Scanning Conductance Microscopy and High Frequency Scanning Gate Microscopy of Carbon Nanotubes and Polyethylene based Nanofibers

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ABSTRACT

We present two new approaches that significantly enhance the analytic power of Scanning Conductance Microscopy (SCM) and Scanning Gate Microscopy (SGM). First, we present a quantitative model that explains the phase shifts observed in SCM, by considering the change in the total capacitance of the tip-sample-substrate system. We show excellent agreement with data on samples of (conducting) single wall nanotubes and insulating polyethylene oxide (PEO) nanofibers. This model is also used to determine the dielectric constant of PEO nanofibers, a general approach that can be extended to other dielectric nanowires. Second, we extend the SGM to frequencies up to 15MHz, and use it to image changes in the impedance of carbon nanotube field effect transistor (CNFET) circuits induced by the SGM-tip gate. We show that these measurements are consistent with a simple RC parallel circuit model of the CNFET, with a time constant of 0.3 µs.

INTRODUCTION

Many types of hybrid Scanning Probe Microscopies (SPM) have been developed to study the local electrical properties of nanoscale objects. Scanning Conductance Microscopy (SCM), and Scanning Gate Microscopy (SGM) are particularly powerful approaches.

SCM can probe the conductivity of nanoscale structures without electrical contacts, and it has been used to image single wall carbon nanotubes (SWNTs), to prove the insulating character of λ-DNA [1], and to distinguish between conducting and insulating polyaniline/polyethylene oxide (Pan/PEO) nanofibers [2]. Although a model for SCM has previously been proposed [1], it does not account for all these observations. We introduce an improved model for the tip–sample–substrate geometry that makes SCM a more powerful quantitative technique. We show that SCM data can be predicted by considering the change in the total capacitance of the tip-sample-substrate system. We also present experimental data for carbon nanotubes and PEO nanofibers that are in excellent agreement with the predictions of the above model. As a very important application we are using this technique to measure the dielectric constant of PEO nanofibers.
SGM is a very powerful technique for measuring the local electronic properties of nanoscale circuits. SGM can be used to image Schottky barriers at the metal contacts of a carbon nanotube field effect transistor (CNFET) [3], and gate-susceptible defects along its length [4]. Here, we combine SGM with Impedance Spectroscopy (IS) in order to extend the frequency range of SGM up to 15 MHz. Using the voltage-biased SGM tip as a nanoscale local gate, we apply this High Frequency Scanning Gate Microscopy (HF-SGM) technique to image the changes in the impedance of a CNFET circuit induced by the SGM tip. We show that the data are consistent with a parallel RC model for the CNFET circuit.

EXPERIMENTAL DETAILS

SCM is a dual-pass technique. In the first line scan, the tip acquires a topography profile in tapping mode. In the second (interleave) line scan (Figure 1(a)), the tip travels at a defined height above the surface. A DC voltage is applied to the tip, and the cantilever is mechanically driven at its free oscillation resonant frequency. The SCM image records the phase of the cantilever oscillation as a function of tip position.

The SCM cantilever can be modeled as a driven harmonic oscillator with resonant frequency $\omega_0$ and spring constant $k$. When the tip is scanned at height $h$ above the bare SiO$_2$ substrate, the electrostatic force between metallic tip and surface leads to a decrease of the resonant frequency of the cantilever [5] and therefore to a negative value $\Phi_0$ for the background phase lag:
\[
\tan(\Phi_0) = -\left(\frac{Q}{2k}\right)C''_1(h)V_{tip}^2,
\]
where $Q$ is the quality factor of the cantilever and $C_1(h)$ is the capacitance of the tip-substrate system. The value of $\Phi_0$ is independent of the tip horizontal position and is used as the reference zero. When the tip is at height $h$ above the sample (SWNT, nanofiber) the total capacitance of the system changes to $C_2(h)$. Again, assuming that the electrostatic forces are small, the phase shift relative to that over the bare substrate is:
\[
\tan(\Phi - \Phi_0) \approx \left(\frac{Q}{2k}\right)\left(C''_1(h) - C''_2(h)\right)V_{tip}^2
\]

For the SCM measurements we use CVD grown SWNTs (likely a combination of single tubes and small bundles) [6], insulating poly(ethylene oxide) (PEO) nanofibers and conducting nanofibers made from a blend of polyaniline doped with camphorsulfonic acid and insulating polyethylene oxide (PAn.HCSA/PEO) [2]. Data for conducting fibers are presented elsewhere [5]. The substrate for all experiments is a 200nm SiO$_2$ layer on top of a p-type degenerately doped Si wafer.

In SGM imaging mode [3], a conducting tip with applied voltage $V_{tip}$ is scanned at a fixed height over an electrically biased sample, and the transport current $I_{sd}$ is recorded as a function of tip position. In contrast to a static backgate that couples capacitively to the entire sample, the tip is a spatially localized gate whose position can be varied. Similarly, in High-Frequency SGM (HF-SGM), the voltage biased SGM tip is scanned over the CNFET at a fixed height (Figure 1(b)) but now the circuit impedance modulus $|Z|$ and phase $\theta$ are measured as a function of tip position. The values for $|Z|$ and $\theta$ are recorded using a HP429A impedance analyzer [7], [8].
CNFET circuits are fabricated from SWNTs, grown by catalytic chemical vapor deposition (CVD) on a SiO$_2$/Si substrate. Au electrodes are patterned using a shadow mask evaporation technique [2]. The devices show a strong field effect transistor response to an applied voltage $V_G$ to the Si backgate, with ON/OFF ratios for the source-drain transport current $I_{sd}$ of $10^3$, and a large transconductance of order $1\mu S$. These values indicate that Au makes excellent contact with p-type CNFET [8].

Both SCM and SGM images were taken on a Digital Instruments Dimension 3000 NS IIIA, using W$_2$C–coated tips with curvature radius $R=30$-60nm, quality factor $Q=150$ and spring constant $k=0.65$-1 N/m.

**RESULTS AND DISCUSSION**

**Scanning Conductance Microscopy**

SCM images for SWNTs, and an insulating PEO fiber, together with the corresponding line scans are presented in Figure 2. SWNTs show a negative phase shift (Figure 2(a)) whereas the phase shift for insulating PEO fibers is always positive (Figure 2(b)).

To explain these images we first note that, according to equation 1 the sign of the phase shift in SCM is determined by the change in the second derivative of the total capacitance of the system. We calculate the capacitances called for in equation 1 using a simplified model for the geometry of the bare substrate, a thin SWNT, and a large diameter polymer nanofiber [5] (Figure 3(a), (b)). Since the PEO fiber diameter $D$ is comparable to the tip radius $R_{tip}$, we model the PEO fiber as an insulating plate of thickness $D$ and dielectric constant $\varepsilon_f$. The geometrical models presented in Figure 3 give simple analytical solutions for the total capacitance of the system. For example, for $h=30$nm over the bare substrate the model predicts $C_1'' = 102\mu F/m^2$; the experimental value [5] (from the slope of the line of $\tan(-\Phi_0)$ vs. $V_{tip}^2$) is: $C_1'' = 95\mu F/m^2$, in good agreement with the predictions.
Figure 2. SCM images of SWNTs (a), and insulating PEO nanofiber (diameter: 10-100nm) (b). Insets show line scans along the white lines. Differences in phase shift are explained in the text.

Using the model of Figure 3(b), the capacitance of the SWNT to each metal plate separately is found analytically [5], and then combined in series to give $C_2(h)$. We find $C_2(h) > C_1(h)$ for all scan heights $h=10-100\text{nm}$. Thus equation 1 predicts a negative phase shift, in agreement with the measurements. The predictions are in excellent quantitative agreement with the data (Figure 3(c)) for intermediate scan heights ($h=30-50\text{nm}$) where the model geometry is appropriate [5]. The observed phase shifts depend on the nanotube length and are almost independent of the tube diameter. The minimum detectable length (limited by the noise in the phase channel [1]) is about $0.4\mu\text{m}$. Also, at least when the measurements are done in atmosphere there is no detectable difference between semiconducting and metallic SWNTs. For insulating PEO fibers the analytical solutions of the geometrical models [5] predict that $C_1(h) > C_2(h)$ for all scan heights, so positive phase shifts (as observed in Figure 2(b)).

As an important practical application, we use the model to determine the dielectric constant $\varepsilon_f$ of PEO $[(\text{CH}_2-\text{CH}_2-\text{O})_n]$ nanofibers. From the slope of the plot of $\tan(\Delta\Phi)$ vs $V_{\text{tip}}^2$ [5], the
predictions for the total capacitance and equation 1, we find the fiber dielectric constant (at the cantilever oscillation frequency of 48 KHz) to be: \( \varepsilon_f = 2.88 \pm 0.12 \).

This measured value is between the tabulated dielectric constants for polyethylene \((\text{CH}_2-\text{CH}_2)n\), \(\varepsilon_{\text{PE}} = 2.28\) to 2.32, and that for polyoxymethylene \((\text{CH}_2-\text{O})_m\), \(\varepsilon_{\text{POM}} = 3.6\) to 4 at 1 KHz and room temperature [9]. This is consistent with the higher polarizability of the C-O bond compared to that of the C-C bond. As expected, the measured value is also higher than \(\varepsilon_{\text{PEO}} = 2.24\) found for PEO at optical frequencies [10]. This method is general and can be used to determine the dielectric constant of other insulating nanowires.

**High Frequency Scanning Gate Microscopy**

We start by presenting low frequency Scanning Gate Microscopy measurements (Figure 4 (a), (b)), which provide information on variation of the low-frequency (DC – 10 kHz) resistance of the sample in response to the tip-gate. In Figure 4(b) a positively biased tip \((V_{\text{tip}} = +8V)\) depletes the carrier (hole) concentration locally, and three spots (defects) are seen along the nanotube length. The diameter of the spots increases linearly with tip voltage, as previously found [4].

We extend this technique to High-Frequency Scanning Gate Microscopy to investigate the effect of the defect regions on the CNFET impedance at frequencies up to 15 MHz. Figure 4 shows the variation of \(|Z|\) (Figure 4(c)) and \(\theta\) (Figure 4(d)) with the tip position for \(V_{\text{tip}} = +8V\) and fixed applied ac bias \(V_{\text{AC}} = 100 \text{ mV}\) and frequency \(f = 300 \text{kHz}\). The same defect regions observed in SGM (Figure 4(b)) also appear in HF-SGM images, implying that changes in the CNFET impedance are due to depletion of these regions by \(V_{\text{tip}}\).

![Figure 4](image)

**Figure 4.** (a) AFM image of a CNFET sample. The diameter of the SWNT is 1nm. (b) SGM image with \(V_{\text{tip}} = +8V\), \(V_{\text{AC}} = 100 \text{ mV}\), \(f = 10 \text{kHz}\), scan height \(h = 15 \text{nm}\). A positive tip voltage depletes holes locally resulting in a decreased transport current when the tip is above defect sites. (c), (d) High Frequency Scanning Gate (HF-SGM) images, of \(|Z|\) (c) and \(\theta\) (d) vs. tip position. Changes in \(|Z|\) and \(\theta\) when the tip is positioned above the defects are consistent with the predictions of a parallel RC circuit for the CNFET.

The HF-SGM setup also allows the measurement of the CNFET impedance spectrum \(|Z(f)|\) and \(\theta(f)\). A parallel RC circuit model for the CNFET, predicts that \(\tan(-\theta) = 2\pi R C\), and \(|Z(f)| = R/(1+(2\pi f R C)^2)^{1/2}\). A fit to the spectra (taken with the SGM tip placed at \(h = 15 \text{nm}\) above the top defect, and \(V_{\text{tip}} = +8V\)) using the above model, yields a capacitance of 2.3pF and a
resistance of 310 kΩ for the circuit [8]. The capacitance is the same as that found from conventional impedance spectroscopy measurements [8], while the resistance agrees with that found from the SGM data (Figure 4(b)). The total capacitance of the circuit is not influenced by the tip gate or the backgate voltage [8]. This is explained by the fact that the capacitance of the SWNT alone (calculated using a coaxial-cable approximation [6]) is ~ 40aF; the circuit capacitance is therefore dominated by parasitics due to the metallic electrodes and wires. Predictions of the parallel R-C model are likewise in quantitative agreement with the variation in |Z| and θ seen in Figures 4(c), (d).

CONCLUSIONS

We have developed a quantitative model for phase shifts in SCM based on the change in the total capacitance of the tip-sample-substrate system. We use simple geometric models and find excellent agreement with data collected on SWNTs and insulating PEO nanofibers. We have also extended the frequency range of SGM up to 15 MHz. By using this technique we have imaged precise locations along the CNFET length, which respond strongly to the tip-gate and change the circuit resistance. The details of the response of |Z(f)| and θ(f) to the tip-gate voltage agree with the parallel RC model of the CNFET. This extension of SGM should prove useful in experiments on other systems including semiconductor nanowires, polymer nanofibers, and the like.

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