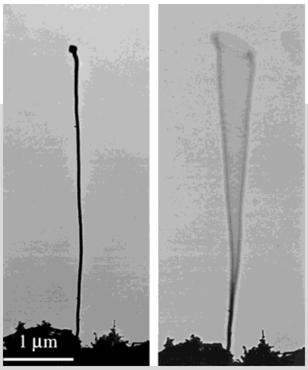
Characterizing the Structure and Properties of Individual Wire-Like Nanoentities**

By Zhong L. Wang*



A new approach to the characterization of the mechanical and electrical properties of individual nanowires and nanotubes is demonstrated by in-situ transmission electron microscopy (TEM). The technique allows a one-to-one correlation between the structure and properties of the nanowires. Recent developments include the determination of the Young's modulii of carbon nanotubes and semiconductor nanowires, femtogram nanobalance of a single fine particle, field emission of carbon nanotubes, and quantum ballistic conductance in carbon nanotubes.

1. Introduction

Nanotechnology is the science of designing and manipulating materials through atom-by-atom engineering. There are four critical challenges in the development of nano-scale science and technology: materials synthesis with controlled structure and precision at the atomic/molecular scale, property characterization of the structurally well understood components, nanodevice fabrication, and system manipulation and integration. There is great diversity in the size and structure of nanomaterials, and thus their properties, which strongly depend on size, size distribution, shape, and chemical composition, vary widely.[1] The properties measured from a large quantity of nanomaterials could be an average of the over all properties, so that the unique characteristics of individual nanoentities could be lost. An essential task in nanoscience is the property characterization of individual nanostructured components with well-defined atomic structures.

A key challenge for today's research is the experimental difficulty in fabricating, manipulating and testing the physical properties of a single nanostructure whose size is in the nano- to micrometer range. The size (diameter and length) is rather small, prohibiting applications of the well-established testing techniques. Tensile and creep testing of a fiber-like material, for example, require that the size of the sample be sufficiently large to be clamped rigidly by the sample holder without sliding. This is impossible for nanostructured fibers using conventional means. Therefore, new methods and methodologies must be developed to quantify the properties of individual nanostructures.

Scanning probe microscopy (SPM), which combines scanning tunneling microscopy (STM) and atomic force microscopy (AFM), has been the most powerful tool in designing, manipulating, and characterizing the structures and properties of nanoentities. But the interior atomic-scale structure of the nanomaterial may not be revealed by the SPM technique. To solve this problem, we have recently developed in-situ transmission electron microscopy (TEM) as an effective tool for measuring the properties of individual wire-like nanostructures.[2,3] This is a new approach that not only can provide the properties of an individual nanowire but also can give the structure of the nanowire through electron imaging and diffraction, providing an ideal technique for understanding the property–structure relationship of a well defined nanostructure. This paper reviews our recent progress in applying in-situ TEM for characterizing the mechanical, field emission, and electrical properties of nanowire-like structures.

2. One-Dimensional Nanowire-Like Structures

One-dimensional nanostructures are ideal systems for investigating the size controlled mechanical and electrical properties. Carbon nanotubes, for example, exhibit a variety of shapes, such as straight, curved, planar-spiral, and helical,[4] simply because of the existence of the hexagon, pentagon, and heptagon carbon-rings. A geometrical combination of the three types of configurations at a different spatial matching

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[*] Prof. Z. L. Wang
School of Materials Science and Engineering
Georgia Institute of Technology
Atlanta, GA 30332-0245 (USA)
Email: zhong.wang@mse.gatech.edu

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and proportion can make any desired geometrical shapes. Helical and zigzag shape carbon nanotubes have been observed (Fig. 1a), which are suggested to be the results of kinetically controlled growth.[5]

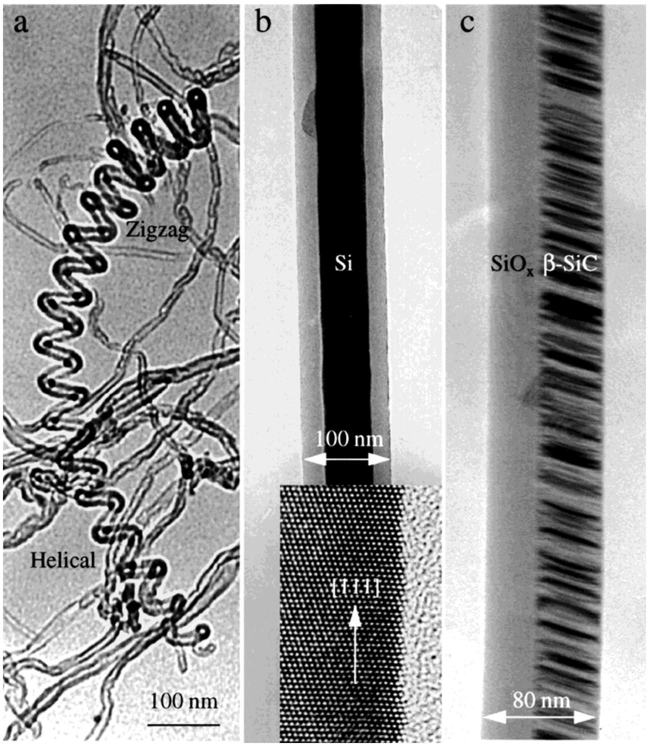

Fig. 1. Typical one-dimensional nanowire structures of a) helical and zigzag carbon nanotubes, b) defect-free Si nanowires sheathed by silica (the inset is an atomic-resolution TEM image of the nanowire), and c) the side-by-side SiC–SiO_x biaxial nanowires.

Nanowires synthesized by vapor–liquid–solid (VLS) technique can be solid cylindrical nanowires[6–8] and coaxial cable nanowires.[9] Devices made using nanowire heterojunctions can be critical for nano- and molecular-electronics.[10–13] Using a modified synthesis technique, we have reported defect-free Si nanowires[14] (Fig. 1b) and biaxially structured silicon carbide–silica nanowires (Fig. 1c),[15] composed of side-by-side sub-nanowires. The success of synthesizing semiconductor–oxide composite nanowires clearly demonstrates that control over growth conditions can produce unique nanostructures, which can be potential candidates for building devices in the wires. The non-uniform passivation of the silica onto the SiC sub-nanowire, as shown in Figure 1c, suggests that it is possible to create p–n junctions across the SiC nanowire using a thickness-controlled diffusion of dopants (such as phosphorous or boron) through the silica barrier.

3. Mechanical Properties of Wire-Like Nanostructures

Mechanical characterization of individual nanowires has been performed by AFM. By deflecting on one-end of the nanofiber with an AFM tip and holding the other end fixed, the mechanical strength has been calculated by correlating the lateral displacement of the fiber as a function of the applied force.[16,17] This type of measurement has two major limitations. The tip–fiber contact and interface sliding are unknown, and the tip could be deformed if the nanowire is harder than the tip. Quantifying the vibration amplitude of a carbon nanotube resulted from thermal vibrations can give the Young's modulus,[18] but the experimental error is quite large.

To carry out the property measurement of a nanowire structure, we have built a TEM specimen holder that allows a voltage to be applied across the nanowire and its counter electrode.[2,3] The nanowire was glued using silver paste onto a gold wire, through which the electric contact was made. The counter electrode can be a droplet of mercury for electric contact measurement or Au/Pt balls for field emission characterization. The measurements can be performed on a specific nanotube whose microstructure is determined by transmission electron imaging and diffraction. If we apply to the nanowire an oscillating voltage whose frequency can be tuned, then mechanical resonance can be induced on the charged nanowire. When the applied voltage frequency equals the natural resonance frequency of the nanowire, resonance is observed directly under the TEM (Fig. 2). The Young's modulus of the nanowire can be derived from the observed resonance frequency. Using this technique, the bending modulii have been measured for carbon nanotubes produced by arc-discharge,[2] carbon nanotubes produced by pyrolysis,[19] carbon nanotubes coated with polymer,[20] and SiC–SiO_x composite nanowires.[15]

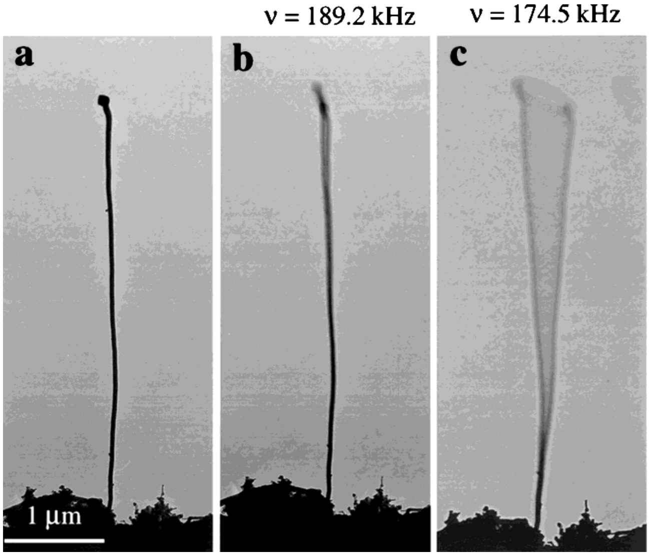

Fig. 2. A selected Si nanowire at a) stationary, b) the first harmonic resonance with the vibration plane parallel to the viewing direction, and c) the resonance with the vibration plane perpendicular to the viewing direction. A slight difference in the resonance frequencies in b) and c) results from the anisotropic structure of the nanowire.

4. Nanobalance for Single Particles of Submicrometer Sizes

It is known that the mass of an atom or a cluster of atoms can be precisely measured by a mass spectrometer. A particle in the picogram range or larger can be measured using quartz balance. But there is a technical gap for measuring the mass of a particle in the femtogram range. This is the range that is most interesting to biological and biomedical sciences, such as the mass of a virus. This problem may be solved using the resonance principle illustrated above.

Analogous to using a spring balance, the mass of a particle attached at the end of the spring can be determined if the vibration frequency is measured, provided the spring constant is calibrated. This principle can also be applied to determining a very tiny mass attached at the tip of the free-end of the nanotube (Fig. 3). The mass of the particle can be derived by the shift in resonance frequency resulted from a change in moment of inertia. This is the newly discovered "nanobalance", which has been demonstrated to measure the mass of a particle of ~22 fg.[2]

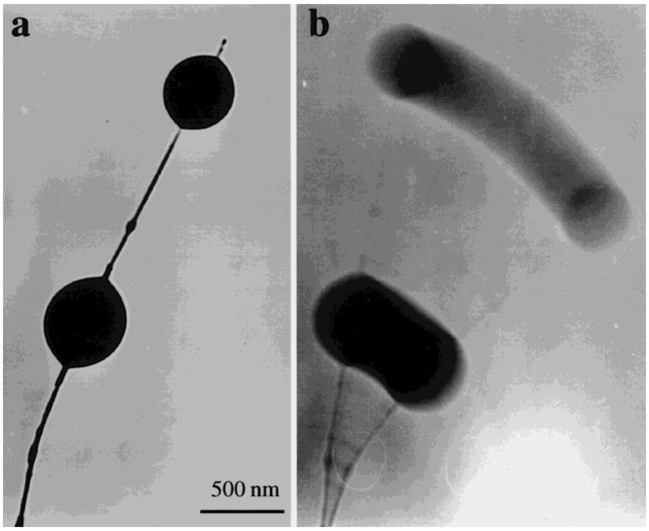

Fig. 3. Submicrometer size small particles attached at a carbon nanotube that is a) stationary and b) at the first harmonic resonance. The effective mass of the particle is estimated to be ~30 fg (1 f = 10^{-15}).

5. Electron Field Emission from a Single Carbon Nanotube

The unique structure of carbon nanotubes indicates they are ideal objects that can be used for producing high field-emission current-density in flat panel displays. The measured *I–V* curve is an averaged contribution from all of the aligned carbon nanotubes, which show considerable variation in diameter and length. Using the in-situ TEM setup we have built, the electric field–induced field-emission characteristics of a single carbon nanotube can be studied. Figure 4 shows a pair of TEM images of carbon nanotubes that are emitting electrons at an applied voltage. The contrast near the tips of the nanotube is due to the potential field induced by the tip charged electrons. A detailed analysis of the field distribution near the tip is expected to provide the threshold field for field emission and many other properties.

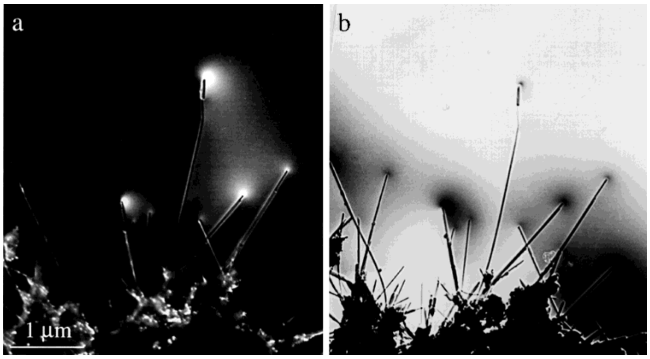

Fig. 4. a) Dark-field and b) bright-field TEM images recorded from carbon nanotubes when a DC voltage of 150 V was applied, showing the distribution of electrostatic potential at the tips of the nanotubes.

Structure damage can be introduced at the tip of a carbon nanotube if the strength of the applied field exceeds a certain limit. Shown in Figure 5 is a series of TEM images recorded from a carbon nanotube during its field emission. As the applied voltage increases from 80 to 130 V, the nanotube is experiencing rapid structural damage starting at the tip. The damage occurs in the form of pilling off, similar to a process of chopping off a wood stunk, and part of the segment is cut off abruptly and completely. This type of damage is believed to leave a high density of dangling bonds on the surface of the carbon tube as a result of the broken graphitic sheets. More importantly, we found that the carbon nanotube vibrates during field emission, resulting in fluctuation in the emission cur-

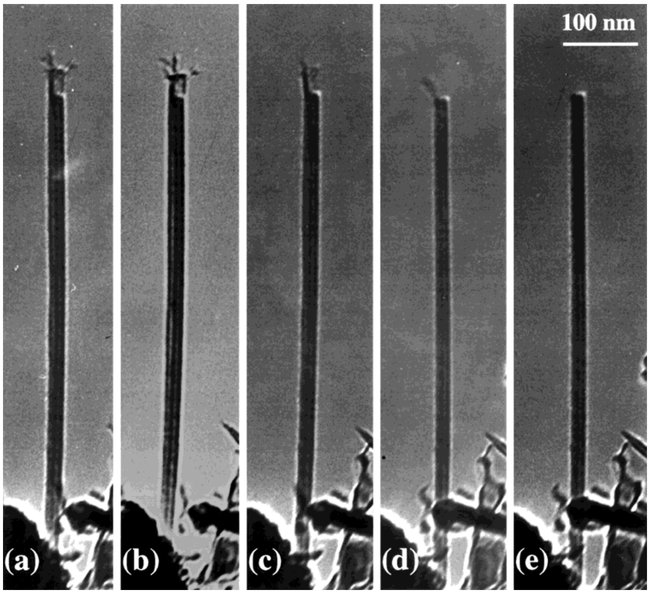

Fig. 5. A series of TEM images showing the electron field emission induced structural damage at the tip of a carbon nanotube as the applied voltage increased from 80 to 130 V.

rent. The quantized conductance observed from multi-walled carbon nanotubes at room temperature[21] has been successfully repeated using the in-situ TEM technique.

6. Conclusions

The small size of nanostructures constrains the applications of well-established testing and measurement techniques, thus new methods and approaches must be developed for quantitative measurement of the properties of individual nanostructures. This paper reviews our progress in the use of in-situ TEM for the measurement of the mechanical, field-emission, and electrical properties of individual nanowires with well-characterized structures. This is a new approach towards nanomeasurements, which can uniquely combine the measured result with the atomic-scale structural information provided by TEM, leading ultimately to a quantitative understanding of structure–property relationships for nanowire-like materials.

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