Physical Property Characterization of Nanotubes, Nanowires, and Nanocoils Using a Zyvex S100 Nanomanipulator System

By Rishi Gupta and Richard Stallcup, Zyvex Corporation

Introduction

Over the last few years, researchers have developed many novel nanostructures, such as tubes, coils, and wires. Much of advanced materials research is being focused on the creation of stronger and lighter materials using these structures[1]. Nanotubes and wires are also of interest for the engineering of molecular electronics[2], biomedical devices[3], and nanoelectromechanical systems[4]. Theoretical models have predicted that these structures exhibit astounding mechanical and electrical properties[1,6], but characterizing the physical properties of isolated nanostructures *in situ* has presented a challenge to the research community.

Many researchers currently employ arduous lithography and microscopy steps to characterize electrical properties of carbon nanotubes. Dispersed nanotubes are first deposited onto a substrate and isolated nanotubes are then found by atomic force or scanning electron microscopy. Once a single nanotube has been located, metal pads are deposited in just the right area so that electrical measurements can be carried out using microprobes. Devices are made using similar methods[7].

In contrast, nanomaterial measurements can be conducted in free space using the Zyvex S100 Nanomanipulator, which eliminates the need for complex processing that can affect the physical properties of the material. The structures can be held, stressed, twisted, rotated, cut, and otherwise manipulated as if they were macroscale objects. The Zyvex S100 Nanomanipulator System effectively solves the problems afflicting researchers working to characterize nanoscale materials.

The Zyvex S100 Nanomanipulator System is designed specifically for manipulating and characterizing nanostructures and can serve as a platform to engineer nanoelectromechanical systems. The S100 System is a piezo-motor based manipulation system, which offers less than 5 nanometers of precision and 12 millimeters of travel range. The center stage rotates 360 degrees clockwise and counterclockwise with a resolution of 3 microradians. Each positioner has 5 electrically isolated input/output lines that can interface with test bench hardware through BNC connectors on the control cabinet. Coupled with low noise amplifiers and the NanoEffector™ suite of end-effectors, the S100 is capable of performing mechanical and electrical characterization on nanostructures in scanning electron microscopes (SEM).

The S100 is capable of performing many types of characterization. For nanowires, the current-voltage (IV) response is typically measured to determine the conductance (or inverse of resistance). This is done by contacting the nanowire with the S100 probes, which are connected to a current source and meter. For semiconducting wires, the IV response is non-linear and is used to determine the saturation limit of the nanowire. The S100 can also perform measurements to determine the field-induced current in a nanowire. By applying a field to a nanotube suspended between two probes, the induced current can be measured using current-meters.

The S100 is also capable of performing mechanical measurements on nanostructures. Typical mechanical measurements that can be performed with the S100 are Young's modulus, breaking strain, and compression strain. Each can be taken by using cantilevered probes of known moduli, or by utilizing Zyvex Corporation's extensive line of microelectromechanical systems (MEMS) -based devices.

One of the purposes of this application note is to describe methods for mounting a multiwalled carbon nanotube (MWNT) to an end-effector, which is the first step towards characterizing any isolated structure or engineering a nano-scale device. This note presents a discussion of the necessary materials, the set-up of the experiment, and the detailed procedure for mounting the nanotube. The reader will also learn about electron beam induced deposition (EBID), which is used as an adhesive binder, much as a weld is used to hold two objects together. Though this note discusses MWNTs, one can use this procedure to mount very small structures of different shapes, sizes, and composition. Finally, procedures are detailed which are useful for characterizing physical properties of nanostructures, such as conductance and Young's modulus.

Multiwalled Carbon Nanotube

The nanostructure discussed in this note is an individual MWNT. There are many suppliers and manufacturers of nanotubes. Unless the nanotubes are in aligned arrays, they will usually need to undergo some processing to loosen and untangle them prior to manipulation and testing. Many processes exist to unbundle tubes, such as sonication and treatment with surfactants, but these processes will not be discussed. See references 8 and 9 for additional information.

The nanotubes should be on a wire or flat surface. It is important that the long axes of the nanotubes protrude from the surface into free space and be orthogonal to the electron beam of the microscope. This allows the probe to gain access to the nanotubes, and it will also help the user to image the tubes under the SEM **(Figure 1)**. A good candidate nanotube tends to be long, relatively thin, and disentangled from bundles or neighboring tubes.

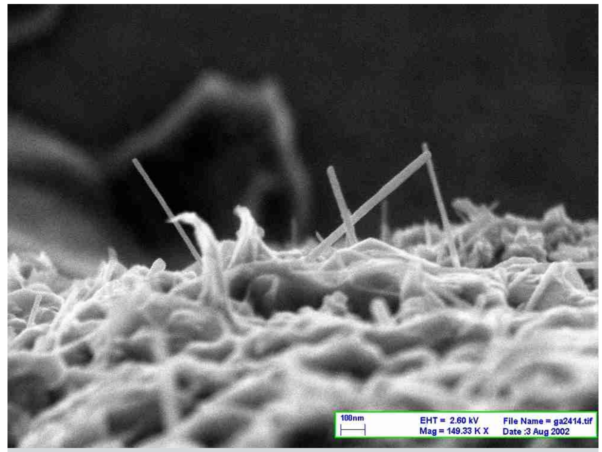

Figure 1 Multiwalled carbon nanotubes (Alfa Aesar).

End-Effectors

End-effectors are defined as the "tools" at the business end of the manipulator. The user selects the type of end-effector according to his/her specific application. The S100 functions with various types of end-effectors.

• NanoEffector™ probes are used for manipulation tasks that require probes with very small tip radii; they can be created with a radius of curvature from hundreds of nanometers to less than 15 nm **(Figure 2)**. The material of the probes is selected depending on the specific application. Tungsten probes are used for picking and placing of nanotubes; palladium (Pd) wires are well suited for electrical measurements and probing nanodevices (Pt and Pd coated tungsten wires are an alternative).

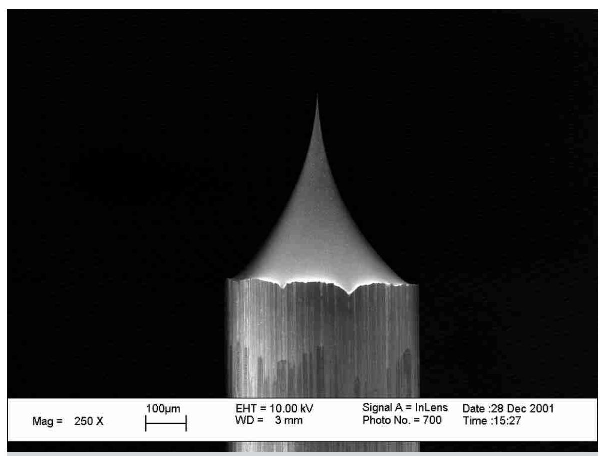

Figure 2 Zyvex NanoEffector™ Probe.

• MEMS-based grippers are used for grasping nanotube bundles and for mechanical characterization work.

• Cantilevered probes with quantifiable moduli are often used for mechanical characterization (**Figure 3**).[10]

The NanoEffector™ product suite is available from Zyvex Corporation. Call 877-ZYVEX99 (877-998-3999) ext. 271 or email sales@zyvex.com for more information.

Set-up

It is very important to set up the S100 properly before starting. All of the probes must make electrical contact to the cabinet. NanoEffector™ probes must be handled carefully to avoid damaging the tips.

The nanotubes need to be on a surface that is accessible to one or more of the probes. The rotational stage is a good place to mount the tubes, as opposed to mounting them in one of the end-effector plugs. In either case, the tubes should protrude from the surface so that they are normal to the electron beam and clear of obstructions. This will allow the probe to approach them while imaging at high resolution.

Once the S100 is in the SEM chamber, verify that the feed-through connectors are mounted properly. Always follow the procedure for handling and operating the S100 as prescribed in the *S100 User's Manual*.

Electron Beam Induced Deposition

EBID is a by-product of electron microscopy, but serves as a useful "welding" agent for nanotubes. EBID is caused by the dissociation of surface adsorbed molecules (hydrocarbons, for example) by high-energy electrons. EBID layers will act as a binder as the deposited amorphous material coats the nanotube.

Optimizing the Deposition

Koops, *et al.,* have investigated this phenomenon for a number of years[11]. From the literature, we see that the density N of adsorbed molecules on the substrate surface varies with time:

$$dN/dt = g * F * (1 - N/N_0) - N/\tau - q * N * f, \quad \textbf{(AppEq 1)}$$

using g as the sticking coefficient, F as the molecular flux density arriving on the substrate, N_0 as the molecule density in a monolayer, τ as the mean lifetime of the adsorbed molecule, q as the cross section for dissociation of the adsorbed molecules under electron bombardment, and f as the electron flux density. The layer growth rate, R, is

$$R = v * N * q * f, \qquad \textbf{(AppEq 2)}$$

where v is the volume occupied by a dissociated molecule or its fractions.

From AppEq 2, we can see that the growth rate depends on the cross section for dissociation of molecules in the path of the electron beam. From quantum mechanics, we know that the differential cross section for scattering is inversely dependent upon the energy of the incident particle. One should adjust the accelerating (EHT) voltage of the electron beam to optimize the deposition efficiency. As a rule, the lower the EHT value, the higher the electron cross section, allowing for a higher probability of electron-molecule interaction. However, there is a point of diminishing returns. The cross section will drop off at very low energies. Also, a lower mean free path will increase the EBID efficiency. Higher pressures result in an increased probability for electron-molecule collisions.

EBID is not a "fire and forget" technique. If the SEM image drifts away from the target region, material will be deposited onto undesirable areas. This could ruin the experiment, so care must be exercised to avoid image drift. Applying EBID to weld a nanotube to a probe is described later in this document.

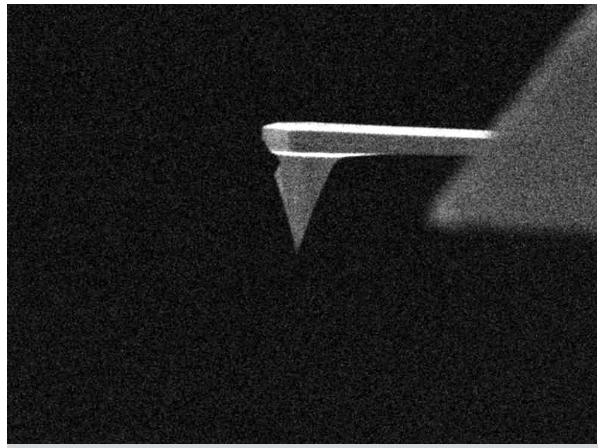

Figure 3 Atomic force microscope tip (Tapping Mode, MikroMasch).

An Alternative to EBID

Scientists have reported that an effective method for attaching nanotubes to probes is to dip the probes in glue before making contact with nanotubes. For example, Dai, *et al.* demonstrated attachment of nanotubes to scanning probe microscopy probes by bringing the probe tip in contact with carbon tape *in situ*[11]. This method is easily performed with the S100.

For this process, carbon tape (acrylic adhesive) is necessary in addition to the aforementioned materials. Apply the carbon tape to an unsharpened wire and place it into one of the inputs on the end-effector plug. It can also be placed on the center stage. Bring the probe into contact with the adhesive. **Figures 4** shows what a bead of adhesive looks like under electron microscopy; **Figure 5** shows the hook-shaped probe immersed in the adhesive. Retract the probe and approach the target nanotube. The drawback of using the adhesive is less control over where, when, and in what state the nanotube sticks to the probe. It may also be difficult to ensure ohmic contact to the probe even though the carbon tape tends to be electrically conductive.

If the SEM has lithography capabilities or a focused ion beam, metals may be used as the binding material. The focused ion beam works in a similar manner as EBID, but one should follow the manufacturer's instructions. An integrated lithography system can be very useful for depositing and patterning materials other than carbon.

Performing the Experiment

This section will describe the procedure for making contact to the nanotube and detail the processes needed to optimize the visual feedback.

SEM Modes of Operation

There are different modes of operation for each microscope (i.e., reduced scan or spot mode). One can observe the motion of the manipulator and the nanotubes with high resolution in near real-time by utilizing the "reduced scan size" operating mode, where the electron beam raster scans across a smaller area. The ideal mode of operation for applying EBID is "spot mode," where the electron beam is fixed upon a single point.

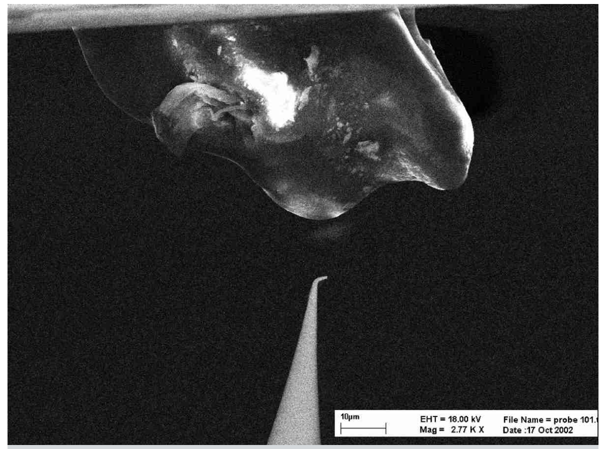

Figure 4 Electron micrograph of a hook-shaped sharpened tungsten wire on approach to a bead of adhesive. The bright region is charge build-up.

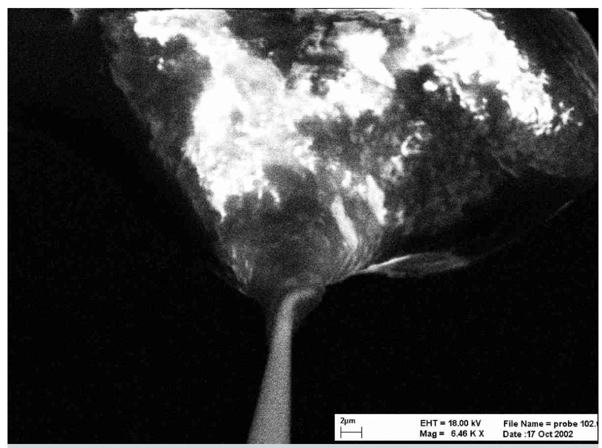

Figure 5 The tungsten wire submerged in the acrylic adhesive.

Approaching the Carbon Nanotube

The best way to start approaching a carbon nanotube (CNT) is to select a target nanotube, as defined above. Begin by using the coarse positioners to bring the end-effector within 10 microns of the nanotube (the range of the fine positioners is 100 microns in the X- and Z-direction and 10 microns in the Y-direction using the "Local Coordinate System"). The coordinate system is best described by taking the positive Y-direction to be towards the center stage for each positioner. The positive Z-direction is out of the plane of the center stage. The X-direction is then orthogonal to the Y- and Z-directions. **Figure 6** shows a probe that can reach a bundle of nanotubes using the fine positioners.

The nanotube is best approached from underneath. This way, you can see it deflect when contact is made, and the probe will be in the best position to apply EBID **(Figure 7)**. Using the Z-axis of the fine positioner, slowly bring the end-effector into contact with the nanotube **(Figure 8)**. Verify contact by watching the nanotube deflect.

If the nanotube is loose enough, the user can remove it from the surface via *van der Waals* forces alone (*van der Waals* forces arise from induced dipoles in neighboring molecules that result in a relatively weak attraction). At this point, retract the probe by moving the fine positioner in the negative Y direction. The nanotube should slip out, being stuck to the probe. If the nanotube needs to be bound more strongly to the probe, try performing electron beam induced deposition to affix it to the probe.

Applying EBID

To apply EBID, use either a reduced scan size or the spot mode of operation. If possible, decrease the electron beam voltage (lower electron energy increases the electron cross section, increasing the probability of dissociation from electron-molecule collisions). We have found that 1.5 – 5.0 kV works well for us. While in focus on the nanotube and the probe, scan the reduced area for several minutes. The electron beam will deposit amorphous carbon material, which tends to be ubiquitous even in high vacuum environments in the form of hydrocarbons. The rate of EBID deposition will depend on the hydro-carbon partial pressure in your vacuum system. In particularly clean systems, the rate of material deposition may be low. This material will bind the nanotube to the probe. Retract the probe as described above once sufficient material has been deposited **(Figures 9-12)**.

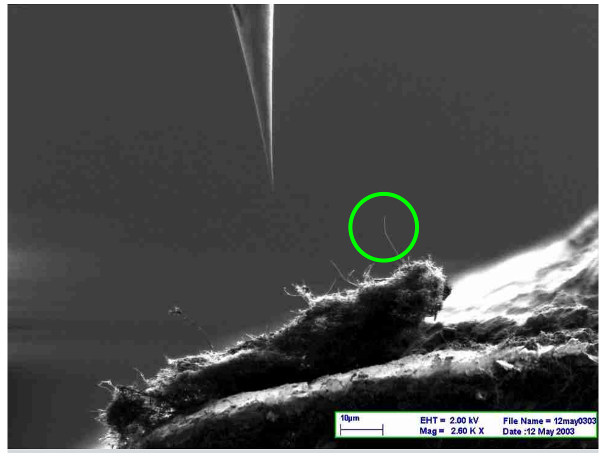

Figure 6 On approach to the nanotube (circled) using the coarse positioners (Mitsui CNTs, Leo 1550 FE-SEM, Zyvex S100).

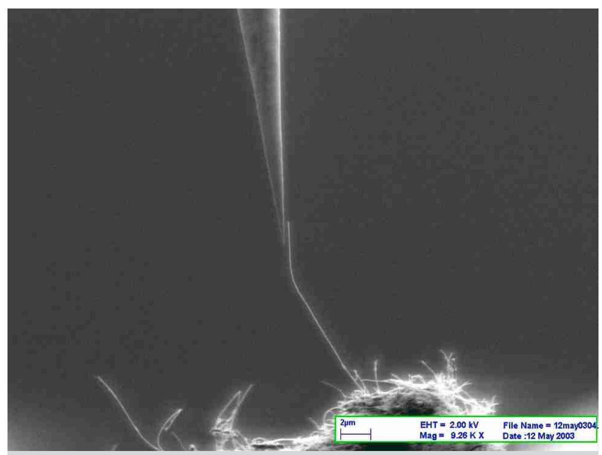

Figure 7 Fine positioner adjustments to maneuver close to the nanotube.

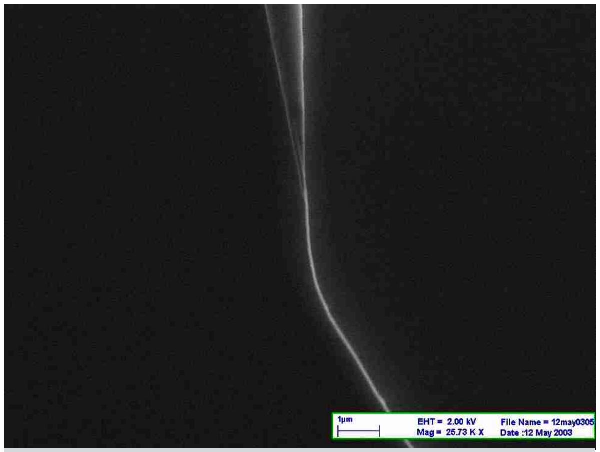

Figure 8 Contact to the nanotube.

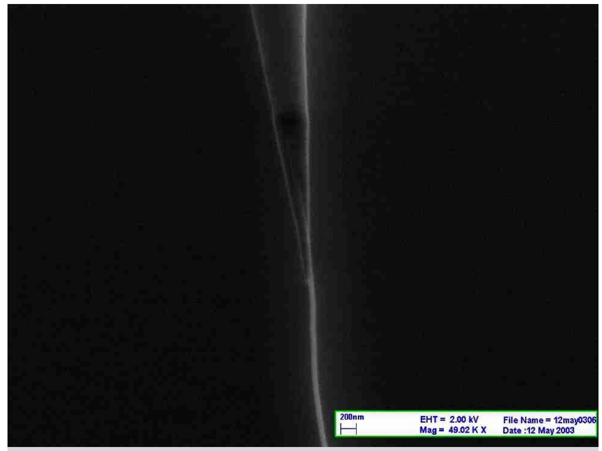

Figure 9 Apply EBID.

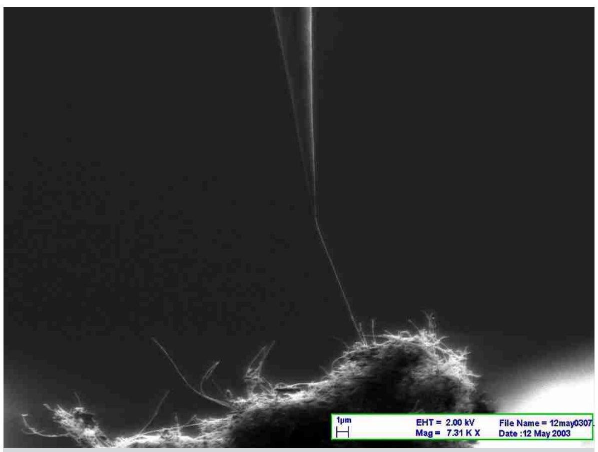

Figure 10 Begin pulling the nanotube from the surface.

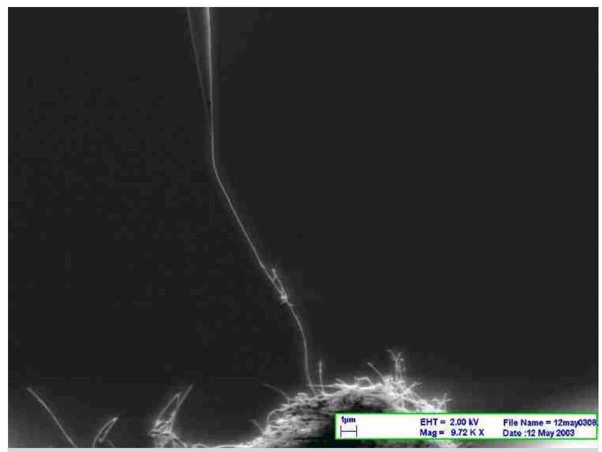

Figure 11 The nanotube loosened and beginning to come out.

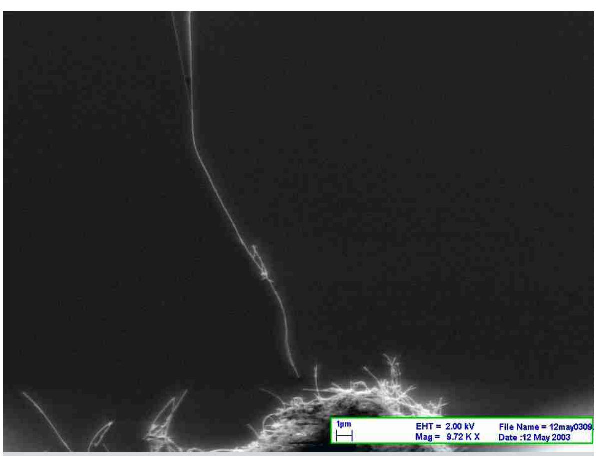

Figure 12 The nanotube free from the surface and attached to the probe.

Towards Characterization

The S100 can perform electrical and mechanical measurements on nanostructures. The suite of Zyvex NanoEffectors™ includes NanoEffector™ probes, MEMS grippers, and AFM cantilevers. Electrical and mechanical measurements can be carried out by utilizing the unique functional characteristics of each.

The electrical properties of multiwalled carbon nanotubes have been studied. Current experimental procedures for measuring the electrical properties utilize lithography processes that not only require time and a fabrication facility but also run the risk of altering the very physical properties that need to be measured[13]. The S100 can be used to make electrical measurements without the complexity of standard experimental techniques.

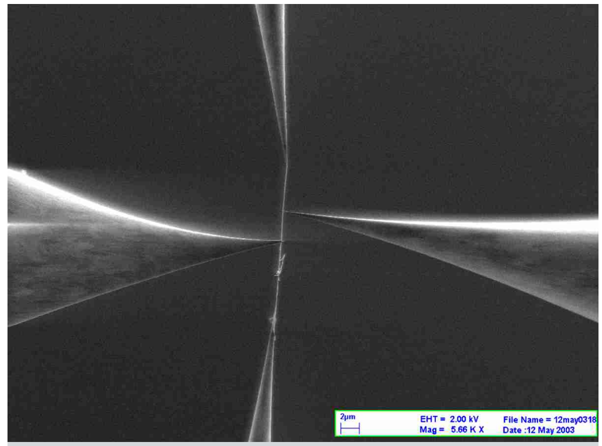

Figure 13 Four-probe configuration for electrical characterization of a multiwalled carbon nanotube.

Electrical measurements can be accomplished using two or four NanoEffector™ probes, depending on user preference. **Figure 13** shows a nanotube in a four-probe configuration. Four-probe electrical measurements are made to compensate for contact resistance between the forcing probes[14]. A current is supplied between the outermost probes. The voltage is then measured between the innermost probe. The IV response depends on the type of nanowire. If the wire is metallic, then the conductance is ascertained by Ohm's law, and a plot of the current *versus* resistance will be linear.

Multiwalled nanotubes however, are complex structures due to the layering of metal and semiconducting tubes. The contribution from inner layers of the multiwalled nanotube can be gauged by successively removing the outer layers[13,15].

CNTs have quantized conductance based on the electrode position on the nanotube[16]. The S100 can position probes at different points along the nanotube to observe the quantized conductance of the nanotube. Another interesting characterization metric is the field-induced electrical response of nanostructures. The S100 can apply an external field to a nanowire that is suspended between two probes. The induced current can be measured with a low-noise ammeter.

Mechanical measurements are made by using cantilevered probes. The nanotube is suspended between the two cantilevered probes, which have disparate moduli. Applying tension to the nanotube by displacing the probes with the S100 positioners causes the weaker cantilever to bend. This bend magnitude can be measured in the SEM and a force can be calculated, which translates to the modulus of the nanotube. Also, the breaking strain and compression strain can be calculated this way[9,17].

A compression strain can be ascertained by bringing the cantilevers together with the fine positioners. A rigid nanowire will cause the cantilevers to bend until the force on the nanowire causes it to buckle. This force is the compressive force and can be determined by measuring the displacement of the cantilevers as the load is applied. This process will not work for nanowires and nanotubes that are very flexible. In fact, long carbon nanotubes will bend before buckling. Rigid nanostructures such as silicon or boron nitride nanowires are better candidates for AFM cantilever based compression testing.

MEMS-based grippers can be used to characterize the force-deflection characteristics of nanotubes[18]. Mechanical characterization of nanotubes with MEMS devices has been performed using complex, AFM-based manipulation systems that require long experiment times and costly equipment [19]. The S100 can position nanotubes between silicon-based, thermally-actuated beams. The beams, or flexures, can be calibrated for moduli in the SEM, and are actuated with a DC voltage source. When the nanotube is positioned between the beams and the beams are displaced, the modulus of the nanotube can be calculated. This is advantageous over other methods since the calculations for the modulus are not solely dependent upon observations of the cantilever displacement ascertained by visual feedback from the SEM. The silicon flexures can be calibrated for displacement per unit voltage, and the supplied voltage measured during the experiment translates into the force applied to the nanotube.

The mechanical properties of the nanotube can also be ascertained from its parametric resonance frequency. A nanotube will oscillate at a particular frequency and amplitude depending on its length and diameter. This resonance frequency translates to a Young's modulus value[20]. Once a nanotube is affixed to a probe, it can be stimulated for resonance using a second S100 probe **(Figure 14)**. The two probes are connected by an alternating current source, and the nanotube feels the effects from the alternating field.

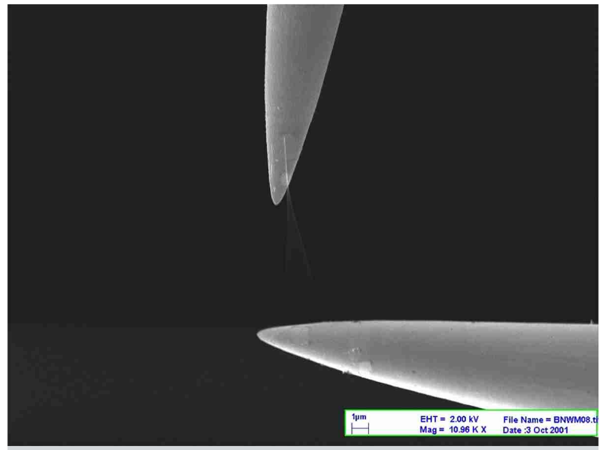

Figure 14 A boron nanowire in resonance. The nanowire is affixed to the top probe and is being excited by field effect from the probe on the right.

Conclusions

The Zyvex platform of nanomanipulator tools was designed to facilitate the physical property characterization of nanoscale structures. The procedure for making contact with a nanotube is straightforward and makes use of the most fundamental capabilities of the S100. Nanotube and nanowire research has long been stifled by the inability of scientists to isolate individual nanostructures. The Zyvex S100 Nanomanipulator simplifies the task by enabling picking, placing, stretching, bending, and stimulating nanotubes with relative ease. The procedures developed are directly applicable for manipulating and characterizing nanostructures of different materials such as germanium or boron. Interfacing to test bench hardware is seamlessly achieved through an easily accessible BNC patch panel. The multiple probe configurations facilitate two, three, and four probe electrical measurements on nanostructures, nanomaterials, and nanodevices. Coupled with Zyvex Corporation's NanoEffector™ suite of tools, the S100 is the most versatile instrument for novel materials characterization and nanoscale device engineering on the market.

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