Carbon nanotube-modified cantilevers for improved spatial resolution in electrostatic force microscopy

S. B. Arnason, a) A. G. Rinzler, Q. Hudspeth, and A. F. Hebard
Department of Physics, University of Florida, Gainesville, Florida 32611-8440

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The resolution of electrostatic force microscopy (EFM) is enhanced when multiwalled carbon nanotubes are used as extensions on conventional silicon cantilevers. Multiwalled nanotubes provide robust, high aspect ratio, conducting tips that minimize topographic dependence of gradients in the capacitance between the tip/cantilever and the substrate. Comparison of simultaneously acquired topographical and EFM images taken at the intersection of overlapping electrodes of electrically biased Al–Al₂O₃–Al tunnel junctions confirm the improved performance. This enhancement enables us to determine the surface contact potential differences between individual nanotubes within a bundle with resolutions of 5 mV and 10 nm. © 1999 American Institute of Physics.

Variations of scanning force microscopy (SFM) techniques employing an electrically conducting tip are presently attracting substantial research attention because of their ability to uniquely characterize the electrical properties of surfaces and interfaces. In contrast to scanning tunneling microscopy (STM), which allows imaging only on conducting surfaces, the SFM techniques can be used on a wide variety of materials including insulating, conducting, or semiconducting surfaces. The conducting tip permits a potential difference to be applied between the tip and substrate. In noncontact mode, electrostatic forces that act on a conducting tip oscillating above the substrate surface are sensed. High-resolution capacitance detection¹ and kelvin probe force microscopy² can detect capacitances on the order of 10⁻¹⁹ F and forces on the order of 100 pN. Measurements using these electrostatic force microscopy (EFM) techniques include contact electrification studies,³ high-resolution imaging of contact potential differences on Au-covered Si(111) surfaces, dopant profiling in silicon,⁴ imaging of potential drops on integrated circuit chips,⁵ and imaging of the conducting and nonconducting regions near the percolation threshold of carbon-insulator⁶ and thin-film silver systems.⁷

In any scanning probe technique the nature of the probe tip can make a significant if not critical impact on image quality. (Note that in the following discussion “cantilever” signifies that portion of the scanning probe responsible for the mechanical resonance, “tip” refers to that portion of the scanning probe that interacts most closely with the sample surface, and “probe” describes the combination of cantilever and tip.) The report by Dai et al.⁸ on the use of multiwalled carbon nanotubes (MWNTs) attached directly onto conventional silicon cantilevers signaled a major advance for SFM techniques. The typical diameter of the tip end is on the order of 5–20 nm, thus allowing high-resolution imaging of surface topography. In addition, its high aspect ratio enables it to probe and image deep recesses in surface topography. The nanotube is also robust, yet flexible enough to survive repeated tip crashes. More importantly, for EFM applications the MWNTs are conducting, thus allowing for the placement of a small-area conducting probe in close proximity to the surface under investigation. Less obvious but equally important is that the elongated shape of the nanotube (as an extension to the cantilever) minimizes the capacitance between the cantilever and the substrate and thus reduces gradients in the capacitance. Finally, carbon nanotubes are less prone to surface contamination, presenting a probe whose work function does not change in time. The results reported in this letter illustrate these advantages and show that significant improvements in EFM imaging are obtained with the use of nanotube-modified cantilevers.

A straightforward analysis of EFM operation, depicted schematically in Fig. 1, reveals the effect of capacitative coupling. The electrostatic force on a conducting tip held a distance z above a conducting surface is

\[ F = -\frac{V^2}{2} \frac{\partial C}{\partial z}, \] ¹

FIG. 1. Schematic representation of the circuit. The output of the lock-in is summed with the ac bias in feedback to null the first-harmonic signal. In general, two independent bias voltages are applied to the two legs of the tunnel junction.
where $V$ and $\partial C/\partial z$ are, respectively, the potential difference between the probe and the sample and the gradient of the capacitance between the tip and the substrate. The potential difference, $V = V_s - V_{dc} + V_{ac} \sin(\omega t)$, comprises three contributions, an intrinsic term associated with nonuniform charge distributions and/or variations in surface work function together with an extrinsic contribution arising from externally applied dc and ac terms, respectively. The force modulation appearing at the applied frequency $\omega$ has an amplitude proportional to the product, $(V_s - V_{dc})/\partial C/\partial z$, which can be conveniently driven to zero when $V_{dc}$ is set to the unknown surface potential $V_s$.

A Park CP AutoProbe SPM was used for the simultaneous acquisition of topographical and EFM images. The cantilever is driven into oscillation just above its resonant frequency ($>100 \text{ kHz}$) and the demodulated signal fed back to the scanning stage to maintain a preset oscillation amplitude. In this “noncontact” mode, topographical images are obtained without shorting the tip to the substrate. Strictly speaking, we cannot guarantee that the tip does not touch the surface. But, we have worked at applied potential levels where we would expect tip ablation if we came into contact with the surface without degradation of the probe. An additional feedback circuit, shown in Fig. 1, was used for the EFM image. An electric potential applied at a significantly lower frequency, $\omega/2\pi = 20 \text{ kHz}$, produces a force modulation that is continuously nulled by the feedback circuit. It is straightforward to show that the output voltage of the lock-in amplifier in Fig. 1 can be written as

$$V_{out} = V_s (G/2) V_{ac} \partial C/\partial z / (1 + (G/2) V_{ac} \partial C/\partial z), \tag{2}$$

where $G$ is the overall gain of the circuit. When $G$ is large, $V_{out} (= V_s)$ becomes a direct measure of the surface potential and is used as the source for the EFM image.

In practice, too much gain will induce oscillations and/or instabilities, forcing one to accept a limited gain to obtain a stable EFM image. The amount of gain that is compromised depends on a variety of factors including scan speed, surface roughness, and the size of the variations in $V_s$. Consequently, as seen from Eq. (2), topographical features relating to the spatial variation of $\partial C(x,y)/\partial z$ will appear in the EFM image. As will be shown below, nanotube-modified tips minimize the contribution from $\partial C(x,y)/\partial z$, and thus help to separate topographical from electrostatic features. This is accomplished primarily because the nanotube extension places the silicon tip of the cantilever further from the substrate, thus diminishing the capacitance between the main body of the cantilever and the substrate. More importantly, the pencil-shaped nanotube presents a uniformly narrow cylindrical cross section which, when convolved with both topographical and surface potential variations, gives improved resolution. This advantage has already been demonstrated for topographical imaging of trenches with steep sidewalls.

All of the measurements presented in this letter are made on Al–Al$_2$O$_3$–Al cross-stripe tunnel junctions (see Fig. 1). By applying a dc voltage bias to a vertically structured tunnel junction with sharply defined edges, a calibrated step function change in surface voltage and topography will simultaneously occur as the tip is scanned across the junction electrodes. This configuration thus allows a meaningful comparison of the suitability of various types of tips in acquiring topographical and EFM images. The junctions are fabricated using standard photolithographic techniques to define the stripes. First, an initial layer of 300-Å-thick Al is deposited from a thermal evaporation source onto a glass substrate. Without breaking vacuum the surface of the Al is oxidized in a dc plasma discharge in 50 mTorr of oxygen. The sample is removed from the vacuum system and the base electrode defined by lift-off. Photoresist is spun onto the resulting sample and patterned to allow the formation of the counter-electrode. The sample is reinserted into the vacuum system and another 300 Å of Al deposited. Again, lift-off defines the top electrode.

These nanotube-modified probes used in these experiments incorporate Carbon Arc-grown, oxidatively purified MWNTs, mounted on standard Si tips (Park 2.0 µm Ultra-levers) by methods previously described by the Rice group. The tubes are mounted to the tips with the adhesive from EMS 77816 conductive carbon tape. This adhesive is not in itself conducting. It is used for its capacity to wet carbon. While we do not characterize the conductivity of each tip, we have checked a representative sample of tips by measuring the current through the tip during the process by which we shorten the tube to a usable length, nanoarc shortening. In about one out of ten cases we have not been able to shorten tips by this technique. A possible explanation for this is that they are not conducting or not well enough electrically coupled to the Si probe. Once the tubes are mounted, 10% of probes have not been usable, 50% have been usable, 20% have given good results, and 20% have been excellent. The differences are in spatial resolution, which depends primarily on the diameter of the mounted tube. Fortunately, with care, an excellent tip can be used for several months of imaging.

Figures 2 and 3 represent simultaneously acquired topographical (left panel) and electrostatic voltage scans (right panel) in the vicinity of the tunnel junction boundary using a conventional silicon tip (Fig. 2) and a nanotube-modified tip (Fig. 3). The labels S, B, and T refer, respectively, to the substrate, the base electrode, and the top electrode. These images are taken with 20 mV of bias between top and bottom plates, 200 mV of bias on the bottom electrode relative to ground, and 500 mV of ac bias on the scanning probe at a frequency of 20 kHz. In the voltage micrograph taken with a
conventional tip (Fig. 2) there is a strong signal from the capacitance gradient as the tip climbs from the portion of the top electrode that is on the substrate, $T_1$, to that portion which covers the bottom electrode, $T_2$. This manifests itself as a diffuse bright area at the edge. By contrast, the edges in the image acquired with a nanotube-modified tip show significantly smaller capacitance gradient effects, clearly resolving all of the step edges. In both of these figures the voltage drop between the electrodes is measured to be $20 \pm 5 \text{ mV}$, equivalent to the applied bias.

Figure 4 represents the simultaneously acquired topographical (left panel) and electrostatic voltage (right panel) scans acquired with a nanotube-modified tip of a bundle of multiwalled nanotubes resting on the oxidized surface of an aluminum cross stripe. The image is taken with an ac bias of 2 V applied at 20 kHz. This sample has no applied dc bias, so the resulting potential image represents solely the surface contact potential of the tubes. The topograph shows a complex tangle of tubes, some of which stretch horizontally across the image, others start vertical and bend to the right at the image center. The potential image presents a distinct picture. Some of the tubes appear to have their potentials pinned to that of the substrate, while others are at a clearly different potential. The lower frame of Fig. 4 shows the potential as a function of distance along the line drawn across the lower extension of the main feature in the potential image. From this line trace we can see that these tubes sit at a potential 15–20 mV below that of the substrate, features with depths of 5 mV are clearly resolvable, and that the spatial resolution possible with the nanotube-modified tip is 10 nm.

In conclusion, we have been able to use the advantageous physical properties of nanotube-modified scanning probe tips to improve the spatial and voltage resolution of our EFM micrographs taken in a scanning kelvin probe configuration. The high aspect ratio of the nanotubes lessens the topographical variation in the capacitance gradients that cause topography to adversely couple into the EFM images. In addition, these tips are robust with consistent performance, producing excellent EFM images over months of use in the best cases. This is to be contrasted with our standard tips which lose spatial resolution with wear and have changing electrical properties as the result of contamination. With these improved properties we are able to make high-resolution measurements of the relative surface contact potential of multiwalled nanotubes.

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