High Lateral Resolution Imaging with Sharpened Tip of Multi-Walled Carbon Nanotube Scanning Probe

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Received: July 23, 2003; In Final Form: November 4, 2003

We report a tip sharpening process for multiwalled carbon nanotube (MWCNT) scanning probes and demonstrate its application in high lateral resolution imaging. The sharpening of the tip is an in-situ process employing the atomic force microscope. The method involves current-induced oxidation in ambient atmosphere by locally stripping away the outer layers at the very tip of the MWCNT. This process requires an applied voltage in the 2−3 V range, which is lower than that required for shortening the nanotube. Direct scanning microscopic data reveal sharpened tips with a radius of curvature normally less than 5 nm. Multiple scan experiments show that the sharpened tips undergo no degradation in image quality, suggesting that the sharpened tips are very robust. Our unique fabrication process for producing a robust multiwalled CNT scanning probe coupled with the tip sharpening method has demonstrated the development of a universal probe for high aspect ratio as well as high lateral resolution imaging applications.

Introduction

The extraordinary mechanical properties of carbon nanotube (CNT) together with its nanoscale diameter and high aspect ratio make it an ideal tip in scanning probe microscopy.[1] These probes are one of the many potential applications of CNTs,[2] and are increasingly used by the research community as well as industry. CNT scanning probe technology is gaining importance in semiconductor metrology both as a profilometer[3] and in the characterization of thin films and surfaces,[4] especially as the critical dimensions of devices approach the nanometer regime. The considerable mechanical flexibility of CNTs—the ability to buckle elastically—allows the tube to buckle without damage and thus retain the structural integrity. Just as important, this buckling limits the maximum force that can be exerted onto the sample, thus preventing damage to delicate samples, especially those of biological origins.

There are two varieties of CNTs:[2] the single-walled and the multiwalled CNT (SWCNTs, MWCNTs). As the name implies the single-walled CNT is composed of a single roll of graphene sheet, and therefore tends to have a smaller diameter than the MWCNTs. The interest in high lateral resolution imaging has attracted much attention to the development of single-walled CNT scanning probes.[4−6] In contrast, multiwalled CNTs with their many layers of concentric tubes have larger diameters, normally ranging from 10 to 50 nm. These multiple layers give MWCNTs a stiffer structure, which in turn results in less thermal vibration compared to SWCNTs. Due to this intrinsic stiffness, a MWCNT is preferred as the tip for scanning probes in high aspect ratio imaging applications. We have recently demonstrated the ability of a MWCNT probe to image a 90 nm critical dimension line and space photoresist pattern derived from 193 nm generation photolithography.[3] A micron long MWCNT has a calculated value of lateral (thermal) vibration amplitude of less than 0.5 nm at room temperature. Our probe images in ref 3 showed a high aspect ratio photoresist pattern with nearly vertical sidewalls. Supported by these data, the tip of a multiwalled CNT probe seems to undergo little or negligible thermal vibration at room temperature. In comparison, a 1 nm diameter SWCNT must have a length of no more than 20 nm in order to have less than 0.5 nm amplitude of lateral vibration.[7] Hence imaging of high aspect ratio features in the hundreds of nanometer length-scale is limited to the MWCNT scanning probes.

The stiffness of MWCNTs also allows for a free-standing structure and thus is easier for manipulation. Nakayama and co-workers[8,9] demonstrated this manipulation in a scanning electron microscope (SEM) where an individual MWCNT was attached to the surface of a Si probe. In our work,[10] we improved the source of the nanotubes, which is composed of spatially separated free-standing MWCNTs grown directly on the surface of a thin wire. This source of low-density MWCNTs enables the manipulation of an individual scanning probe by optical microscopy.[10] Hence we can manipulate an individual multiwalled CNT rather than a bundle as in other processes. Also, our approach does not require an adhesive for attaching the CNT to the surface of the Si probe; instead, an electrical current is used to weld and strengthen the point of attachment of the CNT to the surface of the tip of the cantilever. An electric field is also used to properly orient the CNT with respect to the Si tip. This approach produces probes with a very strong attachment and an optimal directional orientation. The probes retain good structural integrity, and yield the same high-resolution images even after multiple scans over more than a 10 h period.[4]

It is of interest to produce MWCNT tips with tip diameter comparable to SWCNTs. Removing the outer layers in the tip region would undoubtedly afford a smaller diameter probe. Hence, developing a simple method for the local removal of

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10.1021/jp0361529 CCC: $27.50
Published on Web 02/06/2004

the outer graphitic layers at the tip of the MWCNT probe would prove to be an important and practical method for improving its lateral resolution. Cumings et al.[11] have demonstrated in a transmission electron microscope (TEM) that the outer layers at one end of a MWCNT can be stripped away. This paper reports a new tip sharpening process for the MWCNT scanning probes suitable for high lateral resolution applications, as an alternative to the SWCNT probe. This method produces high lateral resolution scanning probes, while still maintaining the robustness associated with a multiwalled CNT probe. Data demonstrating the imaging capability and the durability of these sharpened tips are presented.

Methods

The CVD synthesis of the MWCNT[12] and the fabrication of the MWCNT probes[10] have been reported previously. Typically, MWCNT probes have length ranging from less than 1 μm to as long as 10 μm, which often required shortening by in-situ AFM method using high potential (>7 V). Digital Instrument Nanoscope III Multimode AFM (Santa Barbara, CA) was employed for the in-situ sharpening of the MWCNT probes as well as the acquisition of images with the MWCNT probes. Typical settings for the sharpening procedure are as follows: 1.0 V tapping amplitude, and a Z distance of 1000 nm at 1 Hz. The contact of the tip of the MWCNT probe to the electrode surface was manually adjusted in the force−distance plots such that the MWCNT tip is in soft contact with the substrate (>5 nm past the initial point of contact as monitored with the cantilever amplitude vs distance plot). The electrode substrate consisted of a 20 nm ion-beam-sputtered Ir film on a low resistive (<0.001 ohm cm) Si chip. A 1−2 s pulse of 2−3 V DC field is applied to the negatively biased tip with an HP model E3631A power supply. A Keithley model 237 power supply, with a GPIB/Lab View PC interface for data acquisition, was used for current−voltage measurements.

Results and Discussion

Figure 1 shows a schematic of the AFM manipulation of a MWCNT probe tip to bring it in soft contact with the surface of a metal electrode. The piezoelectric positioning allows for the precise control of the nanotube tip for making contact with the metal electrode. In the AFM force calibration plot (Figure 1b), the white arrow shows the point of contact of the nanotube tip to the surface resulting in the dampening of the cantilever amplitude. A voltage of 2−3 V is applied to the negatively biased CNT tip as it intermittently makes contact with the metal surface in the force calibration routine. SEM images (Figure 2) of the probes that underwent this procedure clearly show that the diameter of the tip is smaller than that elsewhere along the length of the tubes. Consistently, this simple method allows us to produce MWCNT probes with a tapered tip.

This AFM-based technique is commonly employed to shorten the length of the tube of CNT probes,[10] albeit requiring a much higher applied voltage (for example, about 7 V). Since a much smaller voltage is used for sharpening, the damage to the nanotube is minimized during this process. Unlike the previously reported in-vacuo TEM method,[11] our procedure is performed in air and therefore the underlying mechanism for sharpening may also be different for the two methods. For the in-situ AFM sharpening process, we detected a current ranging from 0.01 to 0.1 μA, at a 2 V bias. The in-vacuo TEM process reported a high current of 200 μA at 2.9 V for the removal of the outer graphitic layers; however, at a lower applied voltage, 2.4 V and

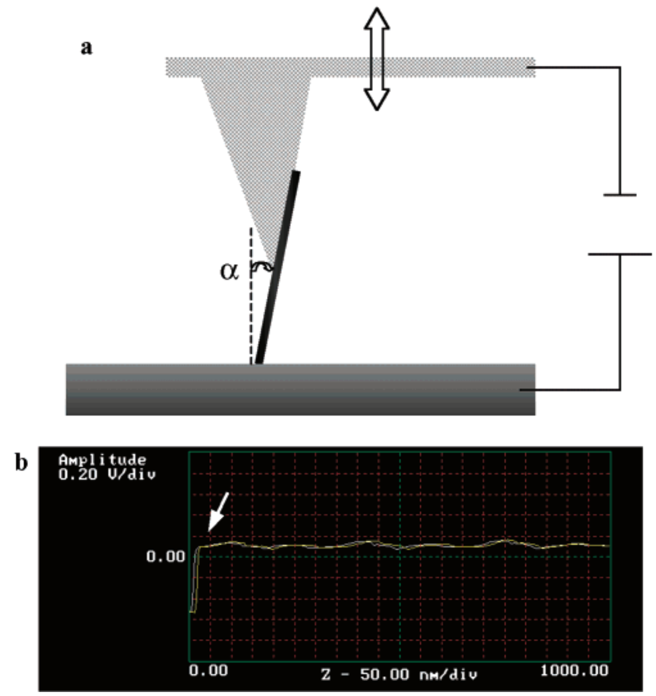


Figure 1. Schematic representation of the in-situ AFM sharpening process for the multiwalled CNT probe: (a) diagram showing the AFM piezoelectric control placement of the tip of the CNT in reference to the metal electrode surface, with the cantilever resonating to allow the CNT tip to make intermittent contact with the metal surface; (b) A plot showing tip amplitude versus distance as obtained from the force calibration mode of the AFM; the initial dampening of the amplitude indicates the point of initial contact with the electrode surface (white arrow).

170 μA, no tip sharpening was observed. In our AFM sharpening technique, a much lower detectable current is still sufficient to cause the etching of the outer layers and reducing the size of the tip of the CNT probe.

There are multiple possibilities for the observation of a low, yet wide range of voltages in the AFM sharpening process. The broad range in the detectable current may be a result of the variation in the nanotube angle (ϕ) relative to the surface normal (See Figure 1a), which in effect changes the configuration and contact area of the nanotube tip with the electrode surface. It is interesting to note that when the CNT is at an ϕ greater than about 30° from the surface normal, an asymmetric tip structure is obtained after sharpening, i.e., uneven stripping of the outer layers (see the TEM images in Figure 2C).[13] Another likely explanation for the observed low current is that the in-situ AFM process is nonstatic. That is, the CNT tip is in intermittent contact with the surface as it resonates with the cantilever (in the 10−100 kHz regime at an amplitude of about 10 nm); in addition, the whole CNT probe assembly is set to approach the surface at a frequency of 1 Hz in force calibration mode.

The use of electrical current in air for the selective removal of the outer layers of the multiwalled CNT has been reported by Collins et al.[14,15] A high current density was reported to be required for the removal of the outer layer completely along the length of the multiwalled CNT. The authors concluded that defect-free graphite along the length of the CNT required high current for current-induced defect formation as the initiation step. Once the defect sites are formed, air oxidation is responsible for the breakdown of successive graphitic layers of the multiwalled CNT. The in-vacuo tip sharpening process also required high current, but because it is an oxygen-free process,

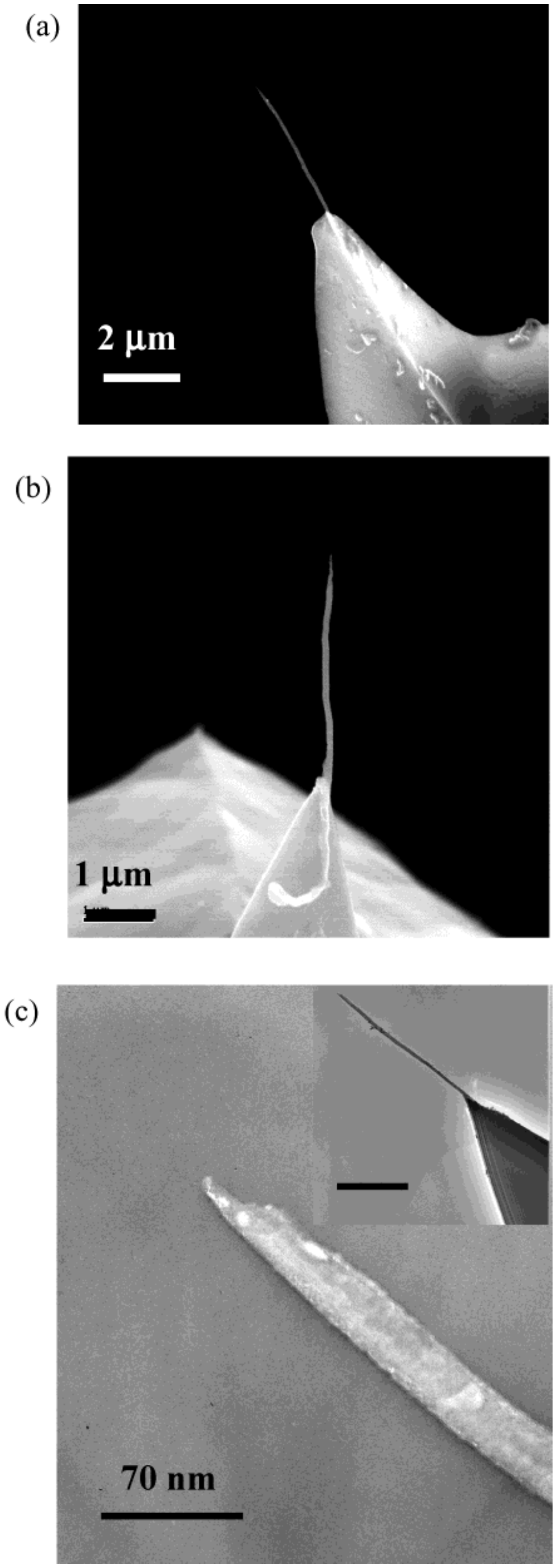


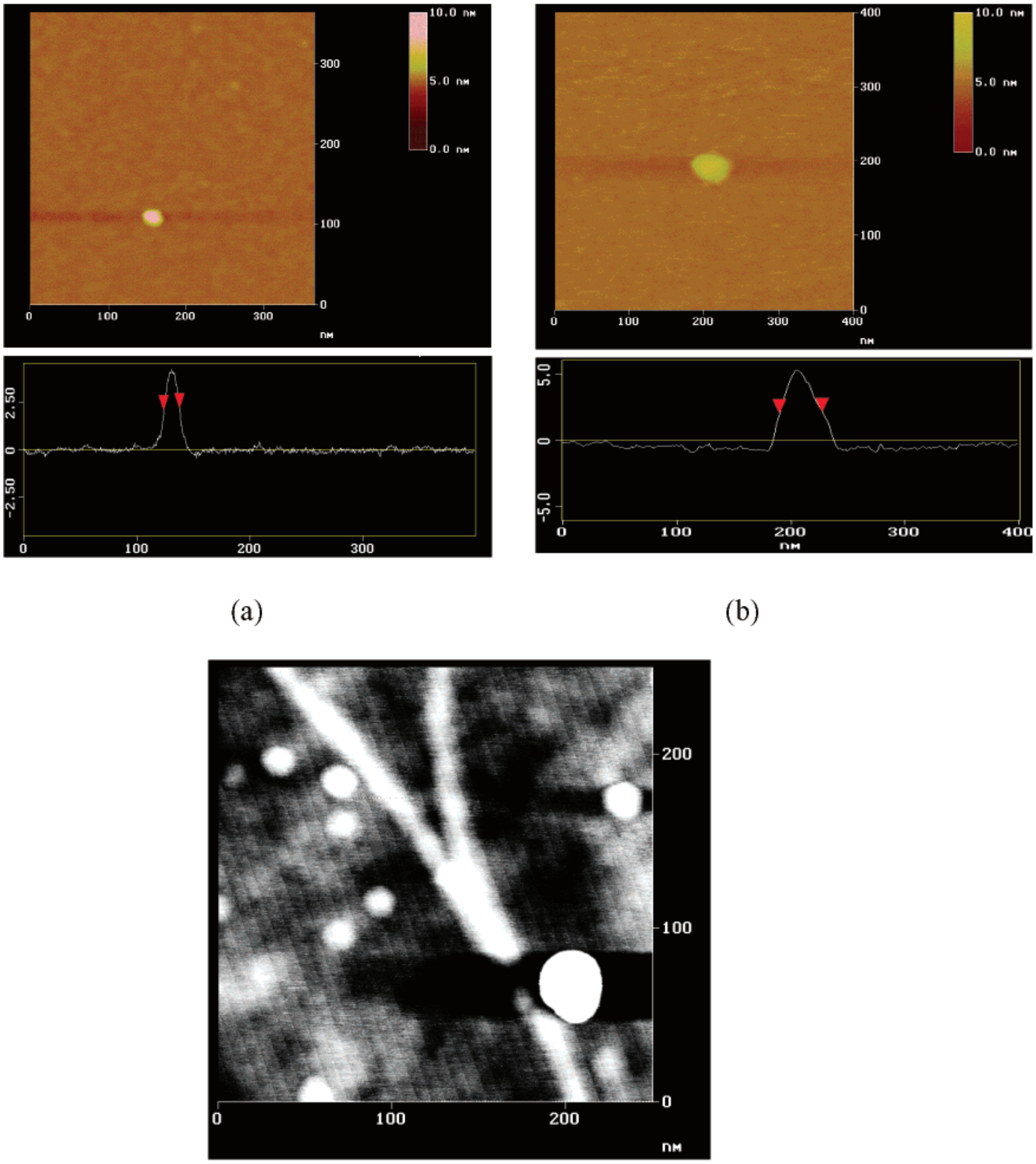
Figure 2. Electron microscopic images of sharpened multiwalled CNT scanning probes. (a) and (b) Scanning electron micrographs of CNT probes (at 5 K and 10 K magnification, respectively) clearly showing the tapered tip after undergoing the in-situ AFM sharpening procedure; (c) Transmission electron micrographs of a sharpened multiwalled CNT probe showing a nonuniform smaller size tip as the result of the MWCNT having a large angular (∼30°) displacement from the surface normal (the scale bar in the inset is 2 μm).

the authors[11] invoked a mechanism based solely on a current-induced breakage of carbon bonds at highly defect sites located at the tip of the CNT. This, coupled with the fact that the ballistic electrical conductivity occurring only through the outer layer, may explain the localized vaporization of carbon atoms from the successive outermost layers at the tip of the CNT. In light of the above proposed mechanisms and the fact that our in-situ AFM sharpening is a process performed in the present of oxygen, we propose another sharpening mechanism involving a current-induced oxygen-assisted oxidation for removing carbon atoms from the outer layers at the tip of the CNT. Because the junction at the CNT tip−metal interface is expected to have a high electrical resistance, this mechanism likely involves current-induced Joule heating of the CNT tip. Oxidation of carbon atoms occurs locally at the tip in the presence of oxygen as the cause for the removal of carbon atoms at the more reactive sites of the outermost layers of CNT, with CO or CO_2 as the products of the reaction (reaction 1). We plan to investigate in detail the proposed mechanism and will report the findings at a later time.

$$[\text{MWCNT}]\ \text{C}_n + \text{O}_2 \xrightarrow[\Delta\ \text{(Joule Heating)}]{\text{AFM Sharpening Process}} [\text{MWCNT}]\ \text{C}_{n-(x+1)}\text{CO}_2\text{H} + x\text{CO}_2 \quad (1)$$

We first investigate the size and shape of the sharpened CNT probe by directly imaging a 5 nm diameter Au nanoparticle dispersed on an atomically flat mica surface. The AFM image and the cross section data of a Au particle acquired with a sharpened MWCNT probe are shown in Figure 3a. The cross section profile of the particle exhibits a symmetrical shape, suggesting a regular uniform tip shape for the sharpened CNT probe. Lateral tip broadening of the 4.8 nm diameter Au particle gives a full-width at half maximum (fwhm) of 13.3 nm. Using a simple model, the deconvolution of these data gives an apparent radius of curvature of 4.3 nm for the sharpened tip.[16] This is consistent with the SEM images seen in Figure 2 of the sharpened CNT probe, where the tip is clearly tapered. Our reproducible CNT sharpening process routinely yields tubes with radii of curvature of less than 5 nm. AFM data for CNT probes before undergoing the shortening process tend to give radii of curvatures generally much larger than 10 nm. Figure 3b shows an AFM image of a 5.0 nm Au particle obtained with the same MWCNT probe before the sharpening process. The fwhm of 37.6 nm gives an apparent tip radius of curvature of 16.3 nm. This comparison categorically demonstrates that the sharpening process produces a MWCNT probe with a much smaller tip.

To further investigate the sharpness of our CNT probes, we also characterized smaller structures, namely SWCNTs on Si substrate, employing the same probe above. Figure 3C shows a high-resolution AFM image of a junction of two SWCNTs diverting from a bundle of nanotubes. Using the same cross-section profile analysis for the gold particle sample, the deconvolution of the cross section data for the 0.8 nm diameter SWCNT gives an appearant radius of curvature of 4.5 nm. In a previous study,[18] a MWCNT probe fabricated through our method was employed for quantitative analysis and comparison study to conventional Si probes. The statistical analysis for a series of sputtered-silicon films demonstrates the superior performance of our probe over that of conventional Si and Si_3N_4 probes. Comparing the roughness exponent, α, and lateral correlation length, ζ, parameters versus film thickness ($\alpha = 0.61$ for MWCNT probe compared to $\alpha = 0.832$ for both Si and Si_3N_4 probes), the MWCNT probe demonstrates the ability to tract the surface more precisely and also closely approaches the intrinsic value for the surfaces.



(a) (b) (c)

Figure 3. AFM images and cross-section plots of a Au nanoparticle obtained with a multiwalled CNT probe comparing the high lateral resolution of the probe after (a) and before (b) the sharpening process. (a) The 13.3 nm full-width at half maximum (fwhm) of the 4.8 nm diameter Au particle gives an apparent radius of curvature of 4.3 nm for the sharpened probe, whereas (b) the fwhm of 37.6 nm for the 5.0 nm Au particle gives an apparent radius of curvature of 16.3 nm for the MWCNT tip before sharpening. (c) Image of single-walled carbon nanotubes (0.8 nm diameter) on SiO_2 surface (the particles in the image are likely to be iron catalysts used for the SWCNT growth).

We have previously reported[4] data in support of the robustness of the multiwalled CNT probes that are fabricated by our unique method. Since the tip sharpening procedure for these CNT probes is achieved in a relatively mild condition, the strength of the point of attachment of the CNT to the surface of the Si scanning probe should not have been altered. The strength of the attachment contributes most to the robustness of the CNT probes. It is nevertheless worthwhile to investigate the stability of the tip structure for the sharpened CNT probe. The sharpened CNT probe discussed earlier was also used for acquiring the two images of a 2 nm thick HfO_2 film deposited on a Si surface shown in Figure 4. The figure compares an image obtained at the 56th scan after undergoing multiple reapproaches for a total of more than 20 h of scanning, with the image from the first scan. The RMS surface roughness values for the two images are about the same, 0.564 and 0.562 nm. The very small change in the roughness data strongly suggests that the sharpened CNT tip structure has not degraded. The SEM micrograph of the sharpened MWCNT probe also shows no change after the multiple scan experiment. From these data, the durability of our multiwalled CNT probe as well as the robustness in the structure of the sharpened CNT tip are clearly demonstrated, as one would expect from the graphitic structure at the tip. In a similar set of control experiments, an image of the HfO_2

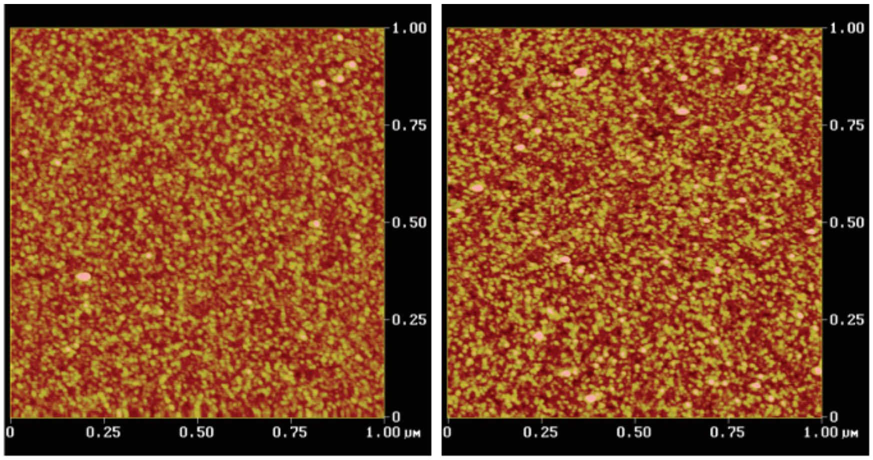


Figure 4. Stability study of the sharpened CNT probe with images of a 2 nm thick HfO_2 film on Si surface. No appreciable change is observed when comparing the (left) initial image with an RMS roughness of 0.562 nm to the (right) 56th continuously scanned image with an RMS roughness of 0.564 nm.

surface obtained with a silicon probe exhibits an initial RMS roughness value of 0.42 nm for a fresh Si probe and shows a degradation to 0.32 nm only after 10 scans.

By removing all the outer graphitic layers of the MWCNTs, leaving only the innermost tube at the tip, the lateral resolution of the sharpened CNT probe should approach that of the SWCNT probe. The MWCNTs, synthesized under the present conditions, tend to favor a large diameter innermost tube. This means that there is opportunity to achieve even higher lateral resolution with this technique for sharpening a MWCNT scanning probe if we improve our CNT source whereby the innermost tube diameter is smaller. Unlike the SWCNT probe, the sharpened MWCNT probe has the advantage of avoiding the problem of jumping to contact due to the bending response of the nanotube as reported by Snow et al.[19,20] The relation for the ratio of the bending response to the compressive response, R_r, for CNT is described by

$$R_r \sim {}^4/_3(L^2/r_o^2)\tan(\phi)$$

where L is the length of the nanotube, r_o is the radius of the nanotube, and ϕ is the angle the nanotube is displaced from the surface normal. By simple analysis, the radius of the sharpened MWCNT, r_o, is larger everywhere along the length of the nanotube except the tip, and therefore R_r, the ratio of the bending response to the compressive response, remains the same for a sharpened MWCNT tip and has a smaller value compared to that of a SWCNT probe with a same length L. The less bending response for MWCNT probes translates to a decrease in the problem of jumping into contact and also no edge blurring image artifact as often encountered with SWCNT probes, particular those SWCNT probes that have a large angular displacement. In fact, we have used many MWCNT probes where the nanotube angle ϕ is displaced far from the surface normal, which would normally exacerbate the bending compression of SWCNT probes, however, no problem with image artifacts was encountered with the multiwalled CNT probes.[18] This lower value of R_r for multiwalled CNT probes also allows for a wider range of force set points where the instrument will not encounter a feed-back problem due to tip−sample adhesion problems.[21] From a practical point of view, the ability to image in a wide range of set points is an added advantage in terms of easier operation. This is due to the fact that most tapping mode AFMs utilize automated software control which may not always pick the same set point.

Concluding Remarks

We have demonstrated a simple in-situ AFM method for locally sharpening the tip of a multiwalled CNT scanning probe. This process involves applying a 2−3 V bias between the soft intermittent contact of the CNT tip and metal electrode surface while in the presence of oxygen. This technique allows for the production of high lateral resolution scanning probes with a radius of curvature for the CNT tips of about 5 nm. A time lapsed study showed no degradation in the quality of the high lateral resolution images after more then 20 h of continuous scanning, indicating the stability of the probe and the robustness of the sharpened CNT tip structure. The coupling of this sharpening method and the superior mechanical properties of multiwalled CNT results in a highly stable scanning probe with universal applications, from high lateral resolution to high aspect ratio imaging.

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(13) Imaging with a MWCNT probe that has an uneven sharpened tip structure occasionally produces image artifacts. For instance, the AFM image of a spherical Au particle may have a nonuniform shape reflecting the uneven sharpening of the tip shape.

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(16) Using the simplest model based on the assumption that (1) a symmetrical hemispherical tip apex structure, (2) the side walls of the CNT tip at normal with surface, (3) neglecting the interaction of the sample with the side walls of the tip, and (4) the sample with perfectly spherical shape, the equation $W = (2R_P) + (2R_T)$ may be used for the deconvolution of the tip size, where W is the width at full-width at half maximum, R_P is the radius of the spherical sample, and R_T is the radius of curvature of the tip. For a more detailed discussion on the topic of tip deconvolution, see ref 17.

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(21) As an example, a multiwalled CNT probe with a length of about 1 μm and a cantilever with a free amplitude set at 1 V (~15 nm amplitude for a etched silicon probe with 2−5 nN/nm force constant), a range of set point from 0.8 to 0.4 V may be used for imaging without any problem in feed- back control.