We observed a linear decrease in height of the VACNT with plasma exposure. Using a commercial digital contact sensor attached to the vertical axis of an optical microscope, we measured an etch rate of = 20 μm/min with an uncertainty of 50 μm (k = 2) for a RF power of 200 W. The large uncertainty is attributed to variation in VACNT height with position and difficulty measuring the same spatial position with successive plasma treatments.

2.4. Imaging

Three samples were imaged with a helium ion microscope (HIM) using a current of 0.2 pA to 0.4 pA and an accelerating energy of 30 keV. The images were acquired in a low-loss regime with a beam current of 0.2 pA and a working distance of 5 mm. The images were processed using a standard analysis software to improve the contrast and resolution of the features. Figure 3 shows a representative image of a VACNT from each sample type. The images reveal a significant reduction in the height of the VACNTs after plasma exposure, consistent with the observed etch rate.

1 NIST standard reference material 2052-01-20 certified in 2002. Calibration was updated in 2013 by personal communication with the optical radiation group at NIST Gaithersburg.

Fig. 1 – (Top) Specular reflectance at an incidence angle of 65° from normal. (Bottom) Ratio of specular reflectance between plasma-treated samples and control sample. (A colour version of this figure can be viewed online.)

Fig. 2 – (Top) Total hemispherical reflectance with uncertainty (k = 2) shown by shaded regions. (Bottom) Ratio of total reflectance between plasma-treated samples and control sample. (A colour version of this figure can be viewed online.)
voltage of 25 kV. A HIM was used instead of a scanning electron microscope because of the combination of superior resolution, increased depth of field, and lack of charging. The images in Fig. 3 show that the oxygen plasma treatment induces agglomeration of the tips VACNT, which has previously been observed after exposure to oxygen plasma [12] and laser light in the presence of oxygen [20]. We speculate that the initial attraction between nanotubes during the plasma treatment arises from charging of nanotube defects and functionalization (oxygen radicals), followed by continued adhesion due to Van der Waals forces.

3. Discussion and conclusion

Carbon nanotube growth is initially randomly oriented, until crowding forces a self-oriented vertical alignment [14,16,21,22]. The initial tangled crust layer, typically ≈ 1 µm thick, ends up at the top of VACNT due to base growth. The crust has a higher reflectance than the bulk VACNT since it has a higher density and is more uniform, so etching away the crust with an oxygen plasma treatment leads to lower reflectance.

Additionally, plasma-induced agglomeration of nanotube ends forms complimentary voids, which together significantly alter the morphology of the VACNT surface. The voids may behave as light traps for a range of optical wavelengths, further lowering reflectance.

In summary, oxygen plasma treatment is a simple post-growth method to reduce the reflectance of VACNT by altering the surface morphology, characterized by etching away the crust and inducing tip agglomeration.

4. Copyright disclaimer

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REFERENCES


