MASTER

Electric force microscopy: method development and application to the problem of toner-transfer

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Electric Force Microscopy: method development and application to the problem of toner-transfer

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“De schrijver/schrijfster werd door Océ-Technologies B.V. in staat gesteld een onderzoek te verrichten, dat mede aan dit rapport ten grondslag ligt. Océ-Technologies B.V. aanvaardt geen verantwoordelijkheid voor de juistheid van de in dit rapport vermelde gegevens, beschouwingen en conclusies, die geheel voor de rekening van de schrijver/schrijfster komen.”
Summary

Scanning Probe Microscopy (SPM) is still a dynamically expanding research field. In the eighties, the invention of the Atomic Force Microscope initiated an immense research effort in surface analysis. Since then, many Scanning Probe Techniques have been developed and even more applications have been investigated.

In September 2000 the department Analysis & Measurements of Océ Technologies purchased a Dimension 3100 of Digital Instruments to perform Scanning Probe Microscopy. Since then, Océ has been exploring the opportunities and possibilities to use the Scanning Probe Microscope as a tool in the research area of interaction between toner and image-forming media and toner-transferring media. This report discusses the systematic exploration of two types of Scanning Probe Microscopy: Electric Force Microscopy (EFM) and Scanning Kelvin Probe Microscopy (SKPM).

EFM and SKPM are two scanning probe techniques which are able to characterize electrical properties of a material. The operation of the techniques is based on the long range Coulomb interaction between a conductive SPM tip and the sample. In an EFM measurement the gradient of the electric force between tip and the sample is imaged. In a SKPM measurement, variations in the surface potential on the sample are imaged. Applications of these techniques include among others electrical failure analysis, detecting trapped charges, quantifying contact potential differences between metals and/or semi-conductors, mapping relative strength and direction of polarization and testing electrical continuity. In our experiments EFM and SKPM are used to solve problems related to Océ printers.

First, a specially prepared Direct Imaging Process drum with 5 different dielectric layers sputtered on it is used to systematically explore EFM and SKPM. The EFM results are also compared to numeric model calculations and theory. From this method development part of the graduation project, it turns out that the Scanning Kelvin Probe Microscope proved its capability to measure surface potentials. The measurement accuracy of SKPM has a maximum deviation of 5% and the minimum detectable potential differences are in the order of mV. The lateral resolution is limited by the size of the used tip (about 50nm). The Electric Force Microscope turns out to be an excellent tool to image local variations in the electric force gradient between tip and sample. The lateral resolution is limited by the tip size (about 50nm). The minimum detectable force gradients are in the range of 0.0001 N/m.

In the application part of the graduation project, EFM is used as a tool to study the problem of surface conduction in the carbon black filled rubber intermediate. It turns out that EFM provides us with a tool to visualise the percolating carbon black network at the surface as well as in the bulk. From these measurements two striking features come to our attention. The first feature concerns the fact that the percolating network “experienced” by the tip at the surface is less fine structured than that in the bulk. This effect is due to the existence of an impoverished carbon skin at the surface layer. The second feature concerns the fact that this impoverished carbon skin reduces the electric force gradient “experienced” by the tip. It turns out that EFM can be used successfully to characterise the “electric thickness” of the impoverished carbon skin. Furthermore, some attention is paid to the characterisation of the distribution of the percolating network. Although a promising methodology has been defined to characterise the distribution, this methodology needs to be developed further.
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1 Introduction

In their CPS 700 printer/copier, introduced earlier this year, Océ has applied for the first time their unique Direct Imaging technology [1,2,3]. With the help of seven development units seven different toner colors are printed separately at a rubber intermediate and successively, in one pass, transferred to paper. See figure 1.1.

Figure 1.1: Side view of the CPS 700. The intermediate is surrounded by 7 different color drums (IMU 1 = black, IMU 2 = blue, IMU 3 = red, IMU 4 = green, IMU 5 = magenta, IMU 6 = Cyan and IMU 7 = yellow).

1.1 Direct Imaging Process drum

The heart of each development unit is the Direct Imaging Process drum. This is an aluminum cylinder at which, under an dielectric surface layer of SiOx, conducting traces in an insulating epoxy coating are created (traces have an axial resolution of 400dpi, or 600 dpi in the newest machines). A potential can be applied to each individual trace with the help of electronics inside the Process drum. See figure 1.2.

Figure 1.2: Schematic view of the Direct Imaging Process drum with 5000 (400dpi) traces. The electronics have been positioned inside the Process drum at four arrays.
1 Introduction

The Process drum turns around against a magnetic knife, that pulls off and transports away the continuous applied toner, unless a potential of 40 V is applied to the traces. In this case the toner particles are bounded to the drum surface by the induced electric force. The toner particles that remain on the drum are successively printed to the rubber intermediate and from there fused to the paper. In figure 1.3 a schematic drawing of this process is pictured.

![Schematic drawing of the Direct Imaging unit.](image)

Figure 1.3: Schematic drawing of the Direct Imaging unit.

1.2 Process drum production

Océ produces the Direct Imaging Process drum in a clean-room. The base is formed by an aluminum cylinder with four internal arrays bonded in grooves at an angle of 90 degrees to the track direction. The arrays consist of standard print board material (FR4) with 900μm copper tracks, which end at exactly the same level as the aluminium cylinder. Very small chisels cut the track pattern in a thin coating of insulating epoxy, which is deposited at the aluminum body. This produces the characteristic "turret shape" of the drum tracks (see figure 1.4) with a depth of approximately 40μm.

![3-D perspective of drum-tracks with toner particles on the drum surface. “Turret shape” drum tracks have been cut in the insulating epoxy.](image)

Figure 1.4: 3-D perspective of drum-tracks with toner particles on the drum surface. “Turret shape” drum tracks have been cut in the insulating epoxy.

The interconnection between a drum trace and the copper tracks at the internal print boards is made by shooting a hole in the epoxy layer with the help of an eximer laser. In this hole a thin copper layer is sputtered and afterwards it is filled with conducting carbon epoxy. Finally, a thin SiO₂ surface layer (about 0.9μm) is sputtered onto the drum. This production process is depicted in figure 1.5.
The SiO$_x$ surface layer actually consists of a SiO$_{3.4}$ bottom layer (300nm thickness) and a SiO$_{1.3}$ top layer (600nm thickness). The more conducting bottom layer serves to mask the insulating areas between the turret shape drum tracks. This ensures that toner is not only printed at the conducting traces but also at the insulating areas between them. The more insulating top layer serves to charge the toner electrically, so that toner remains bounded to the top layer with an electric force. It is also necessary that charges can flow away sufficiently fast from the top layer so that toner can be uncharged. It has to be emphasized that in the transfer pass the electric bonding of toner to the top layer needs to be smaller than the adhesive force of the intermediate! Besides the dielectric conducting function of the top layer, the top layer also forms a hard protection layer, which makes the Direct Imaging Process drum a very robust printhead.

1.3 Intermediate

Toner particles that remain on the drum, are printed to the rubber intermediate ("first step") and from there fused to the paper ("second step"). The first step is taken with the help of adhesive forces. The intermediate consists of a glassy cylinder with a rubber basis layer coated on it (thickness 2mm). On this basis layer, a 100µm thick coating is deposited. It is of great importance that the toner adheres very well to the rubber top layer. The smoothness of the nip (= the transition between drum and intermediate) and the hardness of the rubber are two important parameters in this process. After the images of the seven drums have been collected on the intermediate, the total image is transported to the heater, where the toner is heated to 100°C. Because of this, the toner softens and is pressed on paper more easily. This second step requires the top layer to be not too sticky; else, paper with the toner would stick to the intermediate!

1.4 Challenges

One of the main spearheads in the Océ philosophy is print quality. Therefore, much attention is being paid to so called imaging artefacts. In Direct Imaging one of these, only partially understood, artefacts is the so-called "toner-jumping". "Toner-jumping" means that toner particles are able to jump to a neighboring trace at the moment that 40V is applied to this trace. Simulations [2] suggest that this artefact is strongly influenced by the electric field near the surface of the dielectric SiO$_x$ layer, which is determined by the geometry of the traces. See figure 1.6.

Figure 1.5: Drum production steps, side view of trace pattern: A) Cutting the trace pattern; B) Lasering of interconnections; C) Sputtering process of copper; D) Filling with conducting carbon epoxy; E) Sputtering process of SiO$_x$ layer.
However, one of the reasons that toner jumping is still only partially understood is the fact that formerly no suitable tool was available to measure field variations at the scale of a single trace.

Further, it is a challenge to obtain a good conductive surface layer for the rubber intermediate. This surface conductivity is needed to prevent print artefacts. By adding conductive Carbon Black particles, the silicon rubber intermediate is made more conductive. However, it turns out that an undesired “carbon-less skin” or “impoverished carbon skin” is formed, restraining the essential conductivity of the surface layer. In spite of all the efforts to assess the “impoverished carbon skin”, no adequate tool or method has been available to characterize the skin and its consequences.

1.5 Assignment

In September 2000 the department Analysis & Measurements of Océ Technologies purchased a Dimension 3100 of Digital Instruments to perform Scanning Probe Microscopy. Since then, Océ has been exploring the opportunities and possibilities to use the Scanning Probe Microscope as a tool in the research area of interaction between toner and image-forming media (DIP) and toner-transferring media (intermediate). This report discusses the systematic exploration of two types of Scanning Probe Microscopy: Electric Force Microscopy (EFM) and Scanning Kelvin Probe Microscopy (SKPM).

EFM and SKPM are two scanning probe techniques which are able to characterize electrical properties of a material. The operation of the techniques is based on the long range Coulomb interaction between a conductive SPM tip and the sample. In an EFM measurement the gradient of the electric force between tip and the sample is imaged. In a SKPM measurement, variations in the surface potential on the sample are imaged. Applications of these techniques include among others electrical failure analysis, detecting trapped charges, quantifying contact potential differences between metals and/or semi-conductors, mapping relative strength and direction of polarization and testing electrical continuity. In our experiments EFM and SKPM are used to solve problems related to Océ printers.

First, a Direct Imaging Process drum is used to systematically explore EFM and SKPM. After that, EFM is used as a tool to study the problem of surface conduction in the carbon black filled rubber intermediate.
In this report a general introduction to Scanning Probe Microscopy and some of its most common features are described in chapter 2. In chapter 3 an explanation of EFM and SKPM, including a theoretical background, are given. The experiments that have been performed on several test samples are described in chapter 4. Chapter 5 shows and discusses the results of these experiments. Also a comparison is made between the results obtained by EFM and SKPM. In chapter 6, EFM is used to study the surface conductivity in carbon filled rubbers used in the intermediate. Also some ideas for future work are presented. Finally, in chapter 7 the main conclusions of this work are presented.
2 General Introduction to SPM

The Atomic Force Microscope (AFM) is one of many types of scanning probe microscopes. All of these microscopes work by measuring a local property - such as height, or magnetism - with a force-sensing probe or "tip" placed very close to the sample. This chapter discusses the working principle of the AFM and the most common AFM modes [4]. Since operation of AFM is based on the interaction-force between tip and sample, the forces encountered by the tip as it approaches the sample will be discussed. Furthermore, a few remarks with respect to the various detection methods are made.

2.1 Working principle of AFM

The principles on which the AFM works are very simple. A very sharp tip is scanned over a surface while a feedback system maintains the tip at a constant force on the surface (to obtain height information), or at constant height (to obtain force information) above the sample surface. Tips are typically made from Si₃N₄ or Si, and are mounted at the end of a flat spring, the so-called cantilever. The tip is attached to the bottom of the cantilever. As the tip scans the surface of the sample, the cantilever deflects while the tip moves up and down with the contour of the surface. The AFM head uses an optical system to detect the deflection of the cantilever. A diode laser is focused onto the back of the reflective cantilever and the laser beam is reflected into a dual element photodetector. The photodetector measures the difference in light intensities between the upper and lower elements. This is used as a feedback difference signal, which enables the piezo scanners to maintain the tip at a constant force, or at constant height above the sample surface. In figure 2.1 all of this is shown.

![Feedback loop of the AFM](image)

Figure 2.1: Feedback loop of the AFM

1 The Dimension 3100 series system uses a 4 element photodetector which enables the measurement of frictional forces which cause torsional deflection of the cantilever.
2.2 The Common AFM Modes

In the Scanning Probe community there are three widely used AFM modes: contact mode, non-contact mode and tapping mode. These modes, which are displayed in figure 2.2, will be discussed in the subsequent paragraphs.

Contact Mode

This is the common mode used in the force microscope. In contact mode the tip scans the sample in close contact with the surface. The force on the tip is repulsive with a value in the order of $10^{-9}$ N. This force is set by pushing the cantilever against the sample surface with a piezoelectric positioning element. In contact mode AFM the deflection of the cantilever is measured and compared in a DC feedback amplifier to some desired value of deflection. If the measured deflection is different from the desired value, the feedback amplifier applies a voltage to the piezo to raise or lower the tip relative to the sample surface to restore the desired value of deflection. The voltage that the feedback amplifier applies to the piezo is a measure of the height of features on the sample surface. It is displayed as a function of the lateral position of the sample. The system is thus trying to maintain a constant deflection of the cantilever, and thus also trying to maintain a constant force between the tip and the sample surface.

Problems with contact mode are caused by excessive lateral forces applied by the probe to the sample. The effects can be reduced by minimizing lateral force of the probe on the sample, but there are practical limits to the magnitude of the force that can be controlled by the user during operation in ambient environments. Under ambient conditions, sample surfaces are covered by a layer of adsorbed gases consisting primarily of water vapor and nitrogen which is 10-30 monolayers thick. When the probe touches this contaminant layer, a meniscus forms and the cantilever is pulled toward the sample surface by surface tension. The magnitude of the force depends on the details of the probe geometry, but is typically on the order of 100 nanoNewtons. This meniscus force and other attractive forces may be neutralized by operating the probe and part or all of the sample totally immersed in liquid. In addition, a large class of samples, including semiconductors and insulators, can trap electrostatic charge (partially dissipated and screened in liquid). This charge can contribute to additional substantial attractive forces between the probe and sample. All of these forces combine to define a minimum normal force that can be controllably applied by the probe to the sample.
This normal force creates a substantial frictional force as the probe scans over the sample. In practice, it appears that these frictional forces are far more destructive than the normal force and can damage the sample, dull the cantilever probe and distort the resulting data.

2.2.2 Non-contact Mode

In the non-contact mode the tip hovers 50 - 150 Angstrom above the sample surface. Attractive Van der Waals forces acting between the tip and the sample are detected, and topographic images are constructed by scanning the tip above the surface. Unfortunately the attractive forces from the sample are substantially weaker than the forces used by contact mode. Therefore the tip must be given a small oscillation so that AC detection methods can be used to detect the small forces between the tip and the sample by measuring the change in amplitude, phase, or frequency of the oscillating cantilever in response to force gradients from the sample. For highest resolution, it is necessary to measure force gradients from Van der Waals forces, which may extend only a nanometer from the sample surface. In general the fluid contaminant layer is substantially thicker than the range of the Van der Waals force gradient. Therefore attempts to image the true surface with non-contact AFM fail as the oscillating probe becomes trapped in the fluid layer or hovers beyond the effective range of the forces it attempts to measure. Performing measurements in UHV on cleaved/baked surfaces can solve these problems.

2.2.3 Tapping Mode

Tapping mode is a key advancement in AFM. This technique allows high resolution topographic imaging of sample surfaces that are easily damaged, loosely bonded to their substrate, or are difficult to image by other AFM techniques. Tapping mode overcomes problems associated with friction, adhesion, electrostatic forces, and other difficulties that can plague conventional AFM scanning methods by alternately placing the tip in contact with the surface to provide high resolution and then lifting the tip off the surface to avoid dragging the tip across the surface. Tapping mode imaging is implemented in ambient air by oscillating the cantilever assembly at or near the cantilever’s resonant frequency using a piezoelectric crystal. The piezo motion causes the cantilever to oscillate with a high amplitude (typically greater than 20nm) when the tip is not in contact with the surface (it is said to be in “free air”). The oscillating tip is then moved toward the surface until it begins to lightly touch, or tap the surface. During scanning, the vertically oscillating tip alternately contacts the surface and lifts off, generally at a frequency of 50 to 500,000 cycles per second. As the oscillating cantilever begins to intermittently contact the surface, the cantilever oscillation is necessarily reduced due to energy loss caused by the tip contacting the surface. The reduction in oscillation amplitude is used to identify and measure surface features.

During tapping mode operation, the reduced cantilever oscillation amplitude is maintained constant by a feedback loop. Selection of the optimal oscillation frequency is software-assisted and the force on the sample is automatically set and maintained at the lowest possible level. When the tip passes over a bump in the surface, the cantilever has less room to oscillate and the amplitude of oscillation decreases. Conversely, when the tip passes over a depression, the cantilever has more room to oscillate and the amplitude increases (approaching the maximum “free air” amplitude). A digital feedback loop is used to adjust the tip-sample separation to maintain a constant oscillation amplitude and force on the sample.
2.3 Forces encountered by an AFM probe as it approaches the sample surface

As mentioned before, the working principle of AFM is the interaction-force between tip and sample (since the tip is force-sensing). Therefore some attention is paid now to the forces encountered by the tip as it approaches the sample. In Figure 2.3 an overview of these forces is given.

![Figure 2.3: Forces encountered by an AFM probe as it approaches the sample surface.](image)

**Air damping**

The first boundary is only encountered by probes which are in tapping mode. A damping air film is developed when an oscillating probe comes to within 10 microns of the sample surface. At this distance, air is squeezed between the probe and the surface during each downstroke of the probe. Conversely, as the probe rebounds upward, a partial vacuum results. This pumping effect dampens probe motion somewhat and may lead to false engagement of the surface. If the boundary is passed, however, the phenomenon disappears. Again, tips which are well clear of the surface are said to be oscillating in “free air”.
Electrostatic forces

The next boundary encountered is the electrostatic force zone beginning at 0.100-1.00 microns. Electrostatic forces may be either attractive or repulsive and vary according to the material. Many low-conductivity materials (for example, silicon nitride) exhibit strong electrostatic force properties, while conductors (for example, gold) exhibit smaller electrostatic forces. Electrostatic interaction between tip and sample can be strong enough to interfere with imaging. Using Electric Force Microscopy (EFM), the electrostatic forces on materials may themselves be imaged.

Fluid Surface Tension

Surface tension effects results from the presence of condensed water vapor at the surface. This is an attractive force, and can pull a tip down toward the sample surface strong enough to indent some materials. Depending upon how much water vapor is present, surface tension effects begin at 10-200 nm above the surface. Usually, Tapping mode is employed to alleviate surface tension attraction. (The oscillating tip allows it to break free of the water layer.) Usually, surface tension attraction develops between a “wet” sample and a “dry” tip. If delicate samples are to be imaged, it may be necessary to immerse both tip and sample entirely in fluid to prevent surface tension attraction. Various forms of fluid imaging are available, including contact AFM and tapping mode.

Van Der Waals Forces

At the angstrom level above the surface, Van Der Waals forces cause a weak attraction between atoms in the tip and sample. This attraction is detectable by SPM electronics and is used to monitor non-contacting tip-sample interactions.

Coulombic Forces

The tip and sample are said to “contact” when their respective atoms encounter each others coulombic forces. At this level, electron shells from atoms on both tip and sample repulse one another, preventing further intrusion by one material into the other. Pressure exerted beyond this level leads to mechanical distortion of one or both materials, and the tip may be damaged.
2.4 Detection methods; e.g. Phase Imaging

In tapping and non-contact modes the surface is scanned by an oscillating probe. The oscillations of the cantilever are excited by the cantilever piezo- or bimorph-driver. The tip oscillation amplitude and phase with regard to the harmonic signal applied to the piezo elements (=piezo/bimorph driver generator voltage), depend on the interaction between the oscillating tip and surface. Therefore, the tip oscillation amplitude and the phase depend on the (material) properties of the sample. This is depicted in figure 2.4.

![Figure 2.4: Influence of changes in sample properties on the tip. A change in sample properties will result in a change in oscillation amplitude and/or phase.](image)

Normally, the oscillation phase is more sensitive - compared to the amplitude - to changes in interaction between the probe and the sample. In particular, the oscillation phase is more sensitive to changes related to local variations in surface adhesion and viscoelasticity. Acquiring a phase signal image simultaneously with a surface topography image provides additional information on the surface structure details. This method is called Phase Imaging. In case of a smooth surface the Phase Imaging technique provides contrasting images of the surface structure details related to local variations in surface adhesion and viscoelasticity. Applications include identification of contaminants, mapping of different components in composite materials, and differentiating regions of high and low surface adhesion or hardness.

Anyway, the reader should be aware right now of the possibility to detect not only changes in amplitude, but also changes in phase, due to variations in sample properties.
3 EFM & SKPM

This chapter presents in the first paragraph the Electric Force Microscopy theory in a phenomenological manner. Scanning Kelvin Probe Microscopy is subject of discussion in the second paragraph.

The previous chapter pointed out that the operation of any type of Scanning Force Microscopy is based on the force interaction between a sharp tip (connected to a cantilever) and (the surface of) a sample. The interaction force is measured by the deflection of a cantilever where a sharp tip is mounted at the end of the cantilever. To gain insight in this deflection principle, a theoretical background [5] of the interaction of a sharp tip on a lever mounted on a vibrating bimorph is discussed in Appendix A. In the first subsection of Appendix A, the concept of an effective spring constant, which accounts for force derivatives acting on the sharp tip connected to the lever, is introduced. Then the equation of forced motion of the damped lever, which is mounted on a vibrating bimorph, is solved. In the third subsection the equations concerning the case of an electric force, according to [6], will be presented.

3.1 Electric Force Microscopy

EFM is used to map the vertical and near-vertical gradient of the electric force between the tip and the sample versus the in-plane coordinates x and y.

Consider a conductive AFM tip that can interact with the sample through the long range electrostatic forces. In figure 3.1 the amplitude (white) and phase (yellow) frequency responses of a metal-coated AFM cantilever/tip above a sample of aluminum are depicted around its resonance frequency [7]. The sample is held either at 0V (top) or at 10V (bottom) relative to the grounded tip. The tip is never in contact with the sample. In presence of an electric field (bottom plot), the tip experiences an attractive force toward the sample and the entire resonance curve is shifted to a lower resonance frequency. The amplitude and the phase of the lever are now influenced by the force derivative.

![Figure 3.1: Amplitude (white) and phase (yellow) frequency response of metal coated AFM cantilever/tip above sample of aluminum held at 0V (top) and 10V (bottom) relative to grounded tip.](image-url)
The lever, as it moves down in its excursion, is assisted by the increasing interaction force and moves further down than in the case of an uniform interaction force. As the lever moves up, the interaction force decreases so that the net restoring force acting on the lever increases and the lever will again move up, further than for the uniform case. Consequently, the amplitude of vibration of the lever will increase. Effectively, the stiffness (=effective spring constant \( k' \)) is reduced. This means, according to expression (A.32) in Appendix A

\[
\omega_0' = \sqrt{\frac{k'}{m}}, \tag{A.32}
\]

that the resonance frequency of the cantilever (\( \omega_0' \)) is reduced too. This is in agreement with the shift of the entire resonance curve to a lower resonance frequency in figure 3.1. These changes in the cantilevers amplitude and phase are used to characterize electrical properties on, or just beneath, the surface of the sample.

EFM is performed in one of the following modes:

- amplitude detection,
- phase detection,
- or frequency modulation.

In amplitude and phase detection modes the drive signal that oscillates the cantilever has constant frequency. The EFM image is then generated by plotting the cantilevers phase or amplitude versus the in-plane coordinates. In our experiments frequency modulation has been used. This means that the feedback loop keeps the phase of the cantilever oscillation compared to the piezo-driver oscillation signal at a constant value by changing/modulating the drive frequency. Now, these modulations of the drive signal frequency \(-\delta\omega\) are plotted versus the in-plane coordinates, producing a map of the strength of the electric force gradients, according to Eq. (A.59)

\[
F_1 = 2k \frac{\delta\omega}{\omega_0}. \tag{A.59}
\]

Here \( F_1 \) is the vertical electric force gradient \( (\partial F/\partial z) \), \( k \) is the mechanical spring constant and \( \omega_0 \) is the resonance frequency of the piezo driven cantilever.

Finally, note that all EFM modes produce two images: one of topography and the other of electric force gradients. Since height variations on the sample surface can diminish the fidelity of EFM images, they are compensated for using the “LiftMode” technique. The “LiftMode” technique is explained in figure 3.2 [7].
Figure 3.2: Schematic representation of the Liftmode operation.

In this technique, the height data (topography) is recorded in TappingMode during the first pass. Then, in the second pass, the tip lifts above the surface to an adjustable “Lift Height”, typically 10-500nm, and scans the same line while following the height profile recorded in the first pass. This ensures that topography will affect the electric force gradient image to a minimum. In the diagram the green-colored regions in the sample symbolizes the source of contrast in the EFM image.

3.2 Scanning Kelvin Probe Microscopy

Scanning Kelvin Probe Microscopy (SKPM) allows measurement of local sample surface potential. SKPM is also a two-pass system where the first pass obtains topography and the second pass measures surface potential. The two measurements are interleaved, that is, they each measure one line at a time with both images displaying simultaneously on the screen.

Again, on the first pass, standard Tapping Mode measures the sample topography. In Tapping Mode the cantilever mechanically vibrates near its resonant frequency by a small piezo-electric element in the cantilever holder called the drive piezo. On the second pass, this piezo is turned off. Instead, to measure the surface potential, an oscillating voltage,

\[ V_1 \sin \Omega t, \]  

is applied directly to the tip. This creates an oscillating electric force at frequency \( \Omega \) on the cantilever. This oscillating force equals the following expression, according to Eq. (A.50),

\[ F_\Omega = \left[ \frac{q \cdot V_1}{4\pi \epsilon_0} \frac{C}{z^2} + C' \cdot \frac{V_d}{z} V_1 \right] \sin(\Omega t). \]  

(A.50)

Here \( C \) is the tip-sample capacitance, \( C' \) its vertical derivative, \( V_d \) the external voltage applied between tip and sample (\( V_d = V_{tip} - V_{sample} \)) and \( q \), the charge deposited on a thin insulating film placed on top of the sample. For the case that \( q_s = 0 \), this yields
Thus the force on the cantilever depends on the product of the AC drive voltage and the DC voltage difference between the tip and the sample. When the tip and the sample are at the same DC voltage, $V_{dc} = 0$, the cantilever experiences no oscillating force. Therefore, the effective local surface potential on the sample can be determined by adjusting the DC voltage on the tip, $V_{tip}$, until the oscillation amplitude equals zero. This is called a “nullifying” technique. At this point the tip voltage remains the same as the unknown surface potential. The voltage applied to the cantilever tip, $V_{tip}$, is recorded as function of the in-plane coordinates, creating a voltage map of the surface.

Note that SKPM is a “nullifying” technique. This means that the other terms in expression (3.2) are, theoretically, of no importance to the measurement. In other words $C'$ as well as $V_1$ should have no influence at the measured surface potential.
4 Experiments

In order to gain insight into SKPM and EFM concerning the nature of the methods and the interpretation of the results, it is necessary to perform some exploring experiments. This chapter discusses the structure of these experiments. Later on, in chapter 6, the techniques are applied to an Océ application.

4.1 Method development SKPM

SKPM is a method to monitor variations in surface potential on a sample. In order to test the performance of the Scanning Kelvin Probe Microscope, measurements are performed on several different test structures. These test structures and the experiments performed on them are described in the next two subsections.

4.1.1 Two gold sputtered electrodes

Since the Scanning Kelvin Probe Microscope measures local variations - and their absolute values - in surface potentials of a sample, the first issue that arises is the capability of measuring well-defined voltages. For this purpose, a test sample has been prepared. The test sample consists of a glass substrate (a microscope slide) with a gold layer (approximately 15 nm thickness) sputtered on it. This gold layer is separated into two parts. This is done by covering the substrate with a very tiny tungsten wire (diameter is 45 µm) during the sputtering process. After the sputtering process the tungsten wire is removed, resulting in an insulating barrier of approximately 40-50µm. This barrier between the two electrodes is shown in the Light Microscopic pictures of the sample in figure 4.1 beneath.

![Figure 4.1: Two gold electrodes separated by an insulating barrier.](image_url)

With the help of two conducting wires and some electroconductive paint, the electrodes are connected to a power source, resulting in the following electrical scheme (figure 4.2):
Figure 4.2: Schematic electrical scheme of two gold electrodes separated by an insulating barrier. One electrode is connected to 0 volt relative to ground and one electrode can be adjusted to a preferred value relative to ground.

As can be seen, one electrode is connected to 0 volt relative to ground and the potential of the other electrode can be adjusted to a preferred value relative to ground. Using this setup it is possible to study how good a well-defined potential or potential difference can be measured. Therefore, measurements have been performed as function of applied potential.

Furthermore, in paragraph 3.2 it has been explained that SKPM is a “nullifying” technique and that the first derivative of the tip-sample capacitance, $C'$, should logically have no influence at the measured surface potential values. Since the tip-sample capacitance is among others determined by their mutual distance, a measurement of the surface potential should not depend on the “Lift Height”. Therefore, measurements with a fixed applied electrostatic potential have been performed as function of “Lift Height”.

4.1.2 Special prepared Direct Imaging Process drum for experiments

In order to investigate the distinguishing and reproducing power of the Scanning Kelvin Probe Microscope, it is necessary to develop several samples with different electrical properties. It turned out that the earlier discussed production steps of the drum (paragraph 1.2) and more specific the SiO$_x$ sputtering process, provide us with a tool to develop several samples with different electrical properties. Namely, by changing the sputter conditions, layers with different thickness and different oxygen percentage can be deposited at a bare epoxy drum (= a drum after step D in the production process, in figure 1.5), resulting in several samples usable for gaining insight into SKPM. Hence, using this train of thoughts, 5 different layers have been sputtered at a bare 600dpi epoxy drum. This specially prepared drum is depicted in figure 4.3.
The different layers have the following characteristics:

A) SiO$_{0.4}$ layer, thickness 150nm (half bottom layer);
B) SiO$_{0.4}$ layer, thickness 300nm (bottom layer);
C) Combined SiO$_{0.4}$ layer, thickness 300nm with a SiO$_{1.2}$ layer, thickness 600nm (print layer);
D) SiO$_{1.2}$ layer, thickness 600nm (top layer);
E) SiO$_{1.2}$ layer, thickness 300nm (half top layer).

Note that it is possible to perform measurements in the areas between the deposited layers. So, in this manner, it is also possible to measure at the bare epoxy drum layer.

Since the deposited layers have different thickness and different dielectric constants (bottom layer: $\varepsilon_r = 7$; top layer: $\varepsilon_r = 3.8$), the total resistance of the several layers is different. As a consequence, the effective surface potential should differ for each layer. This means, that these different layers provide us with a tool to investigate the distinguishing and reproducing power of the Scanning Kelvin Probe Microscope!
4.2 Method development EFM

As stated earlier, EFM is a method to monitor the vertical component of the electric force gradient between the conductive SPM tip and the sample. The same specially prepared Direct Imaging Process drum used for SKPM experiments (figure 4.8) is now used to test the performance of the Electric Force Microscope. Since this drum has several deposited layers with different electrical properties, it should be possible to measure differences in the electric force gradient between tip and sample.

EFM, in contradiction to SKPM, does not use a "nullifying" technique. Simplifying expression (A.52) in Appendix A, yields the result for the vertical force gradient acting between tip and sample due the capacitive energy,

$$\frac{\partial F}{\partial z} = \frac{1}{2} C'' V_{dc}^2.$$  \hspace{1cm} (4.1)

In this equation $C''$ is the second derivative of the capacitance of the tip-sample system and $V_{dc}$ is the (applied) potential difference between the tip and the sample. Note that the tip-sample capacitance is determined by the geometry of the tip-sample system as well as their mutual distance. Therefore, it is instructive to investigate in what way the tip-sample geometry (tip shape and sample geometry) and the tip-sample distance (lift height), influence the measurement results. Moreover, model calculations made with the help of the finite element package Quickfield TM and analytic expressions from literature, have been used to explore the influence of the tip-sample geometry and tip-sample distance.
5 Results & Discussion

In this chapter the results of the experiments described in the previous chapter are presented. The exploration of SKPM is subject of discussion in the first paragraph and the exploration of EFM is presented in the second paragraph. Finally, in the third paragraph a comparison of the results and the suitability of SKPM and EFM is made.

5.1 Method development SKPM

Remember that two prepared test samples are used to explore the Scanning Kelvin Probe Microscope, namely the structure consisting of two gold sputtered electrodes and a DIP-drum with 5 different SiO$_x$ layers deposited on it.

5.1.1 Two gold sputtered electrodes

In order to test how good a well-defined potential can be measured, the first series of experiments have been performed on the structure consisting of two sputtered gold electrodes. By varying the potential applied to the adjustable electrode, several things have come to our attention and are discussed in the following subsections.

5.1.1.a Influence on topography measurement of applying a potential to a sample

The first striking feature is the fact that a regular topography measurement (in standard Tapping Mode) is influenced by an applied potential to the sample. Consider figure 5.1 (next page), in which four topography measurements of the insulating barrier between the two gold sputtered electrodes, are depicted. In the measurements performed on this test structure, the electrode to the left of the insulating barrier is connected to ground and the potential of the right electrode is put at either 1V, 3V, 5V or 7V.

The figures clearly indicate that the topography measurement of a sample is influenced by the applied electrostatic potential: the greater the applied potential, the greater the deviation of the true topography. It turns out that the apparent height is bigger than the true height of the surface and that a reduced resolution for fine structures in the surface is observed. In Tapping mode a digital feedback loop is used to adjust the tip-sample separation to maintain a constant oscillation amplitude and thus a constant force at the sample (subsection 2.2.3). This means that in case of an additional electric force present, the tip has to be moved up in order to keep the force at the sample constant. This results in a bigger apparent height and in a loss of fine structures.

However, since SKPM uses an interleaved, or two pass measurement technique, it is possible to overcome this problem. Only by applying zero potential to the sample during the topography (first) scan, the topography is measured properly. The electrostatic potential is applied during the surface potential (second) scan. Practically, this is done by applying a block wave potential (0V alternating with an adjustable value) to the sample, exactly in phase with the topography and surface potential scan! This method is used in all further experiments.
5 Results & Discussion

5.1.1b Measurements of surface potential

Let’s now consider a measurement of a well-defined surface potential. In each measurement, the electrode to the left of the insulating barrier is connected to ground and the electric potential of the electrode to the right of the insulating barrier is set to a given value. In figure 5.2, a measurement above the electrode connected to ground is depicted. The applied potential to the other electrode is set at 3V. All of the experiments discussed in this subsection have been performed with a Lift Height of 500nm.

Figure 5.1: Four topographic measurements of the barrier region. Different voltages are applied to the electrode to the right of the insulating barrier. Note that the upper quarter and the lower quarter do not represent a measured area!
5 Results & Discussion

Figure 5.2: Left: Topography measurement above electrode connected to ground. Right: Surface Potential image above electrode connected to ground. Note that the upper quarter and the lower quarter do not represent a measured area.

The left side of the picture shows a part of the topography of the electrode connected to ground and the right side shows the measured surface potential above this part. It can be seen that the potential is constant (no structure is visible). However, closer investigation shows that the potential measured is not equal to zero volt, but to 250 ± 30 mV. This offset is visualised and discussed later on in figure 5.7.

Further, in figure 5.3 a measurement above the electrode with an applied potential of 3V is depicted.

Figure 5.3: Left: Topography measurement above electrode connected to 3V relative to ground. Right: Surface Potential image above electrode connected to 3V relative to ground. Note that the upper quarter and the lower quarter do not represent a measured area.

The left side of the picture shows a part of the topography of the electrode connected to 3V relative to ground and the right side shows the measured surface potential above this part. It can be seen that the potential is constant (no structure is visible). However, closer investigation shows that the measured potential is not exactly equal to 3V, but to 2.87 ± 0.03V.

In figure 5.4, a measurement above the insulating barrier is depicted. Again the left electrode is connected to ground and the right electrode to 3V relative to ground.
Figure 5.4: SKPM measurements across insulating barrier. The left picture represents the topography measurement and the right side represents the surface potential measurement. The left electrode is connected to ground and the right electrode is connected to 3V. Note that the upper quarter and the lower quarter do not represent a measured area.

In order to gain more insight into this measurement, the surface potential image is depicted in a 3-D plot and in cross section /side view in figure 5.5.

Figure 5.5: Surface Potential image over the insulating barrier, represented as a 3-D plot (left) and represented in cross section / side view (right). Note that in the right plot the red markers are placed at the endings of the sputtered electrodes.

Going from right to left in figures 5.4 and 5.5, the measured potential has a value of 2.87 ± 0.03V in the most right part of the pictures. This agrees with the measurement above the electrode with the 3V applied potential. Then the potential slightly declines near the edge of the right electrode. This is probably an effect due to the neighboring electrode. Theoretically, in case of an ideal insulator and an ideal conductor a step is expected in the surface potential at the edge of this right electrode (the position of the green cross in the right picture in figure 5.4). However, a declination or potential drop is observed across the insulating barrier. Since a leak current through a resistance induces a potential drop, it is concluded that the glass substrate is not an infinite resistance and that a (small) current is present.

Note that with the help of such a measurement across the insulating barrier, it is possible to determine a surface potential difference between the two electrodes. To do this, one has to measure the vertical difference between the outermost left part and the outermost right part in figure 5.5.

Furthermore, it is instructive to compare the measured potential differences across the barrier with the absolute potential measurements above the grounded and above the charged
electrode. In figure 5.6 these measured potentials or potential differences are depicted as function of the applied potential to the charged electrode.

![Figure 5.6](image)

Figure 5.6: Comparison of the measured potential differences across the barrier (blue triangles) with the absolute potential measurements above the grounded (green circles) and above the charged electrode (red squares). Also the 45°-line is included (black). Note that the error bars are negligibly small in size.

The measurements above the charged electrode (red squares), deviate only a small fraction from the defined potential (up to 5% at maximum). However, the potential differences measured across the insulating barrier (blue triangles) indicate a bigger deviation (up to 15%) from the applied potential difference. The offset of the measurements above the grounded electrode (green circles) is also clearly visible. It turns out that this offset determines the deviation of the measured potential difference across the insulating barrier from the charged electrode. This is made visible in Figure 5.7, where the measurements above the grounded electrode (green circles) are compared with the measured potential above the charged electrode minus the potential difference across the insulating barrier (red squares).

![Figure 5.7](image)

Figure 5.7: Comparison of the measured potential above the grounded electrode (green circles) with the measured potential above the charged electrode minus the measured potential difference across the insulating barrier (red squares).
Interpretation of the presented measurements yields the conclusion that the electrode connected to ground is subjected to a remarkable effect. Namely, by applying a potential to the neighboring electrode, the potential of the grounded electrode is "lifted up" by an offset value. Note that the potential measurements above the charged electrode are not influenced and remain at their defined value! Strangely enough, non-reproducible drifting of the offset value is regularly observed, sometimes within hours. This drift ranges from 0 up to 300mV. This effect leads to two possible explanations: either this offset is caused by the Digital Dimension 3100 Nanoscope (perhaps a fluctuating offset is present to the tip) or the ground is not of the expected quality. The first idea is disproved by establishing that the measured potential is always equal to 0 ± 30mV when both the electrodes are connected to ground. The second idea seems a real problem. This remarkable lifting of the ground potential is, however, still not understood.

5.1.1.c Lift height dependence

Because SKPM is a "nullifying" technique, the test sample of the two electrodes is used to check if the tip-sample capacitance indeed does not influence the measured surface potential. Since the tip-sample capacitance is among others determined by their mutual distance, measurements above the electrode connected to 3V are performed as function of the Lift Height. The results of these measurements are depicted in figure 5.8.

Figure 5.8: Measurements above the electrode connected to 3V are performed as function of Lift Height.

Figure 5.8 clearly indicates that the measured surface potential is independent of Lift Height. This proves the fact that the tip-sample capacitance has no influence on the measured surface potential, which is in agreement with the fact that SKPM is a "nullifying" technique!

5.1.2 Specially prepared Direct Imaging Process drum

In order to investigate the distinguishing and reproducing power of the Scanning Kelvin Probe Microscope, measurements have been performed on the specially prepared Direct Imaging Process drum (figure 4.3). In figure 5.9, a typical result of various repeated SKPM measurements on the print layer - that is the combined SiO$_{0.4}$ layer (thickness 300nm) with a SiO$_{1.2}$ layer (thickness 600nm) - is depicted. The Lift Height is set to 200nm during the measurement. Note that all the measurements discussed in this subsection have been
performed with the same Lift Height. As can be seen in the left topography picture, the insulating area (light areas) between two traces is situated typically up to 200nm higher than the traces (dark areas). Note that the width of a trace is about 23.5μm and the width of the insulating area between two traces is about 19μm.

Figure 5.9: Typical result of an SKPM 80x80μm measurement on print layer. Left side of the picture represents the topography and the right side the surface potential. Left trace has been connected to ground and to the right trace a potential of 2V has been applied.

In the right side of the picture, it is seen that the left trace is connected to ground, while the right trace is connected to an applied potential (2 volt in this case). The potential measurements are very smooth above a trace: no influence of topography of any structures whatsoever are visible. Measurements like this give the opportunity to determine:

a) the potential of a trace connected to an applied potential,
b) the potential of a trace connected to ground,
c) the potential difference between two neighboring traces. One trace is “on” (connected to an applied potential) and the other is “off” (connected to ground).

In figure 5.10, typical results of this type of measurements on the bare epoxy drum (upper plot) and on a print layer (lower plot) are depicted.
A few things can be mentioned. The first striking feature is that the measured surface potential at the “on”-trace (red circles) does not correspond with the 45°-line, even in the case of the bare epoxy drum. Apparently, there is a potential-loss. Since measurements at all the different layers yield the same results (see figure 5.11), it can be concluded that the different SiO₂ layers have no detectable influence on the SKPM measurement in the range 0-10V above an “on”-trace and that the observed potential-loss is due to a common property of the drum.
Figure 5.11: Results of surface potential measurements above an "on"-trace on all different layers. Apparently, different SiO\textsubscript{2} layers have no detectable influence on SKPM measurements on an "on"-trace in the measured range.

The question what common property is responsible for the potential loss, is still a point of discussion within Océ. A look at the production steps of a drum in figure 4.7, could lead to the assumption that the used conducting carbon epoxy has to be responsible for the potential-loss. However, a simple calculation using the specifications of the conducting carbon epoxy and the drum (thickness 40μm, resistance ρ ≤ 50Ω·m, radius of DI-drum is about 10 cm, width of a trace is about 23μm), yields a calculated resistance of the epoxy of 138Ω. This leads, in case of a 2V potential drop, to a current of about 15mA. This seems rather unrealistic, since in this situation such a current would run through half of the number of the traces (leading to a total current in the order of Amperes).

Another striking feature in figure 5.10 is the fact that the ground measurement (black curve) increases with the applied potential. It also turns out that each different layer on the specially prepared drum “lifts up” the ground value in a different manner. This explains why the green curves (potential difference between two neighboring “on”-trace and “off”-trace) in figure 5.10 do not coincide. In figure 5.12, measurements of the difference between the “on”-trace and the “off”-trace on all layer structures are depicted.
This figure indicates that the “lifting up” of the ground potential is influenced by the presence of a SiO\textsubscript{x} layer. Under the assumption that the lifting up of the ground potential is a result of transverse conduction across the area between two traces (see figure 5.13), the results in figure 5.12 can be interpreted as follows:

- The bare epoxy drum has the lowest transverse conduction, since the only transverse conduction that takes place is through the insulating epoxy. This means that the “lifting up” of the ground potential is restricted to a minimum and explains why the curve of the bold epoxy drum in figure 5.13 lies closest to the 45°-line.

- The SiO\textsubscript{x} layers are more conducting than the insulating epoxy. This means that in the case of a SiO\textsubscript{x} layer present, more transverse conduction takes place across the area between two traces. Therefore, the ground measurement is now lifted more up, which results in curves in figure 5.13 that lie further away from the 45°-line. More specific, the layers with x=0.4 are more conductive than the layers with x=1.2. This means that the layers with x=0.4 have greater transverse conduction than the layers with x=1.2 and that they lie in figure 5.13 further away from the 45°-line!

- It turns out that no differences occur in the “lift up” of the ground potential in the measured range (0-10V), when the layers have different thickness. The x=0.4 layers with different thickness as well as the x=1.2 layers with different thickness, do not result in different values for the “lift up” of the ground potential.

- Using this line of arguments, the values measured in the case of print layer should lie beneath the x=1.2 curves as is observed.
Transverse conduction across the area between two traces. Green represents the insulating epoxy; brown the SiO$_x$ layer, and white the conducting traces. Transverse conduction can, theoretically, take place by way of the insulating epoxy and by way of the SiO$_x$ layer.

Finally, an undesired effect during experiments has to be discussed. Namely, it turns out that a non-reproducible drift in the lift-up is observed, sometimes within several hours. Although the relative positions of the different SiO$_x$ layers remain the same in most cases, the absolute value of the “lift up” of the ground potential varies. Unfortunately, this remarkable behavior (fluctuating “lift up”) of the ground potential is still not understood. The reader should note that this observed “lift effect” differs from the “lift effect” observed during the measurements at the two gold sputtered electrodes.

5.2 Method development EFM

In this paragraph, the method development for usage of Electric Force Microscopy is discussed. In order to gain insight into EFM, some theory is introduced in the first subsection. The nature of the method is discussed and thoughts have been given to expected dependencies between several parameters that influence the measurement. More specific, in order to investigate in what way the gradient of the force acting on the tip is changed by changes in the geometry of the tip, changes in the geometry of the sample, changes in the electrical / conducting properties of the sample and changes in the mutual distance between tip and sample, simulations have been performed with the help of the finite element package Quickfield TM in the second paragraph. In the third subsection, the results of the EFM measurements are presented and compared to the theoretical findings and simulations.

5.2.1 EFM: theory

EFM is used to map the vertical and near-vertical gradient of the electric force between the tip and the sample. As explained before, modulations of the drive signal frequency $\delta \omega$ are plotted versus the in-plane coordinates x and y, producing a map of the strength of the electric force gradients, according to Eq. (A.59)

$$\frac{\partial F}{\partial z} = 2k \frac{\delta \omega}{\omega_0}.$$  \hspace{1cm} (A.59)

Here $\partial F / \partial z$ is the vertical electric force gradient, $k$ is the mechanical spring constant and $\omega_0$ is the resonance frequency of the piezo driven cantilever. Also in appendix A, an expression for the force acting on the tip due to the capacitive energy is denoted in Eq. (A.47)

$$F = \frac{1}{2} \frac{\partial C}{\partial z} V_{dc}^2.$$  \hspace{1cm} (A.47)
Here $\partial C / \partial z$ is the vertical gradient of the capacitance of the tip-sample system and $V_{dc}$ is the (applied) dc potential difference between tip and sample. To get this reduced expression it is assumed that no ac potential difference is present and that no charge is deposited on a thin insulating film placed on top of the sample. From this expression, the gradient of the force acting on the tip can be determined:

$$\frac{\partial F}{\partial z} = \frac{1}{2} \frac{\partial^2 C}{\partial z^2} V_{dc}^2. \quad (5.1)$$

Taking a closer look at the expressions (A.59) and (5.1) leads to the following expectations for experiments to be performed:

- the measured modulations of the drive signal frequency $-\delta\omega$ should show a dependency to $V_{dc}^2$. In case that measurements at the specially prepared DI drum are performed, this means for example that the measured frequency modulations are quadrupled when the applied potential to a trace is doubled.

- using tips with different mechanical spring constants $k$ or with different resonant frequencies $\omega_0$, results in different frequency modulations $-\delta\omega$, assuming that the tip has the same geometry and thus the tip-sample capacitance remains the same.

- since EFM is not a "nullifying" technique like SKPM, the measurements of the frequency modulations $-\delta\omega$ (=the gradient of the force acting on the tip) depend on the second derivative of the tip-sample capacitance (Eq. (5.1)). The tip-sample capacitance depends among others on the geometry of the tip, the geometry of the sample, the electrical / conducting properties of the sample and the mutual distance between tip and sample. In order to investigate in what way the gradient of the force acting on the tip is changed by changes in these parameters, simulations have been performed with the help of the finite element package QuickField TM. The findings of the simulations are discussed in the next subsection.

### 5.2.2 Simulations of electric force gradient with QuickField TM

Before the findings of the simulations are discussed, a short description of the steps in a QuickField simulation process are listed:

1) Defining the model geometry. The tip-sample system is modeled as a sphere of radius $R$ at a distance $z$ above a metal plate. This means that the tip is represented as a sphere and a trace on the DI drum as a metal plate. The SiO$_x$ layers are drawn on top of the metal plate.

2) Defining the material properties and boundary conditions. The bottom layer has a dielectric constant of $\varepsilon_r=7$ and the top layer has a dielectric constant of $\varepsilon_r=3.8$. The trace is an ideal conductor with a well-defined, applied potential. The tip is an ideal conductor connected to ground and the back wall (placed far away) is also connected to ground. This is necessary to perform calculations of the electric field.

3) Building the mesh.

4) Numeric solving of the electric field.

5) Computing the electric force and the electric force gradient acting on the tip.

These 5 steps have been repeated many times in order to obtain pictures in which the force gradient is plotted as function of the applied potential to the trace, as function of the distance between tip and sample (=Lift Height) and as function of the radius of the sphere (tip shape). Of course, all of this is done for the different SiO$_x$ layers present at the specially prepared DI drum.

In figure 5.14, the results of the simulations of the force gradient above the bare epoxy drum (sphere above metal plate with no SiO$_x$ layer on it) are plotted as function of Lift Height.
(distance between tip and sample). The tip radius (radius of the sphere) has been set to 50nm. This has been done for four different applied potentials (5V, 10V, 15V, 20V).

Figure 5.14: Simulations of the force gradient above the bare epoxy drum plotted as function of Lift Height for a tip radius of 50nm.

It is seen that the simulations confirm the expected qualitative relations: the force gradient between tip and sample decreases as function of increasing Lift Height and the force gradient increases with increasing potential difference between tip and sample. According to our findings in the former subsection, the force gradient between tip and sample should show a dependency to $V_d$. This relation is verified in figure 5.15, in which the simulated force gradients above the bare epoxy drum divided by $V_d^2$ are plotted versus the Lift Height.

Figure 5.15: Simulated force gradient above the bare epoxy drum divided by $V_d^2$ plotted as function of Lift Height for a tip radius of 50nm.

Since the four curves clearly coincide, the expected relation is obeyed. Furthermore, it is investigated how the tip shape influences the force gradient acting on the tip. Therefore, sphere-radii of 50nm and 100nm and a shuttle - or conus - shaped tip with top radius of 50nm are modeled as function of Lift Height. 10 Volt has been applied to the metal plate. The results are depicted in figure 5.16.
Simulated force gradient above the bare epoxy drum connected to 10V for several tip shapes (sphere-radii of 50nm and 100nm and a shuttle- or conus-shaped tip with top radius of 50nm). The upper plot presents the total simulated range, while the lower plot zooms out on a smaller range.

The simulations confirm the expected qualitative relation: the force gradient between tip and sample increases as the tip radius increases. This means that a deteriorated tip (less sharp tip; larger tip radius) experiences a greater force gradient than a new, still sharp, tip. For example, the differences in force gradient acting on the tip at a fixed Lift Height of 500nm is 2.4 times greater in the case of a tip with radius 100nm than a tip with radius 50nm. The shuttle- or conus-shaped tip can also be seen as a deteriorated tip.

Furthermore it turned out that in literature [8] an analytical expression for the capacitance of the used model (conducting sphere with radius $R$ a distance $z$ above a conducting metal plate) has been derived:

$$C_{sphere-platesystem} = 4\pi\varepsilon_0 R \sum_{n=1}^{\infty} \frac{\sinh(n\alpha)}{\sinh(n\alpha)}, \quad (5.2)$$
Results & Discussion

with \( \varepsilon_0 \) the dielectric constant and

\[
\alpha = \ln \left[ 1 + \frac{z}{R} + \sqrt{\frac{z^2}{R^2} + 2 \frac{z}{R}} \right].
\] (5.3)

For the case \( z/R > 2 \), this expression for \( C_{\text{sphere-plate system}} \) converges to

\[
C_{\text{sphere-plate system}} = 2\pi\varepsilon_0 R^2 / z,
\] (5.4)

where \( 2\pi\varepsilon_0 R^2 \) is the effective area of the condenser plate. Note that although this approximate solution is valid only for \( z/R > 2 \), it may sometimes be useful to employ it as a simple analytic tool for describing a certain situation. Eq. (5.4) yields an expression for the second derivative of \( C_{\text{sphere-plate system}} \):

\[
\frac{\partial^2 C_{\text{sphere-plate system}}}{\partial z^2} = 4\pi\varepsilon_0 R^2 / z^3.
\] (5.5)

Combining Eq. (5.5) and Eq. (5.1) leads to the expression

\[
\frac{\partial^2 F}{\partial z^2} = 2\pi\varepsilon_0 R^2 \frac{v_f^2}{z^3}.
\] (5.6)

From this expression it is concluded that \( \frac{\partial F}{\partial z} \) should be proportional to \( 1/z^3 \) and to \( R^2 \) for \( z/R > 2 \). This means that a plot in which \( \frac{\partial F}{\partial z} \) is plotted as function of \( 1/z^3 \) for \( z/R > 2 \) should result in a straight line. When 2 different tip radii (50nm and 100nm) are simulated, this should result in two straight lines with one slope four times as big as the other slope. These relations are verified in figure 5.17. The simulations of the force gradient above the bare epoxy drum connected to 10V are plotted for tip radii of 50nm and 100nm. Also the simulations of a shuttle - or conus - shaped tip with top radius of 50nm) are plotted as function of \( 1/(\text{Lift Height})^3 \) for \( z/R > 2 \).

![Figure 5.17: Simulated force gradient above the bare epoxy drum connected to 10V for several tip shapes (sphere-radii of 50nm and 100nm and a shuttle - or conus - shaped tip with top radius of 50nm) plotted as function of \( 1/(\text{Lift Height})^3 \) for \( z/R > 2 \).](image)

Evidently, the dependency with \( 1/z^3 \) for \( z/R > 2 \) is obeyed. However, the dependency with \( R^2 \) for \( z/R > 2 \) is not followed in the simulations. It turns out that the force gradient is not
quadrupled when the tip radius is doubled, but instead the force gradient is multiply by 2.4. A possible explanation could be the fact that the grounded back wall (see Appendix B) is not placed far away enough from the sphere and that it therefore disturbs the simulations.

Finally, the influence of the different SiO$_2$ layers (at the specially prepared DI drum) on the force gradient acting on the tip is investigated. The results of these simulations are depicted as function of the applied potential to the metal plate in Figure 5.18. Note that in all measurements a fixed Lift Height (500nm) is used.

![Image of Figure 5.18: Influence of different SiO$_2$ layers on the simulated force gradient acting on the tip.](image)

The simulations of the different SiO$_2$ layers confirm the expected qualitative relation: the thicker the SiO$_2$ layer, the further away the tip (sphere) is positioned from the trace (metal plate), and the smaller the force gradient acting on the tip will be! Using this line of arguments, the tip experiences the greatest force gradient in case of the bare epoxy drum (simulated by the metal plate). For the bottom layer and the half top layer, which have the same thickness (both 300nm), it is expected that in the case of the bottom layer the force gradient acting on the tip is greater since the bottom layer is more conductive than the half top layer. This is confirmed in figure 5.18.

### 5.2.3 Measurements and discussion

In order to gain insight into EFM, the derived relations of the former subsection have been tested in experiments at the specially prepared DI drum. In figure 5.19, a typical result of various repeated EFM measurements on the specially prepared drum on a piece bare epoxy is compared with a typical result of various repeated measurements on the print layer (that is the combined SiO$_{34}$ (thickness 300nm) with a SiO$_{12}$ layer (thickness 600nm)). The Lift Height is set to 200nm during both measurements.
Left: Topography. Right: EFM measurement on bare epoxy drum

Left: Topography. Right: EFM measurement on print layer.

Figure 5.19: Typical result of an EFM 80x80μm measurement on the specially prepared drum on a piece of bare epoxy (left picture) and on a print layer (right picture). The left side in these pictures depicts the topography measurement and the right side depicts the EFM measurement. The outer left trace and the outer right trace have been connected to ground and to the trace in the middle a potential of 5 volt has been applied.

It can be seen in the topography plots (left sides in both pictures) that the insulating area (light area) between traces is situated typically up to 200nm higher than the traces (dark areas) itself. The width of a trace is about 23.5μm and the width of the insulating area between two traces is about 19μm. The EFM plots (right sides in both pictures) show a clearly visible frequency modulation -Ω(t)-, located on the trace connected to 5 volt (dark area). Also, some structures or disturbances in this (dark) area are visible. More specific, (great) peaks / variations in the topography plot above a trace connected to 5 volt lead to distinct variations or structure (lighter parts in the dark area) in the EFM plot. The explanation for these variations is simple. In case of a peak in topography, the tip is lifted up during the interleaved scan when the frequency modulation is measured. Since the tip is now further away from the (average) surface it experiences less electric force (gradient) and the measured frequency modulation will be smaller.

Another difference between measurement on a piece of bare epoxy drum and the measurement on the print layer is the course of the electric force gradient across the insulating area between two traces. This is illustrated in figure 5.20.

Figure 5.20: Cross-section of EFM measurements across the insulating area between two traces on a bare epoxy drum (left) and on a print layer (right).
Evidently, the two curves of the measured vertical electric force gradient acting on the tip differ in course. In case of the bare epoxy drum there is a more sudden transition near the border of a “on”-trace than in case of the print layer, in which there is a smoother transition. This smoother transition confirms the idea from chapter 1 that the SiO$_x$ layer serves to mask the insulating areas between the turret shape drum tracks and thus leaks current as seen in the SKPM measurements.

From figures like figure 5.19, a mean difference of the total frequency modulation between an “on”-trace (trace with an applied potential) and an “off”-trace (trace connected to ground) can be deduced. This mean difference is plotted as function of the Lift Height for three applied potentials (5V, 10V, 15V) to a bare epoxy drum in figure 5.20.

![Diagram](image_url)

**Figure 5.20:** EFM measurements on a bare epoxy drum. Mean differences of frequency modulations between an “on”-trace and an “off”-trace (measure for force gradient acting on the tip) are plotted as function of Lift Height.

In analogy to figure 5.15, it is tested whether or not the measurements obey the $V_d^2$ relation by plotting the mean difference in measured frequency modulation (above a bare epoxy drum) between an “on”-trace and an “off”-trace divided by $V_d^2$ versus the Lift Height. See figure 5.21.
Evidently, the curves coincide and thus the $V_{dc}^2$ relation is followed by the measurements. The difference in curve shape of the measurements (figure 5.21) with respect to the curve shape of the simulations (figure 5.15) probably originates from the fact that the used model for the tip shape, a sphere with radius 50nm, is simplified too much. This is confirmed by the check of the $1/z^2$ dependency. It turns out that the expected dependency is obeyed only for $z>1000\text{nm}$ (see figure 5.22). Since this yields a tip radius of 500nm, which is rather unrealistic, it can indeed be concluded that a spherical tip with a radius of 50nm is simplified too much! However, keep in mind that the predicted qualitative relations made with the help of this rather simple model are obeyed by the measurements and that therefore this, rather simple, approximation satisfies reasonably as a first check of the results.

Figure 5.22: Measured mean difference in frequency modulation between an “on”-trace and an “off”-trace above a bare epoxy drum connected to 10V plotted as function of $1/(\text{Lift Height})^3$. 
Now, it is important to discuss an observed problem that arises when the frequency modulations $\Delta \omega$ (measure for the force gradient) are quantified: it turns out that the measurements are not always consistent in magnitude. Figure 5.23 illustrates this problem. The upper and the lower plot represent the same experiment at a bare epoxy drum: at five positions, the difference in frequency modulation between an “on”-trace and an “off”-trace has been determined as function of the applied potential to the “on”-trace.

![Graph 1](image1)

![Graph 2](image2)

Figure 5.23: Two repeated experiments (on different days) of EFM measurements at five positions on a bare epoxy drum. Mean differences in frequency modulations between “on”-trace and “off”-trace are plotted as function of the applied potential.

It is seen that the quantitative determination of the frequency modulation can fluctuate enormously (up to 4 times), although it must be said that the right picture is an extreme exception. Normally, the observed fluctuations of frequency modulations are within a factor 2.5 to the values in the upper plot in figure 5.23. The following list consist sources of errors that contribute to the observed fluctuation in the frequency modulations:

- Environmental conditions. From literature [9] it is concluded that the conductive properties of SiO$_x$ layers are sensitive to changes in relative humidity (RH) of the ambient air. This implies that EFM measurements on SiO$_x$ layers should also be sensitive
to the relative humidity in ambient air. However, measurements of the relative humidity in the measurement room turned out that the ambient air in the measurement room is conditioned very well during daytime (RH = 45±1%).

- Each tip has its own unique mechanical spring constant $k$. According to Eq. (A.59) this leads to an error. The specifications of the lever given by the supplier indicate a range of 1-5N/m for the value of $k$. Since a non-destructive method to determine the actual value for $k$ is not present, the specifications given by the supplier are the most accurate information there is. This means that differences in this parameter could lead - in the worst case scenario - to differences up to a factor 5 in the measured frequency modulations.

- Each tip has also a different resonant frequency. According to the specifications of the supplier, the resonant frequencies are between 60000kHz and 100000kHz. However, during the experiments it turned out that the different tips used in our experiments all have a resonant frequency between 65000Hz and 72000Hz, which means that deviations up to 10% can be explained with this effect. The restriction to the range of the resonant frequency also implies that the variations in the mechanical spring constant are limited to a factor 1.2 since $k \propto \omega^2$.

- Tip shape issues. Different tips can have different radii of curvature. According to the specifications of the supplier, the radii are within the range 25-50nm. Recalling the theoretical model in which the tip-sample system is simulated as a sphere above a metal plate and for which a $R^2$ dependence was predicted, this leads to differences up to a factor 4 in the measured frequency modulations.

- A tip deteriorates as function of time; during measurements the tip becomes less sharp. Therefore a test structure, which makes it possible to de-convolute the tip, has been bought. In the figure 5.24 the same tip has been de-convoluted three times: situation A is the situation in which the tip has not been used in experiments yet, in situation B the tip is de-convoluted after use in several experiments and in situation C the tip has become unusable for experiments.
Situation A:

Situation B:

Situation C:

Figure 5.24: De-convolution of tip shape for three different situations: the unused tip, the tip after several measurements, the unusable tip after many measurements. The left pictures represent the topography measurement (and amplitude measurement). The right picture represents a 3D surface plot, zoomed on the area of one tip.

Clearly a tip deteriorates as function of the number of performed measurements and becomes less sharp. Note that this degeneration of a tip weakens the validity of the used model of a sphere. In order to investigate the influence of this tip deterioration, in situation A and in situation B EFM measurements on the print layer have been performed at the same position. Mean differences in frequency modulations between "on"-trace and "off"-trace are plotted as function of the applied potential in figure 5.25.
In this example, it is illustrated that a deteriorated tip actually yields a different/greater frequency modulation and that therefore a deteriorated tip experiences a different/greater force gradient. This leads to the recommendation that it is only meaningful to quantify and compare EFM measurements when they are taken on a relative short time interval with the same tip. Of course it necessary that a de-convolution of the tip shape is made from time to time during such time interval in order to keep an eye on the deterioration of the tip!

Despite these problems concerning the quantification of the frequency modulations, an attempt has been made to determine the tip radius using the simple sphere-plane plate model and measurement results on the bare epoxy drum. Combining Eq. (A.59), Eq. (5.1) and Eq. (5.5) yields the expression

$$R = \sqrt{\frac{z^3 k \Delta \omega}{\omega_0 \pi \varepsilon_0 V_{dc}^2}}$$

(5.6)

for the radius of the tip $R$. The following values (taken from the left part of figure 5.23; measurements at a bare epoxy drum) have been used for this fitting process of the tip radius:

- $z = 500\text{nm} = 5.10^{-7}\text{m}$,
- $V_{dc}^2 = 10\text{V}$,
- $\Delta \omega = 12 \pm 2\text{Hz}$,
- $k = 1-5\text{ N/m}$,
- $\omega_0 = 65000-72000\text{Hz}$,
- $\varepsilon_0 = 8.85419 \times 10^{-12}\text{F/m}$.

Substitution of these values in Eq. (5.6) gives as a result: $80\text{nm} < R < 210\text{nm}$. Especially if the earlier discussed restrictions of the model and the specifications of the supplier ($25\text{nm} < R < 50\text{nm}$) are taken into account, this result is a fairly good approximation of the radius of curvature of the tip!

Finally, with the help of the specially prepared DI drum, the distinguishing power of the Electric Force Microscope is investigated. A typical result in which the distinguishing power of the EFM method is investigated is depicted in Figure 5.26. This figure contains measurements that are performed on the print layer and the half bottom layer with a Lift Height of $500\text{nm}$. Again the mean difference in frequency modulation between an “on”-trace and an “off”-trace is plotted as function of the applied potential to the “on” trace.
Figure 5.26: EFM measurements on the specially prepared DI drum. The mean difference in frequency modulation between an “on”-trace and an “off”-trace is plotted as function of the applied potential to the “on”-trace. In this plot the distinguishing power of the EFM method is visible.

This figure clearly shows that the thicker the SiO₂ layer is, the smaller the measured frequency modulations are. This is understood by realizing that a thicker layer means that the tip is placed further away from the trace (conducting epoxy) and thus experiences a smaller electric force (gradient). For example, the tip experiences the smallest force gradient in the case of a print layer, which consist of a combined bottom (300nm) and top layer (600nm) and is the thickest layer.

Finally, consider Figure 5.27 in which measurements on all the layers at the specially prepared DI drum are depicted. Mean differences between an “on”-trace and an “off”-trace are plotted as function of the applied potential to the “on”-trace. All measurements have been taken on the same day.
EFM measurements on the specially prepared DI drum. The mean difference in frequency modulation between an “on”-trace and an “off”-trace is plotted as function of the applied potential to the “on”-trace. All measurements have been taken on the same day.

Again, it is seen that the tip experiences the greatest electric force gradient in case of the measurement on the bare epoxy and that it experiences the lowest electric force gradient in case of the measurement on the thickest layer (= the print layer). Actually, it turns out that all the curves are “correctly”, though very subtle, positioned relative to each other in order of layer thickness. Note that the layers with same thickness (bottom layer and half top layer) are also positioned “correctly” relative to each other. It is observed that the tip experiences a greater force gradient in case of the bottom layer than in case of the half top layer, which has also been concluded from the simulations (see figure 5.18). Nevertheless, the differences between the several layers are very subtle and are, unfortunately, not always reproduced in repeated measurements!

5.3 Observed resemblances and differences between SKPM and EFM

As a concluding paragraph of this part of our work, a comparison of observed resemblances and differences between SKPM and EFM is made.

The Scanning Kelvin Probe Microscope proved its capability to measure surface potentials. The measurement accuracy of SKPM has a maximum deviation of 5%. For the lateral resolution of the SKPM measurements, the accuracy of a measurement is limited by the size of the tip. Features or variations in surface potentials smaller in size than the tip cannot be distinguished. Since the used tips have a minimum radius of curvature of 25nm, this leads to the conclusion that features smaller than 50nm cannot be distinguished. The resolution of the surface potential itself has been tested in a simple experiment. Connecting both electrodes on the glass substrate (figure 4.1) successively to 0mV and to 3mV with respect to earth, gives also a difference of 3mV in the SKPM measurements. From this it is concluded that potential variations in the order of mV can be detected. An unpleasant restriction on the SKPM method is the fact that the measurement-range of the surface potential is limited to a range of 0V to 10V. The greatest advantage of the SKPM method is the fact that it is a “nullifying” technique. As a consequence, measurements are not sensitive to geometry parameters like the tip-shape, the distance between tip and sample and the surface of the sample.
The Electric Force Microscope turned out to be an excellent tool to image local variations in the electric force gradient between tip and sample. The greatest disadvantage of the EFM method is the fact that it is not a "nullifying" technique like SKPM. As a consequence, measurements are very sensitive to geometry parameters like the tip-shape, tip-shape deterioration, the distance between tip and sample, and the surface of the sample. This leads to the recommendation that it is only meaningful to quantify and compare EFM measurements on different samples when they are taken with the same distance between tip and sample and when they are taken on a relative short time-interval with the same tip. During such time-interval, it is necessary that the tip shape needs to be de-convoluted from time to time to detect deterioration of the tip! For the lateral resolution of the EFM measurements, the accuracy of a measurement is limited by the size of the tip. Therefore features or variations in the electric force gradient that are smaller in size than 50nm cannot be distinguished. The minimum detectable frequency modulations are within the range of a few Hz (dependents on the smoothness of the surface), which leads to minimum detectable force gradients in the range of 0.0001N/m with the used MESP tips.
6 Applications

After the part of SKPM and EFM method development and method comprehension has been finished, the point has been reached to apply these techniques to Océ related problems. This chapter deals with the problem of the formation of a conductive network in carbon filled rubbers. After that, some considerations with respect to future work are included in the second paragraph.

6.1 Conductive paths in carbon filled rubbers

Some of the artefacts of high speed toner transfer from DI drum to intermediate can be effectively reduced by moving the conductivity of the rubber top layer from the anti-static to the truly conductive regime. Firstly, this paragraph deals with an outline of the background and the problem definition concerning the conductivity of the rubber top layer of the intermediate. Secondly, some questions concerning this problem have been drawn together. After that, a connection is made to the Electric Force Microscope and the Scanning Kelvin Probe Microscope in the third subsection. In the fourth subsection, the experiments that have been performed at several rubbers are discussed. Finally, the results of these experiments are discussed in the fifth subsection.

6.1.1 Background & Problem definition

The so-called conductive route is proposed as a serious candidate to obtain an intermediate with improved performance concerning the print artefacts discussed in [10]. The key issue is to make the intermediate so conductive that it is possible to influence the charge distribution at the toner transfer in the drum-intermediate nip (transition) by applying a potential to the intermediate.

The conduction in the silicon rubber top layer of the intermediate is realised by filling it for about 4% with a special conductive carbon black (Printex XE2). This is a carbon powder that consists of mechanical strong aggregates (approximate diameter 100nm) of primary particles. Because the shape of the primary particles is a hollow half sphere, the aggregates have an irregular shape irregular and they are very porous. The aggregates cluster easily (but reversibly) to bigger agglomerates of several microns. During hardening of the surface layer coating, some agglomeration will have to be realised in order to gain a conducting network in the rubber. Logically, there will be a greater conductive network in the rubber, when a higher percentage conductive carbon black is added. This is confirmed by figure 6.1, in which a typical percolation curve of Printex (XE2) [11] is pictured.
The percolation curve (measured with the help of a “four-contact points” measurement) shows the specific resistance of the bulk as function of the percentage XE2 added. The specific resistance decreases (or the conduction increases) when a higher percentage XE2 is added; more conductive paths are then formed. Note that the specific resistance drops heavily when about 0.75% XE2 is added (“percolation point”).

However, the desired mobility of the aggregates during hardening has an undesired side effect: a so-called “impoverished carbon skin” is formed. As an illustration of this “skin”, figure 6.2 depicts a Light Microscopic picture of a rubber in cross-sectional view with an impoverished carbon skin evidently present.
6.1.2 Actual questions

At this moment, the described problem of the poor surface conduction is the biggest challenge for the application of a conductive network. Questions thereabout are listed here:

- How and why does the impoverished carbon skin exist and is it possible to influence its formation?
- What are the consequences of the presence of the impoverished carbon skin? Pictures like the one in figure 6.2, from which only an optical thickness can be deduced, do not give enough information. Apparently, there is something like an “electric thickness” and unfortunately there seems to be no direct relationship with the optical thickness.
- How can this impoverished carbon skin be characterised? Measurements of the electric resistance, which work well to predict bulk properties, are not sufficient to predict the properties of the impoverished carbon skin.
- Is there a connection between the thickness of the impoverished carbon skin and the %XE2 added to the silicon rubber?
- What about reproducibility? It seems that electrical properties of the impoverished carbon skins are not always reproduced.
- What is the stability of the impoverished carbon skin? Does the (effect of the) impoverished carbon skin (completely) disappear by applying an electrostatic potential to it? How does it happen and how much time does it comprehend? Is there an interaction with %XE2?

In conclusion, it can be stated that there are a number of questions regarding the impoverished carbon skin. All of these questions are connected to the central question: what is the distribution of the percolating conductive carbon black agglomerates at the surface? The two techniques studied in our work, EFM and SKPM, are thought to be suitable for gaining insight in the problematic described.

6.1.3 Connection to EFM and SKPM

In the literature an example [12] is available with EFM measurements on conductive carbon networks in an isolating matrix. Topographic measurements are compared to EFM measurements in order to make a distinction between carbon black agglomerates that participate and carbon black agglomerates that do not participate in the conductive network. This kind of measurement is what we also would like to do: of course, with a special focus on the impoverished carbon skin.

Two different kinds of measurements are performed: measurements on the surfaces of rubbers and measurements on the cross sections of rubbers. This is depicted in figure 6.3.

```
Surface

Carbon Impoverished skin

Cross-section / Bulk
```

Figure 6.3: Measurements are performed on the surface and on the cross-sections of a silicon rubber.
The success of the surface measurements will depend on the measure in which *subsurface* carbon black can be made visible. Therefore, the challenge of this measurement is to make visible how a tip (toner particle) "experiences" the presence of percolating carbon black agglomerates. With the help of the measurements on the cross-section of a rubber, it should be possible to make a profile of the concentration "conductive carbon black" as function of depth. The challenge in this type of measurements is the preparation of the cryogenic cross sections (and coupes) made with the help of the Microtome. The coupes are normally used for Transmission Electron Microscopy (TEM), and the cross section of the remaining rubber sample can be studied with EFM.

Besides using EFM, SKPM could also be used as a tool to study the problem of the impoverished carbon skin. Measurements of the surface potential of rubbers also make it possible to distinguish insulating from conductive areas. However, our experiments on conductive paths have been restrained to EFM since the available experimental time was limited.

### 6.1.4 Experiments

For the EFM measurements a number of silicon rubber samples have been prepared with different percentages of conducting carbon black (XE2) added to it. Since empirical relations exist between hardening conditions (duration, temperature, pressure, environment) and the thickness of the impoverished carbon skin, it is also possible to produce differences in thickness of the impoverished carbon skin on samples with the same bulk properties.

The production of the samples is divided into two parts. Firstly, the preparation process of the substrate and secondly the coating of the substrate with the silicon rubber. The substrate consists of a piece of insulating Melinex foil (thickness approximately 100μm) covered on both sides with a gold layer of approximately 10nm thickness. The gold layers, deposited during a sputtering process, have been interconnected through perforations filled with electroconductive paint. See figure 6.4.

![Figure 6.4: Schematic view of the substrate on which the rubbers used for EFM experiments are coated.](image)

In this manner, the substrate can function as an electrode. The conductive silicon rubber is composed of five components:

- silicon oil (vinyl reactive);
- cross linker (hydrogen reactive);
- inhibitor;
- conductive carbon black;
- catalyst.

After the first four components have been added, they are blended very well. After a homogeneous dispersion has been formed, the catalyst is finally added. Else, the rubber could already harden during the mixing process. The dispersion is put in an exicator vacuum to relieve. During the hardening process (standard in hot oven on a hot plate), the silicon oil forms a network with the cross linker.
Using this process, a number of samples have been created. See table 6.1.

<table>
<thead>
<tr>
<th>Sample name:</th>
<th>Amount XE2:</th>
<th>Used primer</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>2002-20-1 A1</td>
<td>3%</td>
<td>PR1</td>
<td>Standard hardening</td>
</tr>
<tr>
<td>2002-20-1 A2</td>
<td>3%</td>
<td>PR1</td>
<td>Standard hardening; rubber has been extracted in Isobutyl methyl ketone (a solvent).</td>
</tr>
<tr>
<td>2002-20-1 B1</td>
<td>0.75%</td>
<td>PR1</td>
<td>Standard hardening</td>
</tr>
<tr>
<td>2002-20-1 C1</td>
<td>3%</td>
<td>PR1</td>
<td>Standard hardening</td>
</tr>
<tr>
<td>2002-20-1 C2</td>
<td>3%</td>
<td>PR1</td>
<td>Standard hardening; rubber has been extracted in Isobutyl methyl ketone (a solvent).</td>
</tr>
<tr>
<td>2002-20-1 D</td>
<td>2%</td>
<td>PR1</td>
<td>Standard hardening</td>
</tr>
<tr>
<td>2002-20-1 E</td>
<td>0.4%</td>
<td>PR1</td>
<td>Standard hardening</td>
</tr>
<tr>
<td>2002-20-1 F</td>
<td>3%</td>
<td>PR1</td>
<td>Hardening conditions have been changed in order to produce a minimum impoverished carbon skin</td>
</tr>
<tr>
<td>2002-20-1 G</td>
<td>3%</td>
<td>PR1</td>
<td>Standard hardening</td>
</tr>
<tr>
<td>2002-20-1 H</td>
<td>3%</td>
<td>PR1</td>
<td>Hardening conditions have been changed in order to produce a maximum impoverished carbon skin</td>
</tr>
</tbody>
</table>

Table 6.1: Prepared carbon black filled rubber samples for experiments.

With the help of the Microtome, cryogenic cross-sections (and coupes) have been made of sample F, sample G and sample H in order to test if the thickness of the carbon-less or impoverished carbon skins on the different samples agrees with the expected thickness. In Appendix B, pictures of these coupes made with the help of the Light Microscope are depicted. From these pictures it is concluded that the thickness of the impoverished carbon skins obey the expectations:

- Sample II indeed has a visible carbon-less or impoverished carbon skin of about 0.7\textmu m thickness.
- Sample G possibly has a impoverished carbon skin, but if it exists it is smaller than 0.3\textmu m thickness.
- Sample F has no visible impoverished carbon skin.

The scope of our research has been limited to two main subjects of investigation:
1) The prepared samples give the opportunity to study the number and distribution of the “experienced” percolating conductive carbon black agglomerates at the surface as function of the added percentage XE2.
2) The samples F, G and H are made from the same blend and should therefore have the same bulk properties. However, as a result of usage of different hardening conditions, these samples have different thickness of impoverished carbon skins. With the help of these three samples, the possibility to develop a methodology to characterise the impoverished carbon skin is investigated.

6.1.5 Results & Discussion

Note that in all our experiments, the tip is connected to ground and that an adjustable potential is applied to the substrate (electrode) of the rubber samples. Note that all the EFM measurements on the rubber samples have been performed with a Lift Height of 50nm. This paragraph is divided into three subsections. In the first subparagraph, it is verified whether it is indeed possible to visualise the percolating conductive carbon black agglomerates in a silicon rubber with the help of EFM. In the second paragraph, the number and distribution of percolating conductive carbon black agglomerates at the surface are studied as function of the
added percentage of XE2. In the third subsection measurements on the surface are compared with measurements on the bulk. Methodologies to characterise the influence of the impoverished carbon skin and the distribution of the carbon black network are also discussed in this paragraph.

6.1.5a Visualising percolating conductive carbon black agglomerates in the silicon rubbers

The first step in our experiments is to verify if it is indeed possible to visualise the carbon black distribution and the conductive paths in a silicon rubber with the help of EFM. Therefore, two initial measurements have been performed: an EFM measurement on the surface of sample E (0.4%XE2) and an EFM measurement on the surface of sample A1 (3%XE2). The results are depicted in figure 6.5. In both cases, 4V has been applied to the substrate.

![Image of EFM measurements](image)

Figure 6.5: 20x20μm EFM measurement on sample E (0.4% XE2) and a 20x20μm EFM measurement on sample A1 (3% XE2).

The topographic measurements (left side in both pictures) of the rubbers are comparable with topographic measurements published in literature [12]. The EFM measurements (right side in both pictures) are very promising! In case of sample E (0.4% XE2), differences of ca. 0.5 Hz in the frequency modulations have been measured: this is clearly a noise signal. This means that in this case the carbon black particles are positioned too far away from each other to form a conductive network. Note that this observation is confirmed by the percolation curve in figure 6.1: for 0.4% XE2 the specific resistance is very high!

However, in case of sample A1 (3% XE2), there are evidently (dark) areas visible in which there is a modulated frequency and in which hence a greater force gradient acts on the tip. The darker areas in the EFM plot therefore represent conductive areas, while the lighter areas represent insulating areas. Note that the size of the dark areas ranges up to several microns. Recall from subsection 6.1.1 that this is also the size of the agglomerates that exist from the clustering of the aggregates of carbon powder. Hence it is concluded that the dark areas in the EFM picture of sample A1 (3% XE2) indeed represent the percolating conductive carbon black agglomerates at the surface “experienced” by the tip!

6.1.5.b Percolating conductive carbon black agglomerates as function of % XE2

In order to investigate the distribution and the number of percolating conductive carbon black agglomerates “experienced” by the tip as function of the added percentage XE2, EFM measurements on the surface have been performed on all the prepared samples. The results of
the measurement on sample E, sample B1, sample D and sample A1 (increasing percentage XE2) are depicted in figures 6.6 to 6.9. Each figure consists of 4 pictures, which represent different measurements with 4 different potentials applied to their substrate. The discussion of the results follows immediately after figure 6.9

- Measurement at surface: 2 volt applied to sample.
- Measurement at surface: 4 volt applied to sample.
- Measurement at surface: 6 volt applied to sample.
- Measurement at surface: 8 volt applied to sample.

Figure 6.6: EFM measurements performed on the surface of sample E (0.4% XE2). The four cases represent measurements with different potentials applied to the electrode (2V, 4V, 6V and 8V). The left part in one picture always represents the measured topography and the right part represents the measured frequency modulations (electric force gradient acting on the tip).

Note that for sample E (0.4% XE2) no structures, besides noise, are present in the EFM image, when 2V or 4V has been applied to the substrate. When 6V or 8V are applied to the substrate, a few percolating conductive carbon black agglomerates (darker areas) seem to become visible. For the measurements on sample B1 (0.75% XE2), depicted in figure 6.7, remarks like the ones made for sample E (0.4% XE2) are applicable. When 2V is applied to the substrate no structures, besides noise, are present in the EFM image. However, when 4V, 6V or 8V is applied to the substrate, percolating conductive carbon black agglomerates (darker areas) become visible.
Measurement at surface: 2 volt applied to sample.

Measurement at surface: 6 volt applied to sample.

Measurement at surface: 4 volt applied to sample.

Measurement at surface: 8 volt applied to sample.

Figure 6.7: EFM measurements performed on the surface of sample B1 (0.75% XE2). The four cases represent measurements with different potentials applied to the electrode (2V, 4V, 6V and 8V). The left part in one picture represents each time the measured topography and the right part represents the measured frequency modulations (electric force gradient acting on the tip).

In figure 6.8 (next page) the measurements on the surface of sample D (2% XE2) are depicted. The percolating conductive carbon black agglomerates “experienced” by the tip are clearly visible in all the pictures.
Measurement at surface: 2 volt applied to sample.

Surface Measurement: 4 volt applied to sample.

Measurement at surface: 6 volt applied to sample.

Measurement at surface: 8 volt applied to sample.

Figure 6.8: EFM measurements performed on the surface of sample D (2% XE2). The three cases represent measurements with different potentials applied to the electrode (4V, 6V and 8V). The left part in one picture always represents the measured topography and the right part represents the measured frequency modulations (electric force gradient acting on the tip).

Note that the measured differences between insulating (black) and conductive (white) areas become greater when a higher voltage is applied. This can be seen from the adjusted z-ranges in the pictures. This is explained by the fact that the force gradient acting on the tip becomes greater when a higher potential difference exist between tip and sample.

For the measurements on the surface of sample A1 (3% XE2), the percolating conductive carbon black agglomerates “experienced” by the tip are clearly visible too. These measurements are depicted in figure 6.9 on the next page.
6 Applications

Measurement at surface: 2 volt applied to sample.

Measurement at surface: 6 volt applied to sample.

Figure 6.9: EFM measurements performed on the surface of sample A1 (3% XE2). The four cases represent measurements with different potentials applied to the electrode (2V, 4V, 6V and 8V). The left part in one picture always represents the measured topography and the right part represents the measured frequency modulations (electric force gradient acting on the tip).

The measured differences between insulating (white) and conductive (dark) areas become greater when a higher voltage is applied. This can be seen from the adjusted z-ranges in the pictures. This is explained by the fact that the force gradient acting on the tip becomes greater when a higher potential difference exist between tip and sample. Note that these measurements also have been performed at sample C1 and sample G (both 3% XE2, normal hardening conditions) yielding the same typical images. Measurements on sample A2 and sample C2 (both 3% XE2; rubbers have been extracted in Isobutyl methyl ketone (a solvent)) also gave no -optically- different results.

Summarising, from the pictures in the figures 6.6 to 6.9 two features come to our attention:

1. More percolating clusters become visible when a higher electrostatic potential is applied to the substrate.
2. More percolating clusters become visible when a greater percentage of XE2 is added. The number of visible clusters has the same dependency as is expected from the percolation curve in figure 6.1. Namely, when 0.4% XE2 is added to the silicon rubber no conductive paths are visible, corresponding with a high specific resistance in the percolation curve. When 0.75% XE2 is added to the silicon rubber, already some conductive paths are visualised in the EFM plots (lower specific resistance in percolation curve). In case of the addition of 2% XE2, conductive paths are evidently visible and it seems that the degree of percolating paths is in the same order as in the case of the addition of 3% XE2. This is confirmed in the percolation curve, where the specific resistance of 2% XE2 and 3% XE2 is in the same order.
At the moment, we do not have a complete understanding of these phenomena, but it may be
that the following ideas about percolating networks hint in the right direction. The possible
mechanisms of why more percolating clusters become visible when a higher electrostatic
potential is applied to the substrate and when a greater percentage of XE2 is added, will be
discussed now. Consider figure 6.10.

Figure 6.10: Schematic drawings of the sample structure (upper drawing), the conduction band in
case no potential is applied to the substrate (middle drawing), and the conduction
band in case a potential is applied to the substrate.

This figure consists of three schematic drawings. In the first schematic drawing a cross-section
of a rubber sample is depicted. The substrate is positioned at the left side; the circles
correspond to carbon black agglomerates that have been formed during the hardening process
in the insulating matrix. The second drawing represents the (simplified) conduction band of
the sample in case that no potential is applied to the substrate. The potential drops in the
conduction band correspond to the positions of the carbon black agglomerates. The third
drawing represents the (simplified) conduction band of the sample in case that a potential is
applied to the substrate. The potential decreases across the parts of the sample where the
insulating matrix is located. At positions where the carbon black agglomerates are located,
potential drops are visible in the conduction band.

Note that an electron can transfer to neighboring agglomerates by either tunnelling across the
barrier or by thermal emission over the barrier. It is well known that the probability on
tunnelling across the barrier is increased when a smaller barrier is faced. In figure 6.10, the
red arrows indicate the thickness of the barrier. Evidently, the thickness of the barrier
becomes effectively smaller by applying a potential to the substrate. From figure 6.10 it is also
concluded that the effective activation barrier ($\Delta$) is decreased. As a consequence of the
decrease in the effective activation barrier, the probability on thermal emission over the
barrier increases. In summarise, by (further) applying a potential to the substrate, the
probability on tunnelling across the barrier and the probability on thermal emission over the

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barrier increases. Translating this phenomenon to our experiments, this would mean that more percolating carbon black aggregates should become visible when a potential is applied to the substrate. This has also been observed!

Now, the fact that more percolating carbon black particles become visible when a higher percentage XE2 is added is explained. Adding a higher percentage XE2 to the blend, means that the distance between neighboring carbon black agglomerates decreases. As a consequence, it is seen that the barrier thickness (red arrows) and the effective activation barrier ($\Delta$) both decrease (see figure 6.11). This leads to an increasing probability on tunneling across the barrier and an increasing probability on thermal emission over the barrier.

Figure 6.11: Schematic drawings of the conduction band of the rubber sample. In the right plot the carbon agglomerates are at closer distance to each other than in the left plot. This results in a smaller barrier and a lowering of the activation barrier $\Delta$.

This means that more percolating carbon black aggregates should become visible when more XE2 is added to the blend. This has also been observed!
6 Applications

6.1.5.c Measurements on the surface versus measurements on the bulk

It is instructive to study how the conductive carbon black paths are distributed in the bulk. In Figure 6.12 two measurements on sample H (3% XE2, impoverished carbon skin present) have been depicted. The left picture depicts an EFM measurement on the surface, while the right picture depicts an EFM measurement on the cross-section at least 20μm away from the surface. In this bulk measurement as well as in the surface measurement 8V has been applied to the substrate.

![EFM images showing surface and bulk measurements](image)

Measurement at surface: 8 volt applied to sample. Measurement at bulk: 8 volt applied to sample.

Comparing these EFM images, two features come to our attention. The first feature concerns the size of the insulating areas. It turns out that the distribution of the “experienced” conductive network at the surface is coarser (or less fine structured) than the distribution of the “experienced” conductive network in the bulk. This phenomenon turns out to be a typical observation for all samples, except for sample F (3% XE2, no skin present). Namely, in this case the distribution of the conductive paths on the surface is -optically- the same as distribution of the conductive paths in the bulk. This leads to the conclusion that an “electric skin” exists that leads to the blurring of the distribution of the conducting paths. From the frequency modulation (EFM) plots, it is imaginable that toner particles (size 5-15μm) are able to stick to the rubber at insulating areas, which can lead to print artefacts. Therefore it is desirable to have a parameter that says something about the size of the insulating and conductive areas and the distribution of them. Later on, attention is paid to this quantification process.

The second feature concerns the fact that in the bulk measurement the electric interaction between the conductive carbon black agglomerates and the tip is much greater than in the surface measurement. This is concluded from the fact that the differences between the insulating areas and the conducting areas are much greater in case of the bulk measurement than in case of the surface measurement (the range of the z-scale -100Hz versus 10Hz - implies this). This difference in electric interaction is due to the existence of a impoverished carbon skin. Namely, the impoverished carbon skin can be seen as an extension of the Lift Height, which means that at a distance further away from the conductive paths is measured and that therefore smaller force gradients are measured!

Now, the challenge is to quantify this influence of the impoverished carbon skin. Recall from chapter 5 that this is only possible if we assume that tip-shape issues are limited to a
minimum. In practise this means that the tip shape is checked from time to time. In order to quantify the influence of the impoverished carbon skin a suitable parameter is found in the area of Surface Analysis: the $R_z$-value. The $R_z$-value is a roughness parameter, which represents the averaged height difference between 10 maxima and 10 minima in a surface plot. Applying this parameter to the frequency modulation plot (EFM plot), leads to a parameter that is a measure for the averaged difference in frequency modulation between insulating areas (maxima) and the conductive areas (minima). This parameter is therefore a measure for the electric interaction "experienced" by the tip. Comparing $R_z$-values for measurements in the bulk with measurements on the surface, could give a possibility to characterise the influence of the impoverished carbon skin.

Consider figure 6.13, in which the $R_z$-values of samples F, G and H are depicted for measurements on the surface as well as for measurements in the bulk. These values are plotted as function of the applied potential to the substrates of the sample.

![Figure 6.13: $R_z$-values (which is a measure for the electric interaction "experienced" by the tip) of samples F, G and H are depicted for measurements on the surface as well as for measurements in the bulk.](image)

From this figure a few striking features are notified:

- The $R_z$-values become greater when a greater potential is applied to the substrate, which is logical since the conductive paths (minima in EFM plots) differ more from the insulating paths (maxima in EFM plots) when a greater potential is applied.
- The $R_z$-values for the bulk measurements are the same, which is also expected since the samples F, G and H were made from the same blend.
- The $R_z$-values of the measurements on the surface of the sample H have the lowest values. This is also expected since this is the sample with the thickest "optical impoverished carbon skin".
- The $R_z$-values of the measurements on the surface of sample F are within the same range as the measurements in the bulk. This means that in this case no impoverished carbon skin is present, which is in agreement with the expectations.
- The $R_z$-values of the measurements on the surface of the sample G are evidently between the bulk values and the values of surface measurements on sample H. This means that this sample has an "electric skin", although the sample does not have an evident "optical impoverished carbon skin". Remind from the Light Microscopic pictures of sample G in Appendix B that it is concluded that if a impoverished carbon skin is present, it is smaller than 0.3μm.
In order to make the differences between the three samples better visible, in figure 6.14 the $R_z$-values measured at the surface divided by the $R_z$-values measured at the bulk are plotted as function of the applied potential to the substrate.

![Figure 6.14: $R_z$-values measured on the surface divided by the $R_z$-values measured in the bulk are plotted as function of the applied potential to the substrate for samples F, G and H.](image)

In this figure it is confirmed that sample F has no impoverished carbon skin ($R_z$ \textit{surface} divided by $R_z$ \textit{bulk} is normalised to one) and that sample H indeed has a impoverished carbon skin ($R_z$ \textit{surface} divided by $R_z$ \textit{bulk} is about 0.13). Again it is stated that the “electric thickness” of the impoverished carbon skin of sample G is more equivalent to sample H than to sample F ($R_z$ \textit{surface} divided by $R_z$ \textit{bulk} is about 0.35)! From these observations it is concluded that something like an “electric thickness of the skin” exists and that it apparently is not directly related to the “optical skin”.

Now suppose for a moment that the “electric skin” would be directly related the “optical skin”. Combination of figure 6.14 and the $1/z^3$ dependency of the sphere-model then gives an opportunity to calculate back the thickness of the “optical skin” from the thickness of the “electric skin” (see Appendix C). However, the obtained thickness for the “optical skin” of 0.62\textmu m does not agree with the findings of the Light Microscopie pictures (impoverished carbon skin smaller than 0.3\textmu m). This discrepancy confirms that the thickness of the “electric skin” is not directly related to the thickness of the “optical skin” of the sample. Apparently, a still not understood reduction of the electric force gradient between tip and sample takes place in an “electric skin”.

Another striking, nontrivial, feature from figure 6.14 is the fact that the normalised value of $R_z$ \textit{surface} divided by $R_z$ \textit{bulk} is independent of the applied potential to the substrate. This means that in future measurements it suffices to measure at only one applied potential! However, note that this normalised parameter is only a measure for the thickness of the “electric skin”, when the samples have the same bulk properties. Sample A1 (3% XE2), which was made from a different blend -although with the same specifications-, has been used in order to determine whether or not the $R_z$-values of the bulk measurements are reproduced. See figure 6.15.
Figure 6.15: $R_z$-values for bulk measurements on sample A1 at four different positions. Also bulk measurements on samples F, G and H have been included.

Obviously, the bulk measurements are in fair agreement with each other. This means that for future characterisations of impoverished carbon skins an averaged line for the bulk can be deduced from figure 6.15!

Furthermore, the influence of extracting a rubber sample (standard hardening) in Isobutyl methyl ketone (a solvent) is investigated. Recall that no influence of the extraction process is visible on the distribution of the carbon black network. Now, $R_z$ values of bulk measurements on sample A2 (3% XE2; standard hardening, rubber has been extracted) are depicted in figure 6.16, in which also the $R_z$-bulk values of sample A1 (3% XE2; standard hardening) are included.

Figure 6.16: $R_z$-values for bulk measurements on A2 (3% XE2, extracted rubber). Also bulk measurements on sample A1, which was made from the same blend, are included.

Note that the $R_z$-values for sample A2 (3% XE2, standard hardening, rubber has been extracted) are greater than the $R_z$ bulk values of sample A1 (3% XE2; standard hardening), which was made from the same blend. This means that the tip “experiences” greater force
gradients above an extracted rubber. This can be explained by the fact that during extraction insulating oils are removed from the rubber. Since these oils are most likely located at the surface, a thin insulating film is removed and the rubber becomes more conductive.

Finally, attention is paid to the quantification of the size of the insulating and conductive areas and the distributions of them. It turns out from figure 6.12, that it is imaginable that toner particles (size 5-15μm) are able to stick to the rubber at insulating areas, which can lead to print artefacts. Because of this, it is desirable to have a parameter that says something about size of the insulating and the conductive areas and the distributions of them. In our work only a first attempt has been made to characterise the distribution of the conductive paths.

First, the frequency modulation (EFM) images have been binarised into a two colour plot: white represents the insulating areas and brown represents the conductive areas. See figure 6.17.

![Figure 6.17: Binarising the frequency modulation plot into a two colour plot: white represents the insulating areas and brown the conductive areas.](image)

From figures like this, it is possible to deduce a percentage of conductive paths. For this purpose a Matlab routine has been written (see Appendix D). However, it turns out that no evident correlation between our samples has been found. Measurements on different samples all yield a percentage of about 43-48% conductive areas (see Appendix E). From this it is concluded that the percentage of conductive areas is not a suitable parameter to use. Furthermore, the percentage of the conductive areas tells us nothing about the size and the distribution of the conductive areas. However, the fact that the percentages of conductive areas are practically the same on the different samples, justifies the choice to another parameter: $P_c$.

$P_c$ is the averaged number of transitions brown-white in the horizontal direction and the number of transitions brown-white in the vertical direction. This value is, under the assumption that the total white area is equal for all samples, a measure for the size and the distribution of the conductive areas. The bigger the value of $P_c$ is, the smaller the size of the conductive areas or the finer structured their distribution is. Although the written Matlab routine (see also Appendix D) counts the number of transitions correctly, it turns out that the quality of a measurement strongly disturbs the value of $P_c$ (see Appendix E). For example, consider figure 6.18 in which a measurement of less quality is depicted. The small dashes in the binarised plot greatly disturb the number of counted transitions.
Figure 6.18: Binarising of the frequency modulation plot into a two colour plot for a measurement of less quality: white represents the insulating area and brown the conductive paths.

However, if in future work a filtering function is added to the subroutine, the P value should be a suitable parameter to characterise the size and distribution of the conductive paths!

6.2 Challenges and Future work

During this research, several ideas and challenges for future work came up. A few of them are discussed below.

As discussed in the former paragraph, it is imaginable that toner particles (size 5-15µm) are able to stick to the rubber at insulating areas, which can lead to print artefacts. In our research only a first attempt has been made to characterise the distribution of the conductive paths. However, in future work the methodology to characterise this distribution needs to be developed further.

The addition of carbon nano-tubes to the blend instead of Printex XE2 might solve the problem of too large insulating areas. When nano-tubes are added to the blend it is expected that the conductive paths become finer structured. As a result, the size of the insulating areas becomes smaller too. When the insulating areas become (much) smaller than the size of toner particles, the problem of too large insulating areas is solved.

Other challenges for future work are related to the Direct Imaging Process drum. Questions that came up are related to the shape of the measured potential above the insulating area between two traces. Does the potential profile vary with different insulating thickness? Is this potential profile dependent of the applied potential?
7 Conclusions

In order to explore EFM and SKPM to test their performance and reliability, EFM and SKPM experiments are performed at a specially prepared Direct Imaging Process drum, with 5 different dielectric layers sputtered on it. The EFM results are also compared to numeric model calculations and theory.

From the method development part of the graduation project, it turns out that the Scanning Kelvin Probe Microscope proved its capability to measure surface potentials. The measurement accuracy of SKPM has a maximum deviation of 5% and the minimum detectable potential differences are in the order of mV. The lateral resolution is limited by the size of the used tip (about 50nm). An unpleasant restriction on the SKPM method is the fact that the measurement-range of the surface potential is limited to a range of 0V to 10V. The greatest advantage of the SKPM method is that the measurements are not sensitive to geometry parameters like the tip-shape, the distance between tip and sample and the surface of the sample.

The Electric Force Microscope turns out to be an excellent tool to image local variations in the electric force gradient between tip and sample with a lateral resolution that is limited by the tip size (about 50nm). The minimum detectable force gradients are in the range of 0.0001 N/m. The greatest disadvantage of the EFM method is the fact that measurements are sensitive to geometry parameters like the tip-shape, tip-shape deterioration, the distance between tip and sample, and the surface of the sample. This leads to the recommendation that it is only meaningful to quantify and compare EFM measurements on different samples when they are taken with the same distance between tip and sample and with the same tip (shape). During such experiments, the tip shape needs to be de-convoluted from time to time to detect deterioration of the tip.

In the application part of the graduation project, EFM is used as a tool to study the problem of surface conduction in the carbon black filled rubber intermediate. It turns out that EFM provides us with a tool to visualise the percolating carbon black network at the surface as well as in the bulk. From these measurements two striking features come to our attention. The first feature concerns the fact that the percolating network “experienced” by the tip at the surface is less fine structured than that in the bulk. This effect is due to the existence of an impoverished carbon skin at the surface layer. The second feature concerns the fact that this impoverished carbon skin reduces the electric force gradient “experienced” by the tip. It turns out that EFM can be used successfully to characterise the “electric thickness” of the impoverished carbon skin. Furthermore, some attention is paid to the characterisation of the distribution of the percolating network. Although a promising methodology has been defined to characterise the distribution, this methodology needs to be developed further.
This master-thesis is a result of my graduation project that took place at the Analysis & Measurements department of Océ Technologies BV in Venlo. Océ Technologies has a modern, well-equipped Research and Development center, which provides about 1200 people with a challenging, high-tech working environment. My assignment has also turned out to be a very challenging one. Especially, the high degree of freedom in my work and the obvious link to current Océ problematic worked stimulating on me.

Finally, I have come to the very pleasant task of expressing my gratitude to the people who have helped me to make my graduation project a pleasant and successful one. Firstly, I like to thank my daily coaches Pieter Gunter and Henk Rheiter for their support and practical help and my supervisor Paul Koenraad (Eindhoven University of Technology) for our constructive discussions. Next, I like to thank the many colleagues at Océ Technologies who gave me advice, information and their time. Perhaps I might mention a few by name: Margreet Spoelstra (for the introduction into the Dimension 3100 of Digital Instruments), Lei Roodbeen (for the preparation of the DI-drum with the different layers), Guy Verbeek (for the preparation of the rubber samples) and Tiny Ritzen (for the cryogenic preparation of the cross-sections of the rubber samples). And last but not least, I like to thank all the colleagues of floor 3N16 (Marc, Jack, Marjan, Johan, Marlou, Jannie, Novel, Michèle, Robert, Wolfgang and Jacob) for the perfect working environment they provided me with and for showing me how exciting and educational working in a Research & Development center can be!
9 Literature


List of consulted, Scanning Probe Microscopy related websites:

- http://www.topometrix.com/spmguide/contents.htm#Introduction
- http://www.mines.edu/students/a/agilmore/afm/efm.html
Appendix A

The operation of any type of Scanning Force Microscopy is based on the force interaction between a sharp tip (connected to a cantilever) and (the surface of) a sample. Therefore in this Appendix a theoretical background [5] of the interaction between a tip/lever mounted on a vibrating bimorph and an inhomogeneous external force, is presented. In the first subsection, the concept of an effective spring constant, which accounts for force derivatives acting on the sharp tip connected to the lever, is introduced. Then the equation of forced motion of the damped lever, which is mounted on a vibrating bimorph, is solved. In the third subsection the equations concerning the case of an electric force, according to [6], will be presented.

A.1 Effective spring constant

For an ordinary spring the spring constant \( k \) is defined by

\[
k = \left| \frac{F}{z} \right|, \tag{A.1}\]

where \( F \) is the force acting on the spring and \( z \) the resultant deflection. Another definition of the spring constant \( k \) can be derived from the potential energy \( W \) of a deformed spring or lever,

\[
W = \frac{1}{2} k z^2, \tag{A.2}\]

by taking the second derivative of the energy \( W \) in respect to \( z \),

\[
k = \frac{\partial^2 W}{\partial z^2}. \tag{A.3}\]

Equation (A.3) is convenient for finding the effective spring constant in the presence of a force \( F(z) \) that has a derivative in the direction of the deflection of the cantilever. In this case the force can be expanded to first order,

\[
F(z) = F(z_0) + \frac{\partial F(z_0)}{\partial z} \delta z, \tag{A.4}\]

and gets an effective spring constant, \( k' \),

\[
k' = k - F_1, \tag{A.5}\]

where \( F_1 = \frac{\partial F}{\partial z} \).

For convenience, an attractive force derivative is denoted as positive. Therefore, a tip-sample attractive force with a positive derivative decreases the resonance frequency of a lever.

A.2 Equation of forced motion for a bimorph-driven lever

Now consider a tip mounted on a lever that is attached to a bimorph vibrating with an amplitude \( a \) and frequency \( \omega \) (figure A.1). In this case the positions of the bimorph and de lever are given by
\[ u = u_0 + a \exp(i\omega t), \]  
\[ \text{(A.6)} \]

and

\[ z = z_0 + \zeta, \]  
\[ \text{(A.7)} \]

respectively, the position of the sample is given by

\[ g = 0, \]  
\[ \text{(A.8)} \]

and \( \zeta \) is yet an unknown function. Here \( BM \) is the bimorph, \( S \) is the sample and \( t \) is the force-sensing tip.

\[ \text{Figure A.1: The geometry of the bimorph-driven lever where } u \text{ and } z \text{ are the position of the bimorph and the deflected tip, respectively, and } g \text{ is the position of the sample.} \]

Using the defined geometry, expressions for the amplitudes of vibration of the lever and the phase angle \( \theta \) between the vibration of the bimorph and the lever will be derived for two cases. In the first case, the interaction force \( F \) acting between the tip at the end of the lever and the sample is constant, and in the second case, it has a derivative along the direction of vibration of the lever.

**Constant Interaction Force**

The equation of motion of the lever, in case of a uniform interaction force \( F = F_0 \), is given by

\[ m \frac{\partial^2 z}{\partial t^2} + \gamma \frac{\partial z}{\partial t} + k(z - u) = F_0, \]  
\[ \text{(A.9)} \]

and has three independent parameters: the effective mass of the lever \( m \), the mechanical spring constant of the lever \( k \), and a dissipation term \( \gamma \). According to [13] an appropriate expression for \( k \) of a solid rectangular lever is given by

\[ k = \frac{16w(\pi \omega L)^3(n\rho)^{3/2}}{\sqrt{E}}. \]  
\[ \text{(A.10)} \]

Here \( w \) is the width of the lever, \( L \) the length of the lever, \( \omega \) the oscillation frequency, \( \rho \) the mass density and \( E \) is the modulus of elasticity.

Inserting (A.6) and (A.7) in the equation of motion of the lever gives
\[
\frac{\partial^2 \xi}{\partial t^2} + \gamma \frac{\partial \xi}{\partial t} + k[\xi - u_0 - a \exp(i\omega t)] = F_0 .
\]  
(A.11)

Since at equilibrium the sample-lever force equals the restoring force of the lever

\[
F_0 = k(z_0 - u_0) ,
\]  
(A.12)

we get

\[
\frac{\partial^2 \xi}{\partial t^2} + \gamma \frac{\partial \xi}{\partial t} + k[\xi - a \exp(i\omega t)] = 0 .
\]  
(A.13)

The vibration of the lever will have the same frequency as that of the bimorph and can be written as

\[
\xi = A_b(\omega) \exp[i(\omega t - \vartheta)] ,
\]  
(A.14)

where \( \vartheta \) is a time-independent phase angle. Using (A.14) in (A.13) yields

\[
A_b(\omega)[k - \omega^2 m + i\omega\gamma] = ak \exp(i\vartheta) .
\]  
(A.15)

Isolating the amplitude of vibration of the lever by taking the absolute value of Eq. (A.15) gives

\[
A_b(\omega) = \frac{ak}{\left[(k - \omega^2 m)^2 + \omega^2 \gamma^2\right]^{1/2}} .
\]  
(A.16)

Here the dissipation term can be expressed as

\[
\gamma = m \omega_0 / Q ,
\]  
(A.17)

where

\[
\omega_0 = \sqrt{\frac{k}{m}}
\]  
(A.18)

is the resonance frequency of the free lever for \( Q >> 1 \). \( Q \) is the quality factor and is given by the ratio of the resonance frequency \( \omega_0 \) and the full bandwidth, at 0,707 of the maximum amplitude,

\[
Q = \frac{\omega_0}{\Delta \omega}.
\]  
(A.19)

It is helpful to define a bimorph-driven lever response function, \( G_b(\omega) \), by

\[
G_b(\omega) = \frac{A_b(\omega)}{a} ,
\]  
(A.20)

where

\[
G_b(\omega) = \frac{Q}{\left[Q^2 \left(1 - \omega^2 / \omega_0^2\right)^2 + \omega^2 / \omega_0^2\right]^{1/2}}
\]  
(A.21)
Decomposing Eq. (A.15) into imaginary and real components gives for the sine and cosine functions
\[
\sin \theta_b = G_b(\omega) \frac{\omega}{Q\omega_0} \quad (A.22)
\]
and
\[
\cos \theta_b = G_b(\omega) \frac{\omega^2 - \omega_0^2}{Q\omega_0} \quad (A.23)
\]
On resonance, where \( \omega = \omega_0 \), the above expressions lead to
\[
G_b(\omega_0) = Q, \quad (A.24)
\]
\[
A_b(\omega_0) = aQ, \quad (A.25)
\]
and
\[
\theta_b(\omega_0) = \frac{\pi}{2}. \quad (A.26)
\]

**Non-uniform Interaction Force**

In this case, Eqs. (A.6) through (A.8) still hold, but the interaction force and the equation of motion become
\[
F(z) = F_0(z_0) + F_1(z_0)\zeta \quad (A.27)
\]
and
\[
m \frac{\partial^2 z}{\partial t^2} + \gamma \frac{\partial z}{\partial t} + k(z - u) = F_0(z_0) + F_1(z_0)\zeta, \quad (A.28)
\]
respectively. Note that we expanded the non-uniform interaction force to first order in the perturbation term \( \zeta \) around \( z = z_0 \). The equivalent of Eq. (A.11) is now
\[
m \frac{\partial^2 \zeta}{\partial t^2} + \gamma \frac{\partial \zeta}{\partial t} + k[z_0 + \zeta - u_0 - a \exp(i \omega t)] = F_0 + F_1\zeta, \quad (A.29)
\]
and, since Eq. (A.12) still holds, we get for Eq. (A.29)
\[
m \frac{\partial^2 \zeta}{\partial t^2} + \gamma \frac{\partial \zeta}{\partial t} + k[\zeta - a \exp(i \omega t)] = F_1\zeta. \quad (A.30)
\]
The amplitude of vibration of the lever, \( A_b(\omega,F_1) \), denoted now by two parameters \( \omega \) and \( F_1 \), will now be given by
\[
A_b(\omega,F_1)[k' - \omega^2 m + i \omega \gamma] = ak \exp(i \theta), \quad (A.31)
\]
where \( k' = k - F_1 \). The physics is in this case somewhat more involved than that of the uniform force case, because the motion of the lever is now influenced by the force derivative. It is clear, for example, that for an attractive force derivative, the lever, as it moves down in its
excursion, will be assisted by the increasing interaction force and will move further down than the lever in the uniform interaction force case. As the lever moves up, the interaction force decreases so that the net restoring force acting on the lever increases and the lever will again move up, further than for the uniform case. Consequently, the amplitude of vibration of the lever will increase. Of course, the opposite will happen when the tip traverses a repulsive force derivative, namely, when \( k' > k \). See figure 6.2.

![Comparison of attractive and repulsive force derivatives.](image)

The resonance frequency, namely, that frequency at which the amplitude is maximized, changes from \( \omega_0 \) to \( \omega_0' \), where

\[
\omega_0' = \sqrt{\frac{k'}{m}}. \tag{A.32}
\]

Note that the effective spring constant \( k' \) must remain positive. From Equations (A.18) and (A.32) it can be seen that an attractive force derivative \( (k'<k) \) leads to a decreasing resonance frequency and a repulsive force derivative \( (k'>k) \) leads to an increasing resonance frequency.

Using the definition of \( \gamma \) in Eq. (A.17) and \( \omega_0' \) in Eq. (A.31) gives for the amplitude of vibration in the presence of \( F_1 \)

\[
A_b(\omega, F_1) = a \frac{\omega_0^2}{\omega_0^2/\omega_0^3 + \omega^2/\omega_0^3} / Q^{1/2}, \tag{A.33}
\]

which can also be written as

\[
A_b(\omega, F_1) = a \frac{\omega_0^2}{\omega_0^2/\omega_0^3 + \omega^2/\omega_0^3} Q / \omega_0^3 \left[ Q^2 (1 - \omega^2/\omega_0^2)^2 + \omega^2/\omega_0^2 \right]^{1/2}, \tag{A.34}
\]

or as

\[
A_b(\omega, F_1) = a \frac{\omega_0^2}{\omega_0/\omega_0^3} Q / \omega_0^3 \left[ Q^2 (1 - \omega^2/\omega_0^2)^2 + \omega^2/\omega_0^2 \right]^{1/2}. \tag{A.35}
\]

In terms of the bimorph-driven lever response function,

\[
G_b(\omega, F_1) = \frac{\omega_0^2}{\omega_0^2/\omega_0^3} Q / \omega_0^3 \left[ Q^2 (1 - \omega^2/\omega_0^2)^2 + \omega^2/\omega_0^2 \right]^{1/2}, \tag{A.36}
\]

we get
for the amplitude,

\[
\sin \theta_b = G_b(\omega, F_1) \frac{\omega}{Q \omega_0}
\]  \hspace{1cm} \text{(A.38)}

for the sine angle, and

\[
\cos \theta_b = G_b(\omega, F_1) \frac{\omega_0^2 - \omega^2}{\omega_0^2}
\]  \hspace{1cm} \text{(A.39)}

for the cosine angle. On resonance, where \(\omega = \omega_0\), this leads to

\[
G_{b0} = Q \sqrt{\frac{k}{k'}}
\]  \hspace{1cm} \text{(A.40)}

\[
A_{b0} = a G_{b0}
\]  \hspace{1cm} \text{(A.41)}

and

\[
\theta = \pi / 2.
\]  \hspace{1cm} \text{(A.42)}

Now that general expressions have been derived that give the change in amplitude of vibration of the lever supporting the force-sensing tip, these expressions will be applied to the case of a present electric force.

### A.3 Equation of motion for a bimorph-driven lever due to an electric force

Consider again, the typical system where the lever is mounted on a bimorph vibrating with amplitude \(a\) and frequency \(\omega\) in figure A.1. Again, in this configuration we have for \(u, z\) and \(g\),

\[
u = u_0 + a \exp(i \omega t),
\]  \hspace{1cm} \text{(A.6)}

\[
z = z_0 + \zeta,
\]  \hspace{1cm} \text{(A.7)}

\[
\zeta = A_\phi(\omega) \exp[i(\omega t - \vartheta)],
\]  \hspace{1cm} \text{(A.14)}

and

\[
g = 0.
\]  \hspace{1cm} \text{(A.8)}

Here \(A_\phi\) and \(\omega\) are the amplitude and frequency of vibration of the lever and \(\vartheta\) is a phase angle. The equation of motion for this system is

\[
m \frac{d^2 z}{dt^2} + \frac{\omega_0 m}{Q} \frac{dz}{dt} + k(z - u) = F(z),
\]  \hspace{1cm} \text{(A.43)}

where \(Q\) is the quality factor of the lever, \(m\) its mass, and \(\omega_0\) its free motion resonance frequency. To find \(F(z)\) for this case, external voltages \(V_p\) and \(V_e = V_p \sin(\Omega t)\) applied between the lever and sample together with a charge \(q_s\) deposited on a thin insulating film placed on
Appendix A

top of the sample are considered. Now the simplest approach is to assume that the voltage $V_{dc}$ and $V_{ac}$ induce charges on the tip given by

$$q_{dc} = CV_{dc}$$  \hspace{1cm} (A.44)

and

$$q_{ac} = CV_{ac},$$  \hspace{1cm} (A.45)

respectively, with a total charge given by

$$q_t = q_s + q_{dc} + q_{ac}.$$  \hspace{1cm} (A.46)

The force acting on the tip will then be due to the charge-charge interaction and the capacitive energy,

$$F = \frac{q_t q_t}{4\pi\varepsilon_0 z^2} + \frac{1}{2} C'(V_{dc} + V_{ac})^2.$$  \hspace{1cm} (A.47)

Substituting for the total charges gives

$$F = \frac{1}{4\pi\varepsilon_0 z^2} [q_s^2 + q_s q_{dc} + q_s q_{ac}] + \frac{1}{2} C'(V_{dc} + V_{ac})^2.$$  \hspace{1cm} (A.48)

Decomposing the force into components at dc and at the frequencies $\Omega$ and $2\Omega$, yields

$$F_{dc} = \frac{q_s^2}{4\pi\varepsilon_0 z^2} + \frac{q_s V_{dc}}{4\pi\varepsilon_0 z^2} + \frac{1}{2} C'[V_{dc}^2 + V_{i}^2],$$  \hspace{1cm} (A.49)

$$F_{\Omega} = \left[ \frac{q_s V_{i}}{4\pi\varepsilon_0 z^2} + C' V_{dc} V_{i} \right] \sin(\Omega t),$$  \hspace{1cm} (A.50)

and

$$F_{2\Omega} = -\frac{1}{4} C' V_{i}^2 \cos(2\Omega t).$$  \hspace{1cm} (A.51)

The force derivatives, which are readily obtained from the force, are

$$F_{1dc} = \frac{2q_s^2}{4\pi\varepsilon_0 z^3} + \frac{q_s V_{dc}}{4\pi\varepsilon_0 z} \frac{C' z^2 - 2Cz}{z^4} + \frac{1}{2} C'' \left[ V_{dc}^2 + \frac{1}{2} V_{i}^2 \right],$$  \hspace{1cm} (A.52)

$$F_{1\Omega} = \left[ \frac{q_s V_{i}}{4\pi\varepsilon_0 z^2} + C' V_{dc} V_{i} \right] \frac{C' z^2 - 2Cz}{z^4} + C'' V_{dc} V_{i} \sin(\Omega t),$$  \hspace{1cm} (A.53)

and

$$F_{12\Omega} = -\frac{1}{4} C'' V_{i}^2 \cos(2\Omega t).$$  \hspace{1cm} (A.54)

The average position of the lever will be determined by equating the electrostatic and restoring forces, yielding
The effective spring constant, which is given in terms of the derivative of the force by

$$k(z_0 - u_0) = F(z_0). \quad (A.55)$$

by

$$k' = k - \langle F_z(z_0) \rangle, \quad (A.56)$$

shifts the resonance frequency of the lever from

$$\omega_0 = \sqrt{k/m} \quad (A.57)$$

to

$$\omega'_0 = \sqrt{k'/m} \quad (A.58)$$

Again, the feedback-driven lever, which operates at $\omega = \omega_0$, directly measures the force derivative from the frequency shift,

$$F_1 = 2k \frac{\delta \omega}{\omega_0}. \quad (A.59)$$

The amplitude of vibration of the bimorph-driven lever is given by

$$A_b(\omega) = a \frac{k}{k'} \frac{Q}{[Q^2(1 - \omega^2/\omega_0^2)^2 + \omega^2 \omega_0^2 / \omega_0^4]^{1/2}}, \quad (A.60)$$

which, at $\omega = \omega_0$, is

$$A_b(\omega_0) = aQ \sqrt{k/k'}. \quad (A.61)$$

Finally, note that the tip-sample capacitance is determined among others by the geometry of the tip and the geometry of the sample as well as their distance, and that a first approximation is the use of a spherical tip above a conducting plate.
Appendix B

The Light Microscope has been used to make pictures of the coupes made with the help of the Microtome of sample H, sample G and sample F. Here, the results are depicted.

Figure B.1: Light Microscopic pictures of the coupes made with the help of the Microtome on sample H, sample G and sample F. The black spots or points refer to the conglomerates present.

It can be concluded that the thickness of the carbon-less skins obey the expectations:

- Sample H indeed has a visible carbon-less or impoverished carbon skin of about 1,5μm thickness.
- Sample G possibly has a carbon-less skin, but if it exists it is smaller than 0,4μm thickness.
- Sample F has no visible carbon skin.
Appendix C

If it is assumed that the model of a sphere above a metal plate and its theoretical $1/z^3$ dependency is valid, combination of figure 6.11 and the $1/z^3$ dependency gives an opportunity to calculate back to an optical thickness of the carbon-less skin of sample G. Consider therefore figure C.1.

![Image](image_url)

Figure C.1: Normalised $R_z$ values ($= R_z\text{-surface} / R_z\text{-bulk}$, taken from figure 6.11) plotted versus the measured thickness of the carbon-less skin ($\mu m$) plus the Lift Height ($=0.05\mu m$).

The $1/z^3$ dependency leads to the following function for the thickness of the carbon-less skin plus Lift Height

$$f(z) = 1 - Az^3.$$

(C.1)

In this function $A$ is a constant. Note that the condition $f(0) = 1 - 0 = 1$ is obeyed.

Using point $(0.75; 0.13)$ leads to the determination of $A$. Namely

$$f(0.75) = 1 - A(0.75)^3 = 0.13 \Rightarrow A = 2.06.$$

Now the function is complete

$$f(z) = 1 - 2.06z^3.$$

(C.2)

This yields for the thickness of the carbon-less skin of sample G plus Lift Height

$$f(z) = 1 - Az^3 = 0.35 \Rightarrow z = 0.67\mu m,$$

resulting in a thickness for the carbon-less skin of sample G of $0.62\mu m$.

Note that this value does not correspond with the findings of the Light Microscopic picture. (With the help of the Light Microscopic pictures, it has been determined that the carbon-less skin is smaller than $0.3\mu m$).
Appendix D

A Matlab routine has been written in order to calculate the percentage conductive paths in a binarised image. Here, this routine is depicted:

```matlab
img= imread('filename.TIF');
img2= img(81:592,49:560);
imagesc (img2);
colormap gray;
imagesc (img2);
axis image;
wit= find(img2>0);
zwart= find (img2==0);
perc_zw= length ( zwart ) ./ length(img2(:));
perc_wit= length(wit) ./ length(img2(:));
perc_zw
perc_wit
imagesc (img2);
axis off;
```

In order to calculate the number of transitions (from insulating to conductive area and vice versa) in horizontal as well as in vertical direction, another Matlab routine has been written. If it is assumed that the percentages of the conductive paths are equal for all samples, this number is a measure for the size of the conductive paths. Now, the extension of the routine is depicted:

```matlab
Nhor=0;
Nvert=0;
afm=size(img2);
X=double(img2);

for i = 1:(afm(1,1)),
    for j = 1: (afm(1,2) -1 ),
        if X(i,j)-X(i,j+1) -=0
            Nhor=Nhor+1;
        end
    end
end

for j = 1:(afm(1,2)),
    for i = 1: (afm ( 1, 2) -1 }
        if X(i,j)-X(i+1,j) -=0
            Nvert=Nvert+1;
        end
    end
end

Nhor
Nvert
Ntot=Nhor+Nvert
Ngem=(Nhor+Nvert)/2
```
In the depicted table, the results of the matlab routines are depicted.

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**Table E.1:** Results of the Matlab routines. Sample stands for the sample name, volts stands for the applied potential to the substrate, surf/bulk indicates whether the measurement has been performed at the surface or at the bulk, Perc.con stands for the percentage conducting area, Perc.ins stands for the percentage insulating area, Nhor is the number of transitions in horizontal direction, Nvert is the number of transitions in vertical direction, Pc is the averaged number of Nhor and Nvert and Quality gives a short description of the quality of the binarised image.