Mechanical Testing of Carbon Nanotube Arrays

Application Note

Jennifer Hay,
Agilent Technologies

Dr. Matthew R. Maschmann,
Air Force Research Laboratory, AFRL/RXBC Hybrid and Composite Materials,
Universal Technology Corporation

Dr. Jeffrey Baur,
Air Force Research Laboratory, AFRL/RXBC Hybrid and Composite Materials

Introduction

Carbon nanotubes (CNTs) are allotropes of carbon with a hollow cylindrical structure. Because CNTs feature extremely strong carbon-carbon bonding and excellent transport properties, CNTs have a wide variety of potential applications [1].

Chemical-vapor deposition (CVD) may be used to grow CNTs from a seeded substrate. Because of the significant relative density of CNTs originating from a growth substrate, resulting CNT arrays look like a fibrous carpet [2]. Within the array, Van der Waals forces bind nanotubes to each other.

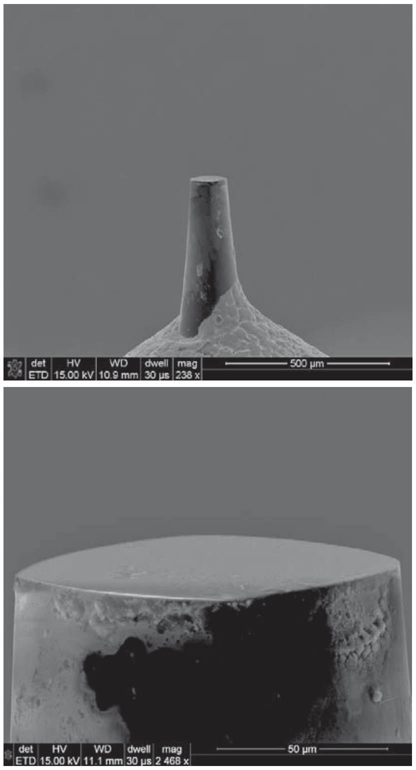

Figure 1. Flat-ended diamond cylindrical punch, D ≈ 100 µm.

CNT arrays have potential application beyond being a means for producing CNTs. CNT arrays, which provide a large surface area, may be used to efficiently dissipate heat. Single-walled CNTs feature a band gap that strongly depends on the chiral vector of individual tubes, so CNT arrays might potentially be used as conductors, semi-conductors, or insulators, especially within microelectronic devices. CNT arrays might also be useful as sensors, because conductivity depends strongly on mechanical strain. Successful incorporation of CNT arrays into a product requires the ability to both measure and control the mechanical properties of the CNT array as an array. Thus, the goal of the present work was to use an Agilent NanoIndenter to mechanically characterize CNT arrays.

In this situation, the data achieved with the NanoIndenter cannot be analyzed using standard data analysis, because we do not have contact between two uniform materials. Nevertheless, the NanoIndenter gives accurate and useful force-displacement data, even when that data must be analyzed in new ways.

Experimental Method

Two samples were tested: (1) A CNT array of 650 µm-long CNTs, and (2) an array of 35 µm-long CNTs. CNT arrays were grown on a silicon substrate by CVD reaction with an iron-based catalyst, following methods described elsewhere [3-5]. Growth was initiated and controlled so as to produce arrays of similar densities.

An Agilent NanoIndenter XP having the CSM option was used for this work. The CSM option allows the continuous measurement of stiffness. The cylindrical flat-punch indenter pictured in Figure 1 was used so that the resulting contact area would be known and consistent throughout a single test

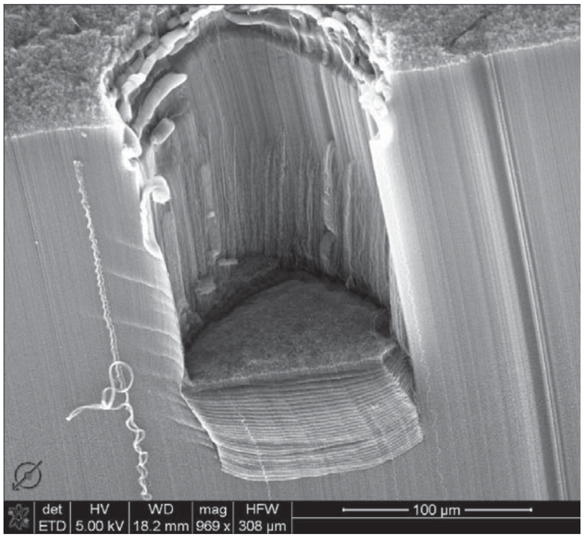

Figure 2. Residual impression of a 200 µm test at the edge of the long-CNT. Testing at the edge clearly shows accordion-style deformation. This image explains the saw-tooth features of the force-displacement data (Figure 4).

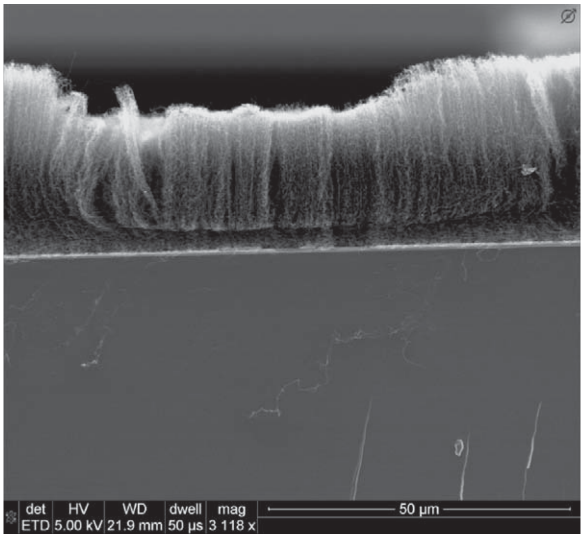

Figure 3. Residual impression of a 25 µm test at the edge of the short-CNT array. The image shows simpler mode-2 deformation.

and from test to test. (A NanoIndenter G200, configured in the same way would be able to do the same work.) This work required compressing CNTs a long distance: up to 200 µm. Thus, the XP-style actuator/sensor (also available on the NanoIndenter G200) was necessary for this work, because it provides the largest travel of any commercial nanoindentation device: up to 1.5 mm!

The continuous stiffness measurement (CSM) option measures contact stiffness (S) dynamically; to accomplish this measurement, the indenter was oscillated at a frequency of 50 Hz with amplitude of 2 nm. For each test, loading was controlled such that the loading rate divided by the load (P′/P) remained constant at 0.05/sec; loading was terminated when the indenter reached a penetration depth of 200 µm for the first sample (650 µm CNTs) and 25 µm for the second sample (35 µm CNTs). Twenty tests were performed on each sample.

In order to see the behavior of CNTs below the array surface, some indents were performed at the edge of the array and then imaged in a scanning-electron microscope.

Results and Discussion

Figures 2 and 3 show the “edge indents” on the long-CNT and short-CNT arrays, respectively. Force-displacement traces for indents into the midst of the long-CNT and short-CNT arrays are provided in Figures 4 and 5, respectively. Although the images in Figures 2 and 3 are not for the tests plotted in Figures 4 and 5, they are helpful in understanding the force-displacement traces.

The most intriguing result from this work is the deformation mode for the long-CNT array. Under the punch,

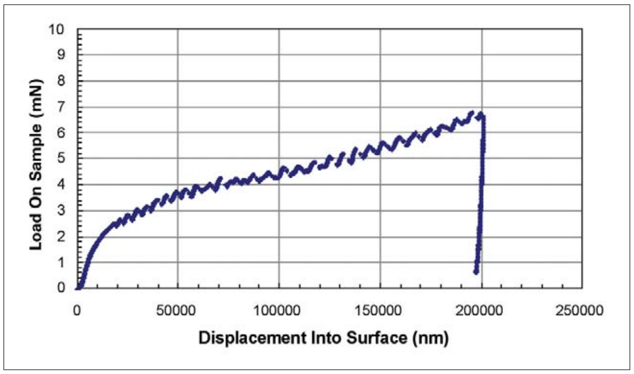

Figure 4. Exemplary force-displacement curve for a single test to 200 µm in 650 µm CNT array. Buckling events cause the “saw-tooth” appearance.

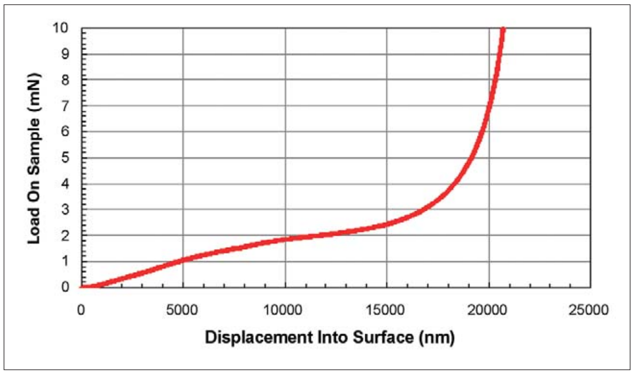

Figure 5. Exemplary force-displacement curve for a single test to 25 µm in 35 µm CNT array. Material becomes very stiff at large displacements.

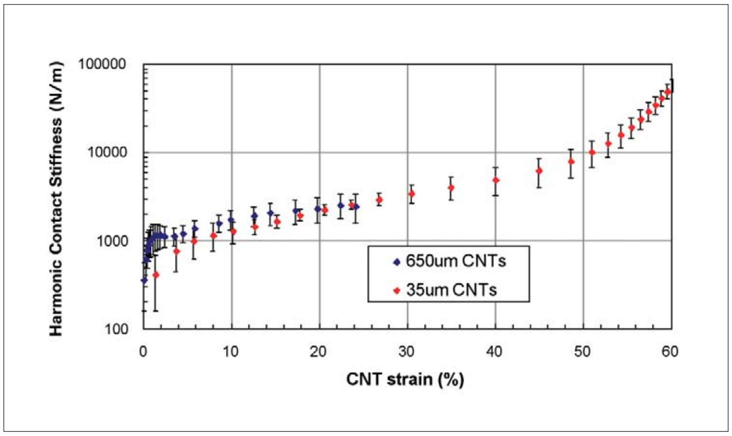

Figure 6. Average stiffness over all tests on each sample as a function of CNT strain (defined as surface penetration divided by original CNT length). Though modes of deformation are different, effective stiffness is comparable.

the longer nanotubes collapse like an accordion. Discrete buckling events are evident in the force-displacement data (Figure 4). Such a clear "saw-tooth" pattern confirms that the CNTs are behaving collectively; that is, all CNTs under the indenter locally buckle at the same time. The field of permanent deformation does not seem to incorporate any material below the "accordion". That is, the part of the CNT that doesn't collapse recovers completely. The force-displacement curve in Figure 4 shows about five microns of elastic recovery during unloading.

The short-CNT array also buckles (Figure 3), but not in the same way. The buckling seems to be of mode 2. The deformed CNTs have an "S" shape at the conclusion of the experiment. Moreover, the force-displacement data for these tests do not show any evidence of discrete events. However, at a consistent penetration, the array does become very stiff—the slope of the force-displacement curve increases dramatically.

The CSM option allows the continuous measurement of stiffness by means of a small oscillation. This measurement is particularly interesting for these samples. Figure 6 shows that despite the differences in deformation mode, both arrays exhibit the same stiffness as a function of CNT strain, where strain is defined as the indenter penetration divided by the original CNT length (either 650 µm or 35 µm).

Although we can't apply standard nanoindentation analysis to these CNT arrays, it is still useful calculate a modulus for the array. When using a flat punch indenter, elastic modulus, E, is calculated as:

$$E = S/D,$$

where S is the stiffness and D is the diameter of the punch [6]. At 20% strain, the array modulus is similar for both samples: about 20 MPa. The Young's modulus for individual carbon nanotubes is estimated to be on the order of teraPascal [1].

Conclusions

An Agilent NanoIndenter was used to mechanically test two CNTs arrays. Post-test imaging revealed significant differences in the mode of deformation and explained unusual features in the force-displacement data. Determining the cause(s) of the different deformation modes is the focus of ongoing work. Potential influencing factors include CNT density, alignment, aspect ratio, and boundary conditions.

As a function of CNT strain, the two arrays had similar stiffness. Array modulus was determined by dividing the measured stiffness at 20% strain by the diameter of the flat punch. At this strain, both arrays had a modulus of about 20 MPa.

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