Charge Writing and Detection by EFM and KPFM Scanning Probe Techniques

Nikolaus Knorr¹ and Stefan Vinzelberg²
1. Materials Science Laboratory, Sony Deutschland GmBH, Stuttgart, Germany
2. Atomic Force F&E GmBH, Mannheim, Germany

INTRODUCTION
Understanding the generation mechanisms and dissipation behaviour of electric charge on the surface and in the bulk of insulating materials is of importance to the study of a variety of phenomena, such as triboelectrification and electrostatic discharge (ESD), as well as to several current and future applications, such as cable insulation, laser printer and photocopier xerography, charge based data storage, plastic material recycling, and electret field-effect transistors, microphones, and dust filters. Remarkably, the charging and discharging mechanisms of insulators are often not understood in detail, and even today the identity of the charge carriers remains obscure in many cases [1-3].

A convenient tool for investigating these mechanisms is the atomic force microscope (AFM) because the charging can be realized with the same probe used for the analysis, and electric field sensitive AFM modes such as electrostatic force microscopy (EFM) and Kelvin probe force microscopy (KPFM; also known as scanning Kelvin probe microscopy, SKPM) provide highly resolved spatial information of the charge distribution with extremely high sensitivity. Accordingly, these methods have been used since their invention for the study of charging and discharging phenomena on insulators [4,5].

Biased AFM-probe-induced charge writing has found widespread interest, often in conjunction with data storage or nano-xerography. Charge pattern and xerographically assembled nanoparticles with feature sizes below 100 nm have been generated [6]. Another topic well suited for investigation by EFM and KPFM is triboelectric (frictional) and contact charging, because both the morphology and the charge distribution of the contacted surface are detected simultaneously in high resolution. Trboelectrification is a common phenomenon experienced any time two materials come into contact. Tribocharging affects us frequently in our daily lives due to the widespread use of highly insulating synthetic fibers and plastics with low surface and volume charge dissipation. Research on triboelectric charging mechanisms has recently found renewed interest [3,7,8], and AFM studies have helped in revealing new insights such as prevalent bipolar charging characteristics on micrometer length scales and the link of morphological features to the charge distribution [9].

In this article, biased-probe induced and triboelectric charging of thin insulating films is covered, with the focus on practical aspects of the AFM techniques. An Asylum Research MFP-3D AFM was used for all work described.

EFM AND KPFM MODES FOR CHARGE DETECTION
The EFM and KPFM methods are useful for high resolution studies of any system where external electric fields are present, such as for biased electrodes and devices or for contact potential differences of materials. Here, we are interested in the electric fields generated by uncompensated charge carriers deposited on or injected into insulators. The physical system under study is that of a thin insulating sheet or film of thickness d, with its free face charged by the biased AFM probe, by rubbing, or by evaporation of water drops, and its opposing face in good mechanical and electrical contact to a grounded back electrode. For both EFM and KPFM scans, the so-called dual-pass method is applied, with a first scan in dynamic contact mode recording the topography and a second scan for electric field recording along the same scan path in the non-contact mode but with an adjusted lift height h added to the previously recorded height information.

Typically, bare or metal-covered (Au, Pt, or Ptlr) AFM probes made of strongly doped Si with medium range force constants are used for EFM and KPFM. Here, Pt-covered AFM probes with relatively stiff cantilevers (40 N/m force constant) have been used to reduce the distortion of the topographic scan by the attraction between probe and charged surface, and to increase the resolution and sensitivity of the EFM scans by small EFM amplitude...
scanning (typically $h = 10$ nm, measured with respect to the height of contact in the topographic scan).

**ELECTROSTATIC FORCE MICROSCOPY**

Vertical force gradients generated by the electric fields emanating from the charged sample and interacting with the probe modify the harmonic potential of the cantilever spring (Figure 1). Attractive force gradients weaken the restoring cantilever force while repulsive force gradients cause the opposite effect (Figure 2A). This results in a negative or positive shift of the resonance frequency of the cantilever (Figure 2B). In EFM mode, these resonance shifts are detected by measuring the phase or the amplitude change of the cantilever oscillation which is mechanically excited by a piezo element at or near its resonance frequency. For small resonance shifts, the phase signal is proportional to the resonance frequency shift. Larger frequency shifts can be tracked by using a phase lock loop-type feedback that adjusts the drive frequency such that the phase remains at $90^\circ$. In this work, the phase signal ($\psi$) was evaluated.

Attractive force gradients make the cantilever effectively ‘softer’, reducing the cantilever resonant frequency and increasing the phase. Conversely, repulsive force gradients make the cantilever effectively ‘stiffer’, increasing the resonant frequency and reducing the phase.

A quantitative interpretation of the EFM signal is difficult because it depends in a complicated fashion upon the geometries of the probe, sample, and charge pattern due to the increasing the resonant frequency and reducing the phase. For approximate scanning of the charge, the force on the probe can be derived by considering that the energy of the capacitor ($\varepsilon_{p} = q^{2}/2$) is equal to the surface potential ($V_{SP}$) generated by the charge at the probe with respect to the grounded back electrode. Mapping $V_{AC}(x,y)$ thus reflects the distribution of the surface potential on the sample surface. The origin of the force on the probe can be derived by considering that the energy of the capacitor ($C$) formed by the probe and the electrode is given by:

$$E = \frac{1}{2} CV^{2}$$  \hspace{1cm} \text{Eq. 1}

The $z$ component of the electrostatic force is $F = \frac{1}{2} dC/dz V^{2}$. Because $V = (V_{AC} - V_{SP}) + V_{AC} \sin(\omega t)$, the vertical electrostatic force is the sum of three terms: a static term, one term oscillating with a frequency of $\omega$, and one with $2\omega$. The $\omega$ term is:

$$f_{EM} = dC/dz (V_{DC} - V_{SP}) V_{AC} \sin(\omega t)$$  \hspace{1cm} \text{Eq. 2}

which is nullified by a feedback loop for $V_{DC} = V_{SP}$. For a proper operation of the feedback loop, the insulating film has to be thin enough ($d < 20$ nm) also due to the attraction of $Q_{p}$ and $Q_{p}$, which have however interchanged signs. Close to the charge, $\psi$ is reduced due to the repulsion of $Q_{p}$ and $Q_{p}$ which is however somewhat attenuated by the attraction of $Q_{p}$. For smaller positive $V_{AC}$, these opposite forces result in camel-shaped phase scans.

**KELVIN PROBE FORCE MICROSCOPY**

Just as for EFM, there are several different KPFM modes. In our experiments, the cantilever is no longer driven mechanically by the piezo in the second pass, but an AC voltage $V_{AC} \sin(\omega t)$ is applied to the AFM chip, with $\omega/2\pi$ at the resonance of the cantilever. Any electric fields reaching the probe will exert a

![Figure 2](image1.png)

**Figure 2:**

(A) The harmonic potential of the cantilever spring is modified by an attractive or repulsive force gradient.

(B) This modification leads to a shift of the cantilever resonance frequency and an associated phase shift which is detected by the AFM control electronics.

![Figure 3](image2.png)

**Figure 3:**

Centre lines of EFM phase-scans of a positively charged spot at $x = 0$ on a 40 nm PMMA film. For $V_{AC} = 0$, no force acts on the probe ($\psi = 90^\circ$) and thecantilever oscillation which is mechanically excited by a piezo element at or near its resonance frequency. For small resonance shifts, the phase signal is proportional to the resonance frequency shift. Larger frequency shifts can be tracked by using a phase lock loop-type feedback that adjusts the drive frequency such that the phase remains at $90^\circ$. In this work, the phase signal ($\psi$) was evaluated.

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A quantitative interpretation of the EFM signal is difficult because it depends in a complicated fashion upon the geometries of the probe, sample, and charge pattern due to the long range nature of the Coulomb force. For example, a point charge $q$ on the surface of the insulting film will induce mirror charges in the probe apex ($q_{p}$) and the back electrode, which will all be mirrored again ad infinitum at the probe, dielectric, and electrode surfaces. For proximate scanning of the charge, the dominant force on the probe will be generated by the interaction of $q$ and $q_{p}$, yielding an attractive force which is proportional to $q^{2}$ (Figure 3). For strong or extended charge patterns, the fields reaching the cone of the probe and the cantilever will also considerably affect the cantilever oscillation. To obtain stronger and better defined charge signals, usually constant DC bias ($V_{DC}$) is applied to the probe during scanning of the second pass. In this case, for a point charge $q$ often only three forces need to be considered: the forces between the charge in the biased probe ($Q_{p}$) and its mirror charges in the dielectric and the electrode ($Q_{p}$), between $Q_{p}$ and $q$, and between $q$ and $q_{p}$ (Figure 3) [10]. For $V_{DC}$ above the surface potential of $q$ at the probe, $\Delta \psi$ is approximately proportional to $q$.

**KELVIN PROBE FORCE MICROSCOPY**

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which are constant on an area large enough to be resolved by KPFM are proportional to the measured surface potential [11]. Under these assumptions, the surface density $s$ of charges that are located on the surface of the insulating film can be approximated by the capacitor equation:

$$s(x,y) = \frac{\varepsilon \varepsilon_0 V_{SP}(x,y)}{d}$$  \hspace{1cm} \text{Eq. 3}

where $\varepsilon$ is the dielectric constant of the insulating film and $\varepsilon_0$ the electric permittivity of free space [12]. Eq. 3 follows from the fact that the charge induced in the probe/back-electrode capacitor by the applied voltage has to match the charge at the insulator surface in order to nullify the electric fields between the charge and the probe. For a uniform space charge density $\rho$ in the insulating film, it follows from the Poisson equation that:

$$\rho = 2\varepsilon \varepsilon_0 V_{SP}$$  \hspace{1cm} \text{[3]}$$

The lateral resolution of KPFM and EFM probes can not be determined easily. It is, however, generally advisable to use long and slender probes for higher resolution [14]. In addition, the use of rather thin insulating films is beneficial, because the range of the electric fields of the charges at the surface is reduced by the compensating fields of the mirror charges in the proximate back electrode. It should, however, be noted that, for biased-probe charge writing on very thin films ($d < 50$ nm), electric breakdown can easily damage the probe [15].

**BIASED-PROBE INDUCED CHARGE WRITING**

Many different types of insulating material are suitable for AFM charging experiments. Insulating sheets can be either glued to an electrode substrate, or a metal film can be evaporated onto the backside of the sheet. Alternatively, insulating films can be deposited directly on an electrode sample, for example, by thermal evaporation or by spin- or dip-casting from solution. The latter methods have the advantage of typically providing discharged and well-attached films of low surface roughness. The quality of the contact of the film to the sample is crucial because, for loose contacts, charge will also accumulate on the side of the sheet facing the electrode. Frequently used systems are oxide layers grown on doped Si wafers and thin ($d < 100$ nm) spin-coated films of poly(methyl methacrylate) (PMMA),

**Figure 5:**
Surface potential scan of a charge pattern written on PMMA in ambient air in contact mode using the Asylum Research lithographic tool software. Scan size: 8 $\mu$m x 8 $\mu$m. Colour scale: 1V.

**Figure 6:**
Surface potential scans of charge spots written in 2% RH on (A) glass, and (B) PTMSP, by 20 V, 40 V, 60 V, 80 V with 0.5 s pulses. Scan size: 10 $\mu$m x 5 $\mu$m. Colour scale: 5V.

**Figure 7:**
KPFM study on different aspects of charge spot writing for data storage. (A) 25 x 25 array of spots written on a large scale by (5 V, 0.5 s) pulses. (B) 9 x 9 array of charge spots (7 V, 0.5 s) with a 3 x 3 array erased by (7 V, 0.5 s) pulses. (C) Spots rewritten by 1, 10, and 100 (-30 V to 30 V, 10 Hz) square wave cycles, from bottom to top. For higher cycling numbers, peak widths are increased. This spot broadening can be reduced by the use of asymmetric pulses of shifted bias or pulse width. (D) From bottom to top: charge spots written in contact with load forces of 1 $\mu$N and 10 $\mu$N (+30 V, 5 ms), and with lift heights of h = 100 nm, 150 nm, and 200 nm by (+40 V, 10 s) pulses. (E) Charge spots written (+15 V, +18 V, +20 V with 1 s pulses, from bottom to top) and scanned with a high aspect ratio (~7:1) AFM probe. (A, B) on 20 nm PMMA; (C, D) on 40 nm PMMA; (E) on 30 nm CDC.

**Figure 8:**
Peak volumes, heights and widths of the KPFM charge peaks, as a function of applied voltage pulse height and width. Charge spots written on PTMSP (black squares), glass (blue triangles), and PVAc (red circles), all in 2% RH. Pulse widths in (A) are 0.05 s for PVAc and 0.5 s for glass and PTMSP. Pulse heights in (B) are +80 V for glass, +80 V and -60 V for PTMSP; and +60 V for PVAc (closed symbols for negative, open symbols for positive voltages). Lines indicate power law fits in (B) and square law fits in (A) with $V_{th} = +3$ V for glass, +9 V for PTMSP, and -10 V and +24 V for PVAc.
which can be strongly and persistently charged by comparatively low voltages (<50 V) under ambient conditions. Charging of insulators has been found to be highly variable in different laboratories and for different experimenters due to, amongst other things, its strong dependence on the humidity. Therefore, for quantitative charging experiments it is advisable to work under a well-defined atmosphere by performing the AFM experiments in a glove box (Figure 4) or in a humidity cell. A low humidity will also reduce the charge dissipation rate [16].

AFM charge writing can be accomplished by applying a constant bias or voltage pulses to the continuously scanning probe, or point-by-point applying a voltage pulse to the probe at a fixed location. In Figure 5, the surface of a 160 nm PMMA film has been charged continuously while scanning in contact mode by application of 50 V bias voltages using the lithographic tool of the Asylum Research software. To avoid damage to the AFM electronics, bias voltages above ±10 V were applied to the back electrode, electrically connected by a metal clamp which touches the electrode at a point where the insulating film has been removed. In this case the cantilever substrate was held at ground. For ±10 V, the authors verified that charge writing is symmetric for the two alternatives of bias application (cantilever substrate versus back electrode). In AFM charge writing of insulators, a probe which is positively biased relative to the back electrode usually yields positive charging and surface potential values at the sample surface and vice versa. To avoid confusion, voltages stated in the following text always refer to potentials applied to the cantilever substrate relative to the back electrode.

**CHARGE SPOT WRITING**

Charge spots were written in Figure 6 by square voltage pulses of up to 80 V on a 12-µm thick float glass slide and on a 1.4µm thick spin-cast film of poly(1-trimethylsilyl-1-propyne) (PTMSP), which is a high-free-volume glassy polymer of intrinsic porosity (inner surface: 550 m² g⁻¹) [11]. First, the probe was brought into contact with the polymer film by using contact mode AFM feedback with a controlled, low load force (typically 25 nN). Next, a square voltage write pulse was applied by triggering an external function generator connected to an external high voltage amplifier, and then the tip was retracted before moving to the next spot location. Usually, no modification in the topography at the contact position due to indentation of the tip is observed, because of the low load forces and relatively low voltages (<1000V) used.

Figure 7 summarizes the performance of some functions of AFM based charge writing which are relevant for data storage. All charge spots shown have been written and scanned in ambient air. Figure 7(A) indicates the high reproducibility of the method over a 90 x 90 µm² scan area, 7(B) demonstrates the targeted reversing in polarity (erasing) of single bits, 7(C) their re writable, 7(D) illustrates the insensitivity of charging to the applied load and that writing from a lift height is possible, and 7(E) demonstrates high resolution scanning of charge spots which are as small as 30 nm FWHM.

**CHARGE SPOT WRITING CHARGING MECHANISM**

The surface potential peak heights and widths of the charge spots are not correlated to the applied pulse voltages in a simple manner, one reason being that the size of the charged surface area is often too small to be resolved by the probe, yielding average values of the surface potentials above the charge pattern and the neighbouring uncharged areas [16]. It has been shown that the KPFM peak volumes, which are proportional to the total amount of surface-near charge, approximately follow a square law in the applied pulse voltage, offset by a threshold voltage $V_{th}$. The pulse width dependencies of KPFM peak volumes, heights, and widths can be approximated by power laws of positive exponents smaller than one [15]. Figure 8 shows results for glass and PTMSP (including data from Figure 6), and for which charge writing on a 1.0-µm thick polyvinyl acetate (PVAc) spin-cast film. $V_{th}$ is a key parameter shedding light on the charging mechanism. $V_{th}$ is increased for more hydrophobic materials of low water permeability and water uptake capacity. Based on this and other observations, such as the comparably weak effect of the probe load on the amount of injected charge (Figure 7), an electrochemical charging mechanism of ionic charge carriers mediated by the field-adsorbed water meniscus at the biased probe has been proposed [15]. Supposedly, either water ions are injected from the water meniscus into the insulating film (Figure 9) or, for materials with easily dissociable surface groups, ions from the insulating material are removed to the water phase driven by the high electrochemical potential of the biased water meniscus. According to the former mechanism, $V_{th}$ will be reduced for polymers with a high degree of free volume or high water swellability, because the penetrating ions may keep a larger fraction of their hydration shell when entering the polymer. The validity of the proposed charge injection mechanism is supported by the fact that charging is strong and achieved at low applied voltages for dried amor phous materials with a comparably high degree of water permeability such as SiO₂, Al₂O₃, PMMA, PVAc, polycarbonate (PC), polyacrylamide (PAAm), poly(acrylic acid), and PTMSP.

**TRIBOELECTRIC CHARGING**

Pronounced triboelectric bipolar charge patterns can be generated easily by rubbing an insulating film with almost any other material. Strong $V_{th}$ signals in the few voltage range can be achieved by using comparatively thick films ($d = 1 \mu m$) according to Eq. $3$. It is advisable to either use pointed rubbers, so that the entire width of rubbed track can be scanned (the maximum scan range of the MFP-3D scanner is 90 µm x 90 µm), or to scan the edge of broader rubbed tracks with the cantilever facing the untouched surface, in order to reduce the interaction of the AFM cantilever with the charge pattern and to have a pristine surface.
Interesting observations are: rubbed tracks are much higher mobilities on the surface and in the volume of most materials at increased RH [16]. At low RH (<10%), strong charge patterns can be generated when at least one rubbing partner is made of a somewhat hydrophilic copolymer (COC), PMMA, and PAAm. Some charge (for example by dissociation of the water molecules into positive and negative ions), but it can also act as a sink of water ions, which may, interestingly, be caused by adsorbed water can be the source of the triboelectric charge (for example by dissociation of the water molecules into positive and negative water ions), but it can also act as a sink of charge, because ionic charge carriers have much higher mobilities on the surface and in the volume of most materials at increased RH [16]. At low RH (<10%), strong charge patterns can be generated when at least one rubbing partner is made of a somewhat hydrophilic material and the charge patterns are generally fairly durable over many days. Examples are given in Figures 10 and 11 for PAAm, PVAc, and PMMA films rubbed by cyclic olefin copolymer (COC), PMMA, and PAAm. Some interesting observations are: rubbed tracks are generally charged bipolarly, at onsets of tracks material from the rubber is deposited and surfaces are strongly charged, nanoscopic strongly charged particles are frequently observed along the rubbed track (Figure 11), and stick-slip friction is reflected in the charge pattern.

At higher RH, however, the charge patterns are often rapidly dissipated, especially for materials with a high degree of water uptake capability or water permeability. Rubbing combinations of two hydrophobic materials (such as Teflon, poly styrene, polydimethylsiloxane (PDMS), cyclo-olefin polymers (COP), polyvinylchloride (PVC), silicone rubber, polyethylene (PE), polypropylene (PP)) will generate much weaker charge pattern at low humidity, but stronger ones at higher humidity (RH >50%), and charge patterns on such materials are stable even in higher humidity.

TRIBOELECTRIC CHARGING MECHANISM

The mechanism of triboelectric charging is under debate. To explain the complexity of the observations, assumedly several different mechanisms contribute to the charging, their prevalence depending on the type of materials involved and the conditions under which the triboelectrification is generated. In Ref [9], an insulator/insulator triboelectric charging mechanism by separation of dissociated water ion pairs stemming from adsorbed water has been proposed: the positive water ions, i.e. hydrated protons, are preferentially dragged along the surface together with an excess of adsorbed water in front of a conformal rubbing contact due to their lower adhesion to and increased separation from the surface, leaving behind the relatively stronger bond and near-surface negatively charged water ions. This explanation finds support in the observation that water droplets evaporating on hydrophobic surfaces generate a pronounced bipolar charge pattern of a negatively charged dewetted circumferential boundary and a strongly positively charged core (Figure 12). Presumably, negative water ions are preferentially left behind on the surface by the receding three-phase line due to their higher affinity than the positive water ions to the polymer/water interface, leading to an accumulation of excess positive ions in the shrinking evaporating droplet.

CONCLUSIONS

The EFM and KPFM methods have been discussed, including interpretation of the measured variables with regard to uncompensated charge deposited on insulating dielectric films. Practical hints have been given for the controlled generation of charge patterns by triboelectrification and biased-probe induced charging, as well as methods for quantification of the measured signals for the latter. Possible charging mechanisms have been discussed, which may, interestingly, be caused by dissociation and ion separation of adsorbed water in both cases.

REFERENCES

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