Electric charges and forces in atomic force microscopy and nano-xerography

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Abstract. Electrostatic forces generated by contact potential differences, localized charges, or externally applied voltages play a crucial role in atomic force microscopy. Electrostatic forces mediate the non-contact measurement of local potentials by the Kelvin probe technique, enabling compositional mapping of surfaces. However, if not compensated properly, electrostatic forces lead to height errors in topography images acquired in tapping mode. We present a single scan Kelvin probe force microscopy technique that compensates local electrostatic forces and allows simultaneous height and potential measurements in tapping mode. Electrostatic forces also direct the localized assembly of structures in nano-xerography. Here we describe how positive charges, written into a thin film of poly(methyl)methacrylate with the conductive tip of an atomic force microscope, guide the deposition of carboxyl-functionalized multiwalled carbon nanotubes suspended in isopropyl-acohol.

1. Introduction

Atomic force microscopy has proven very powerful in visualizing nanoscale structures and even atomic details on surfaces of a wide range of materials in vacuum, ambient air, or liquid. At the heart of these instruments is a very sharp tip, mounted on a microfabricated cantilever serving as force sensor. While scanning across the specimen, the tip either is kept in steady contact with the specimen surface, or is oscillating in close proximity to sense force gradients above the surface. In air, dynamic imaging modes such as tapping mode allow one to minimize interaction forces and, in particular, to prevent the detrimental effects of capillary forces as experienced when the tip is scanned in continuous contact across delicate specimens. In addition to surface topography, qualitative maps of surface chemistry are accessible by measuring the local contact potential difference between tip and specimen in Kelvin mode [1-5]. A major challenge, however, is the proper discrimination between van der Waals and electrostatic forces acting simultaneously on the tip. As we will show below, uncompensated electrostatic forces cause the tip to lift away from the surface, leading to erroneous height information and a reduction in lateral resolution due to the increased tip-sample distance.

Beyond imaging, the atomic force microscope (AFM) also opens new avenues in nanofabrication. In nano-xerography, patterns of surface charges, written into thin electret layers by applying voltage pulses to a conductive tip, guide the deposition of nanomaterials suspended or emulsified in a carrier liquid [6]. Materials suitable for nano-xerography range from metal and solid dielectric particles to carbon nanotubes and biomolecules. The deposition process is driven by a superposition of Coulomb
and polarization forces, the ratio between the two depending on the electret material, the fluid medium, the size of the objects, the amount of charge deposited, and the geometry of the pattern [7].

In the following sections we report on our recent advances towards true topography measurements in air by compensating electrostatic forces in a single scan Kelvin probe force microscopy set-up. We further demonstrate very good pattern definition in nano-xerography of functionalized carbon nanotubes, directly deposited from alcohol-based solutions.

2. Single scan Kelvin probe force microscopy

In the presence of a contact potential difference $U_c$, an attractive electrostatic force $F_z$ acts on the tip:

$$F_z = 0.5 \left( \frac{dC}{dz} \right) U_c^2,$$

where $C$ is the tip-sample capacitance at the actual tip location. In Kelvin probe force microscopy (KFM) the cantilever is kept oscillating above the surface by applying a voltage $U_{AC} \cos(\omega_{KFM} t) + U_{DC}$ between the conductive tip and sample [1, 2, 8]. The resulting electrostatic force has spectral components at DC, $\omega_{KFM}$, and $2\omega_{KFM}$, with the $\omega_{KFM}$ component given by

$$F_\omega = -\left( \frac{dC}{dz} \right) \left( U_c - U_{DC} \right) U_{AC}.$$ 

A feedback circuit with lock-in amplifier adjusts $U_{DC}$ such that the oscillation amplitude of the cantilever at the driving frequency $\omega_{KFM}$ vanishes, corresponding to $F_\omega = 0$. $U_{DC}$ then equals the contact potential difference between tip and specimen. To prevent crosstalk between van der Waals and electrostatic forces, KFM usually is performed in a two-pass technique in air [4]. For each scan line, first topography is determined in normal tapping mode and subsequently the measured topography is retraced at a set lift height above the same line in Kelvin mode, i.e. with applied AC and DC voltage. The rationale behind this strategy is that, with increasing distance from the sample surface, the strength of van der Waals forces decreases much faster than the strength of Coulomb forces.

However, in this standard protocol of KFM the topography scan is subject to height errors in areas of nonzero contact potential difference. Figure 1 depicts such electrostatically induced height errors for different operating conditions in tapping mode on a gold electrode in air at ambient pressure and humidity. In tapping mode higher amplitude setpoints (i.e. closer to the free amplitude of the cantilever) lead to weaker tip-sample interaction forces, but at the same time this operating regime is subject to large electrostatic height offsets up to several tens of nanometers. Although electrostatic forces need to exceed the tip-sample interaction before the height offset rapidly increases, one should note that contact potential differences of a few hundred millivolt are sufficient to completely mask molecular adsorbates in topography scans. The observed height offset results from the feedback circuit

![Figure 1](image_url). Height offset in tapping mode due to electrostatic forces generated by potential differences between tip and sample. Measured in air on a gold electrode with a gold-coated cantilever. Free oscillation amplitude of the cantilever was 20 nm. Setpoint indicates amplitude maintained by feedback circuit when the tip is positioned close to the sample surface. Decreasing setpoints correspond to shorter tip-sample distances.
withdrawing the sample to compensate for the electrostatic attraction of the tip that would lead to a reduced oscillation amplitude of the cantilever if the average distance between tip and sample was not increased.

To compensate electrostatic forces in topography scans we have implemented a new set-up for single scan KFM. In this new method the cantilever is excited at two frequencies simultaneously while two independent feedback circuits for topography and Kelvin probe separately track the signals at the two frequencies. Tapping mode is performed as usual slightly below the first eigenfrequency of the cantilever whereas the Kelvin modulation frequency $\omega_{KFM}$ is matched to the second eigenfrequency, which for most cantilevers is not a multiple of the first resonance. This strategy is necessary to prevent interference from higher harmonics of the first eigenfrequency that get excited due to nonlinear intermittent tip-sample interactions in tapping mode. We excite the second eigenfrequency both mechanically (via the tapping mode piezo) and electrically (via the standard AC and DC voltages) with a $\pi/2$ phase shift between the two types of induced cantilever oscillations. This excitation scheme ensures that electrostatic forces resulting from small tip-sample potential differences act conservatively on the oscillating cantilever, i.e. potential differences only induce phase variations while the oscillation amplitude remains constant. The phase of $\omega_{KFM}$ is a monotonous function of the potential difference with a linear slope around $(U_c - U_{DC}) \approx 0$, well suited for control by the Kelvin feedback circuit. Electrical excitation alone, as in standard KFM, would result in zero amplitude at $\omega_{KFM}$ and a phase jump of $\pi$ when $U_{DC}$ matches the contact potential difference, a situation hardly suitable for setting up a stable KFM controller.

Figure 2. Compensation of electrostatic forces leads to true topography measurements in tapping mode atomic force microscopy. Topography (a) of a gold-coated silicon grating showing height offsets when forces due to an externally applied bias voltage (b) are not compensated. True topography (c) when electrostatic forces are compensated locally by applying a voltage corresponding to the measured surface potential (d).

Figure 2 illustrates how electrostatic height offsets are eliminated with our new single scan KFM set-up. For comparison, figure 2(a) documents the height offsets experienced in standard tapping mode for various bias voltages between tip and sample as indicated in figure 2(b). With increasing bias voltage less details are detected in surface topography of the gold-coated silicon grating since the height offset adds to the average tip-sample distance and, therefore, weakens van der Waals interactions. Figure 2(c) depicts the topography when in a similar experiment the electrostatic forces exerted by an applied bias voltage are compensated by the single scan KFM method. The simultaneously acquired map of locally measured surface potential is depicted in figure 2(d).

The presented single scan Kelvin probe force microscopy technique will benefit precise and simultaneous height and potential measurements on active semiconductor and microsystem devices. We also expect this new method to offer higher sensitivity in composition and potential mapping on various kinds of surfaces, including minerals, Langmuir-Blodgett films, and structures used for molecular electronics.
3. Nano-xerography

Easy-to-use and versatile techniques for the precise positioning of molecules and nanoparticles on solid substrates play a crucial role in the emerging field of (bio)nanofabrication, for example to build molecular sensors or nano-electronic devices. Nano-xerography, i.e. the directed assembly of nano-objects onto electrostatic templates presents a particularly attractive process offering high selectivity, precision, and speed. Here we focus on electrostatic templates generated by writing electric charges into thin electret layers using the conductive tip of an atomic force microscope (figure 3). The latent charge image is developed in a solution carrying suspended nanoparticles or emulsion droplets [9, 10]. After rinsing, the carrier liquid is allowed to evaporate and the nano-objects remain firmly attached to the substrate by van der Waals forces. Alternatives to this process include charge writing with a patterned conductive stamp brought into conformal contact with the substrate [11] and development of the latent charge image in a gas atmosphere [12].

![Figure 3](image)

**Figure 3.** Nano-xerography. (a) Charge patterns are written into an electret layer on a solid substrate by applying voltage pulses to a conductive AFM tip. (b) The sample is developed in a suspension of nano-objects. (c) After rinsing and drying, the nano-objects remain selectively attached to the predefined pattern.

Carboxyl functionalized multiwalled carbon nanotubes with a nominal diameter of 10 nm and lengths between 100 nm and 10 \( \mu \)m were deposited directly from isopropyl-alcohol suspensions (20 \( \mu \)g/ml). Prior to deposition, the nanotube suspension was sonicated with a high-power probe for 30 min. Positive charge patterns, written into 100-120 nm thick poly(methyl)methacrylate (PMMA) layers spin-coated onto p-doped silicon wafer pieces, attracted the negatively charged nanotubes (figure 4) [13]. To write the charge patterns, voltage pulses of 70 V and duration of 1 ms were applied.

![Figure 4](image)

**Figure 4.** Nano-xerography of carboxyl functionalized multiwalled carbon nanotubes.
to a conductive AFM tip while it was drawn across the grounded substrate surface, resulting in a line pattern of charge dots with a potential of 5.5 V as determined by KFM immediately after charge writing.

In the past, mainly polarization forces have been used to guide the deposition and orientation of carbon nanotubes [14, 15]. In our case, however, Coulomb forces dominate because the carboxyl groups are negatively charged in isopropyl-alcohol. In addition, carboxyl groups increase the solubility of carbon nanotubes in isopropyl-alcohol, resulting in deposition patterns consisting of single tubes predominantly. Last but not least, direct deposition from suspension ensures high resolution and pattern definition.

We conclude that surface functionalization is a key factor controlling the deposition characteristics in nano-xerography. We expect that the presented process scheme can be extended to further classes of nanoscale objects.

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