Charge imaging and manipulation using carbon nanotube probes

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(Received 15 July 2002; accepted 23 October 2002)

Due to their high aspect ratio, well-defined cylindrical structure, and good electrical conductivity, carbon nanotubes (CNTs) are ideal probes for “true” local imaging of electric domain structures at the nanoscale. By performing force–distance measurements and tip-shape profiling with a uniformly charged oxide square, we clearly demonstrate the local nature of the CNT tip for electrostatic force microscopy. We show that CNTs can be used to probe long-range electrostatic forces with a lateral resolution better than 5 nm. © 2002 American Institute of Physics.

[DOI: 10.1063/1.1530377]

Direct imaging and manipulation of electric and magnetic domain structures (spontaneously or artificially formed) at the nanoscale has become increasingly important because of the recent developments in ultrahigh-areal-density storage devices using charge-trapping, ferroelectric, or ferromagnetic materials. Electrostatic force microscopy (EFM) and magnetic force microscopy (MFM), variations of scanning force microscopy (SFM), are two of the most widely used techniques for this purpose. To date, the major difficulty related to the long-range force imaging is to decouple the short-range interactions without degrading the spatial resolution. This problem is especially severe for the conventional micromanipulated EFM and MFM probes with conical or pyramidal shaped tips. Carbon nanotubes (CNTs) have great potential to be used as the probing tips for the scanning probe techniques. Several groups have already reported experimental approaches to attach a single CNT to a conventional SFM tip. Both high-resolution imaging and lithography applications of CNT probes have been reported. Since CNTs are electrically conducting, mechanically robust, and having a perfect cylindrical geometry with very large aspect ratio, they are also very suitable for imaging long-range forces.

We used a specially designed field-emission scanning electron microscope (FE-SEM) to attach individual multiwall carbon nanotubes to PtIr-coated Si tips of commercial EFM probes (70 kHz resonance frequency, ~2.8 N/m force constant, and ~10–15 μm tip length). To separate the electrostatic force information from the total interaction of probe and sample, we used a dual-modulation scheme (operating in the dynamic mode), where a near-resonant mechanical modulation (ωm ≈ ω0 ~ 70 kHz) was applied to the cantilever and a nonresonant electric modulation (ωe ≈ 20 kHz) was applied to the sample bias voltage. The average tip–sample separation (dynamic mode) used in this study was ~15–30 nm. Two types of charge-storage media were used in this work for EFM imaging. One type consists of a Si3N4/SiO2 bilayer (4 nm/3 nm thickness); and the other is a single Si3N4 layer (3.5 nm thickness), both grown on p-type Si(001) substrates.

Figure 1(a) shows dynamic force–distance curves of PtIr-coated Si tip and CNT-attached tip measured by the same type of EFM probes on a gold film in air. Figure 1(b) shows quasistatic force–displacement curves used to determine the closest tip–sample distances before the tip snap-in. The drastic difference in the contact force (surface adhesion due to the absorbed humidity layer) between these two types of tips can be directly observed in Fig. 1(b). From the measurement shown in Fig 1(a), we can confirm that the force–distance relationship of a conventional EFM probe with a metal-coated Si tip is in qualitative agreement with the results simulated by S. Belaidi et al.

We can use a sphere/cone/cantilever probe geometry to understand the measurement results of a conventional EFM probe. In the large-distance regime (tip–sample distance > 10 μm), the detected electrostatic force is mainly a long-range capacitive force resulting from the cantilever and the Au sample. In the intermediate regime (~10 μm), the electrostatic force between the tip cone and the Au sample begins to contribute significantly to the detected force. Only in the proximate regime (~40 nm), the main detected electrostatic force is from the interaction between the tip apex and the sample. However, in this regime, van der Waals and various chemical interactions also become dominant. Therefore, to separate these interactions between the sample and the conventional Si tip, the conventional approach is to “lift” the tip above the sample some tens of nanometers. However, in this case, reduction in lateral resolution would occur due to the increase in the tip-to-sample distance and the occurrence of electrostatic interaction between the sample and the cone structure of Si tip. By contrast, the force–distance curve of CNT-attached tip shows much less contribution from the Si cone structure in a wide range of tip-sample distance. This is the main reason CNT probes enable true local sensing of electrostatic interactions under typical noncontact or intermittent-contact operating conditions. Two dotted lines in the CNT force curve of Fig. 1(a) show the regions of interaction transition. The actual CNT length (~380 nm) acquired by FE-SEM imaging is also indicated in the curve.

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The measured power-law exponents for force versus tip–sample distance are: $-1 \sim 1/d$ for the spherical tip apex of the conventional probe and $-0.45$ for the nanotube, while the exponent for the common tip cone structure is $-0.25$, consistent with the expected sphere-like, rod-like, and cone-like behaviors, respectively.

For nitride charging experiments performed on nitride films in air, we have previously discovered\(^1\) that anodic oxidation could occur in the proximity of the local probe due to the intense electric field built between the grounded probe and the humidity-layer-covered nitride film on top of a positively biased Si substrate. We have found that the main oxidation by-product ions (positive charge state) could be trapped at the anodic–oxide/nitride interface with a long retention time. Therefore, a well-prepared oxide pattern on nitride can be used as a uniformly charged “mirror” for imaging the tip shapes of EFM probes. Figure 2 shows an example of such experiments on an oxide–nitride–oxide–silicon (ONOS) structure with two types of probes. A positively charged oxide square was prepared by locally oxidizing the Si$_3$N$_4$/SiO$_2$ bilayer film using a conducting probe under ambient conditions. Instead of the center-protruded EFM image taken with a conventional EFM probe, using a CNT probe, we can resolve the sharp boundary of the charged and uncharged regions, and the electrostatic force signal is quite uniform within the charged region.

To obtain the information of optimum resolution for EFM imaging with a CNT probe, an array of alternative positively and negatively charged regions was written in a...
probe displays much finer topographic features of the nitride film. We found that the topographic images taken with the CNT tip correspond to the interaction of the tip with the surface topography and the electrostatic force signal corresponding probed volume of the nitride film with a PtIr-coated Si tip, while images (d), (e), and (f) were acquired with a CNT-attached tip (the corresponding image sizes are the same). All images were taken in high vacuum with imaging conditions similar to that used in Fig. 2, except that the ac component of the bias voltage was 2 V (peak-to-peak). The arrows in images (d) and (e) point to some sub-5-nm features for comparison.

Si₃N₄ film with ±10 V voltage pulses (1-ms-width for the PtIr-coated Si tip and 1-s-width for the CNT tip) applied between the conducting tip and the p-type Si substrate as shown in Fig. 3. In order to avoid the complication of field-induced oxidation in ambient air, the local charging experiments were performed in high vacuum (~10⁻⁶ Torr) with an environment-controlled SFM system (SPA300HV, Seiko Instruments) such that field-induced anodic oxidation did not occur during the charging and subsequent imaging process. We found that the topographic images taken with the CNT probe displays much finer topographic features of the nitride surface with small feature sizes of the order of ~5 nm. Since the Z-feedback of the probe position is controlled by the surface topography and the electrostatic force signal corresponds to the interaction of the tip with the bulk charge trapping sites within the nitride film, the true local sensing of electrostatic force should reflect the local surface topography because that the tip moves conformationally with the surface topography during simultaneous EFM imaging, and the effective probed volume of bulk charged sites should change accordingly. This is observed only with the EFM image using the CNT probe because of its local probing capability. By comparing the fine features displayed in Figs. 3(d) and 3(e), the achievable EFM resolution using a CNT probe is determined to be better than 5 nm. In contrast to the much-improved lateral resolution, the EFM signal obtained with the CNT probe is weaker due to the fact that the effective probed sample volume is much smaller than that of the conventional probe. This is consistent with the line profiles of EFM images shown in Fig. 2(e).

The areal bit density of the charged array demonstrated here is ~64 Gbit/in², and the charged regions are erasable and rewritable by applying reverse voltages. From the known trap density of an electron or hole in Si₃N₄ film, we estimate that each charged bit contains a few tens of electrons or holes. It is interesting to note that, although CNT probes can provide an extremely high lateral resolution for EFM imaging, the charged dot diameter induced by the CNT tip is not significantly smaller than that induced by the tip of a conventional EFM probe (45–50 nm versus 60–65 nm). The reason might be that, during the writing process, the intensive charging field causes significant lateral relaxation of the trapped charges similar to the known phenomenon of electric-field-induced thermal excitation of trapped charge carriers at room temperature. Although we demonstrate only the capabilities of imaging and manipulation of charges on insulating films, the drastically improved spatial resolution of EFM imaging with single CNT tips can open up new applications of nanometer-scale surface potential measurements.

We thank the National Science Council and the Program for Promoting Academic Excellence of Universities, the Ministry of Education in Taiwan for supporting this research, and J. A. Dagata for enlightening discussions. The SEM manipulation work performed in AIST, Tsukuba was partially supported by the New Energy and Industrial Technology Development Organization, Japan.

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