Doctoral Thesis

Electrostatic field-directed assembly of particles and molecules from polar solution

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Electrostatic Field-Directed Assembly of Particles and Molecules from Polar Solution

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presented by

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Abstract

The fabrication of structures with nanoscale resolution and the positioning of individual nanoscale objects on solid surfaces is of increasing interest because it is one of the key requirements for building up nanotechnological devices and sensors. Since established lithographic methods have only limited capabilities regarding the handling of individual nanoscale objects, new concepts are needed which target their precise and selective assembly on surfaces. Electrostatic fields in particular appear to be a promising option to direct the assembly process, due to their long-range nature and their ability to attract many objects in a parallel fashion.

This thesis focuses on a method - referred to as nanoxerography - employing electrostatic fields for directed assembly of particles and molecules dispersed in polar solvents. In nanoxerography, we write patterns of local surface charges into thin electret layers, such as poly(methyl methacrylate) (PMMA), by applying voltage pulses between a conductive atomic force microscope tip and the sample. These charge patterns act as templates for the selective deposition of particles or molecules in a subsequent development step.

We demonstrate for 50 nm and 100 nm carboxylate functionalized polystyrene microspheres, carboxylate functionalized multi-walled carbon nanotubes, single-walled carbon nanotubes stabilized by the non-ionic surfactant Synperonic NP10, C\textsubscript{60} molecules stabilized by the nonionic-ionic surfactant Triton X-100 and citrate-stabilized 5 nm gold colloid, that direct deposition from alcohol- or water-based suspensions yields higher resolution compared to water-in-oil emulsions used in earlier work. Dissociation of surface groups or local dipoles in the polar head groups of the surfactants lead to either net or partial negative charges on the suspended particles, resulting in Coulomb attraction to positively charged patterns written into the PMMA. We show that the magnitude of the local surface potential provides considerable control over the deposition characteristics such as approximate number of particles deposited per charge dot or alignment of individual and small bundles of carbon nanotubes along charge lines, allowing the
Abstract

creation of nanoparticle arrays with pitches down to 250 nm or networks of carbon nanotubes. We further study additional parameters influencing deposition behavior, such as the stabilizing agents involved, dispersion treatment such as ultrasonication and centrifugation in the case of single-walled carbon nanotube dispersions, or the particle concentration in suspension in general.

Vertical transfer of structures assembled by nanoxerography from the electret surface to an underlying substrate broadens the range of applicable substrate materials much beyond electrets. By these means, we document how thermal removal of the thin PMMA layer transfers patterns of 5 nm gold nanoparticles vertically down onto an underlying SiO₂ substrate. In addition, anisotropic growth of silicon nanowires from the gold nanoparticle patterns provides evidence for the retained catalytic activity of the gold nanoparticles.

We further explore the possibility of using positively charged patterns written into PMMA for the direct patterning of ionic molecules, such as polyelectrolytes, from aqueous solutions. Although the process developed serves its basic purpose in yielding selective deposition behavior of polyanions as well as polycations, further improvement would be inevitable to gain a valuable alternative to existing strategies for polyelectrolyte patterning.

Our results obtained in this thesis demonstrate the capability of nanoxerography to assemble diverse nanoscale objects from polar suspensions on solid surfaces with a considerable degree of control and accuracy, may providing a promising new route for maskless nanoscale fabrication.
Zusammenfassung


Wir zeigen für 50 nm und 100 nm grosse, mit Carboxylgruppen funktionalisierte Partikel aus Polystyrol, für mit Carboxylgruppen funktionalisierte, mehr wandige Kohlenstoff-Nanoröhren, für einwandige Kohlenstoff-Nanoröhren, welche mittels des Tensids Synperonic NP10 stabil dispergiert werden, für C_{60} Moleküle, welche mittels des Tensids Triton X-100 stabil dispergiert werden sowie für Zitrat-stabilisierte 5 nm grosse Goldkolloide, dass gezielte Anlagerung aus Alkohol-basierten oder wässrigen Suspensionen eine höhere Auflösung der resultierenden Strukturen zulässt, verglichen mit Wasser-in-Öl-Emulsionen, welche bisher oft benutzt wurden. Dissoziation von chemischen Oberflächengruppen oder lokale Dipole in den polaren Kopfgruppen der Tenside führen entweder zu
Zusammenfassung


Die Resultate, die in dieser Arbeit erzielt wurden, zeigen auf, dass es die Nanoxerographie erlaubt, verschiedenste Nano-Objekte, dispergiert in polaren Lösungsmitteln, präzise auf Oberflächen anzuordnen. Der entwickelte Prozess bietet gute Prozesskontrolle und stellt somit eine möglicherweise vielversprechen-
de neue Strategie für die Fabrikation von Strukturen im Nanometer-Bereich dar.
Zusammenfassung
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# Abbreviations

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<th>Abbreviation</th>
<th>Full Form</th>
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<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
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<td>AuNP</td>
<td>Gold Nanoparticle</td>
</tr>
<tr>
<td>COOH-MWCNT</td>
<td>Carboxylate functionalized Multi-Walled Carbon Nanotube</td>
</tr>
<tr>
<td>DPN</td>
<td>Dip-Pen Nanolithography</td>
</tr>
<tr>
<td>EG</td>
<td>Ethylene Glycol</td>
</tr>
<tr>
<td>FC</td>
<td>Fluorocarbon (Layer)</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full Width at Half Maximum</td>
</tr>
<tr>
<td>HMDS</td>
<td>Hexamethyl Disilazane</td>
</tr>
<tr>
<td>IPA</td>
<td>Isopropyl Alcohol</td>
</tr>
<tr>
<td>ITO</td>
<td>Indium Tin Oxide</td>
</tr>
<tr>
<td>KFM</td>
<td>Kelvin (Probe) Force Microscopy</td>
</tr>
<tr>
<td>LM</td>
<td>Light Microscopy</td>
</tr>
<tr>
<td>MWCNT</td>
<td>Multi-Walled Carbon Nanotube</td>
</tr>
<tr>
<td>NOS</td>
<td>Nitride-Oxide-Silicon (Si₃N₄-SiO₂-Si)</td>
</tr>
<tr>
<td>PAH</td>
<td>Poly(allylamin hydrochloride)</td>
</tr>
<tr>
<td>PAH-FITC</td>
<td>Poly(fluorescein isothiocyanate allylamine hydrochloride)</td>
</tr>
<tr>
<td>PDMS</td>
<td>Polydimethylsiloxane</td>
</tr>
<tr>
<td>PEM</td>
<td>Polyelectrolyte Multilayer (System)</td>
</tr>
<tr>
<td>PEO</td>
<td>Poly(ethylene oxide)</td>
</tr>
<tr>
<td>PMMA</td>
<td>Poly(methyl methacrylate)</td>
</tr>
<tr>
<td>PS</td>
<td>Polystyrene</td>
</tr>
<tr>
<td>PSS</td>
<td>Poly(styrene sulfonate)</td>
</tr>
<tr>
<td>PTFE</td>
<td>Poly(tetrafluoroethylene)</td>
</tr>
<tr>
<td>SAM</td>
<td>Self-Assembled Monolayer</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>SiNW</td>
<td>Silicon Nanowire</td>
</tr>
<tr>
<td>SPM</td>
<td>Scanning Probe Microscopy</td>
</tr>
<tr>
<td>STM</td>
<td>Scanning Tunneling Microscopy</td>
</tr>
<tr>
<td>SWCNT</td>
<td>Single-Walled Carbon Nanotube</td>
</tr>
<tr>
<td>Synperonic NP10</td>
<td>Poly(ethylene glycol) nonylphenyl ether</td>
</tr>
<tr>
<td>Triton X-100</td>
<td>Poly(ethylene glycol)tert-octylphenyl ether</td>
</tr>
<tr>
<td>UHQ</td>
<td>Ultrahigh Quality (Water)</td>
</tr>
<tr>
<td>VLS</td>
<td>Vapor-Liquid-Solid (Process)</td>
</tr>
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Chapter 1

Introduction

1.1 Structuring of materials at the nanoscale

In 1990, Eigler presented a fascinating experimental result, showing single xenon atoms arranged into 5 nm small “IBM” letters [Eigler90]. The atoms were placed one by one using the tip of a scanning tunneling microscope (STM) as manipulator, acting at the nanoscale. The experiment evidently revealed the contrast to conventional photolithography techniques best known from microelectronic processes, which are not capable to create such small structures. Although Eigler’s single atom manipulation was inefficient from the technological point of view, and restricted to special conditions such as vacuum and low temperatures, the result came very close to the ultimate vision of nanostructuring, the assembly of matter on the atomic scale to obtain full control over the physical and chemical properties of a material.

Top-down approaches, such as lithographic techniques, which rely on the downscaling of macroscopic techniques, are still away from this limit of resolution. Immersion photolithography has reached a resolution of 32 nm. Electron beam lithography, the best of the lithographic techniques, achieves a resolution of 3 to 10 nm [Broers96, Vieu00]. Furthermore, lithographic techniques are often expensive and demanding in terms of clean room equipment and vacuum technology, and usually limited to specific material combinations of resists, etchants and substrate materials.

The ability to create nanoscale structures on solid surfaces is a key requirement in nanotechnology. Molecules, nanoparticles, nanotubes, -wires and -rods are considered as functional units to build up nanoscale devices. The selective immobilization of biomolecules on surfaces is highly considered for bioelectronic
Introduction

systems [Franks07] and biosensing [Zaytseva05, Staedler07]. Patterns of ordered monomolecular layers known as self-assembled monolayers (SAMs) are often used for creating patterns of high chemical contrast, one example are hydrophilic and hydrophobic regions [Liu04]. The unique electronic, catalytic and thermal properties of nanoparticles deriving from the large surface area to volume ratio make them attractive components for electronic [Shipway00, Thelander01] and optic [deWaele07, Sannomiya09] devices and sensors, as catalysts for the growth of nanotubes [Durrer08] and nanowires [Wagner64, Schmid08, Albuschies06], or for molecular electronics [Dadosh05]. Nanotubes, -wires and -rods are known to have considerable potential as key components in field-effect transistors [Bachtold01], nanoscale actuators [Yuzvinsky06], memory elements [Rueckes00], or sensors measuring chemical [Kong00] or physical quantities [Helbling08].

A major challenge still presents the immobilization of individual or small numbers of these functional units onto exact substrate locations. New approaches are required for the assembly, which may take more advantage of the local, chemical or electrical surface forces than the top-down approaches. Since single particle manipulation is too inefficient, the particles or molecules have to be arranged on a surface in a parallel fashion, based on self-assembly. In nature, structures on the molecular and cellular scale are built up by pure self-assembly, without any external control. Regarding specific integration of nanoscale objects into devices, however, the assembly must be guided or directed by an external force.

Capillary forces for instance are used to direct colloidal particles into lines [Ray05] or into predefined topographical features for subsequent transfer printing [Kraus07]. Most of the recent approaches for directed assembly are based on selectively patterned surfaces, in an either chemical, electrical or structural way [Garno02]. Chemical patterning is very often achieved on SAMs, where local electrochemistry can induce oxidation of molecular head groups [Liu04, Maoz99]. Such chemical patterns often serve as adsorption sites of proteins [Hyun02], polyelectrolytes [Clark97b] or particles [Hoeppener02]. Patterned electrodes can serve as electrostatic pattern to direct the selective deposition of microparticles via dielectrophoretic forces [Suzuki04].

For manipulating surfaces in ambient conditions or in liquids, scanning probe-based methods have shown to be promising tools. Due to the small size of the probes and the sensitive actuation provided by feedback control, structures of a resolution of a few nanometers can in principle be achieved. A general review on
scanning probe microscopy (SPM)-based fabrication techniques can be found in [Nyffenegger97, Samori04], and an overview on electrical SPM-based techniques is given in [Naujoks05b].

Direct mechanical structuring has been performed by scratching or indentation, for example on soft polymer surfaces [VanLandingham01]. Mechanical scratching of thiol-based SAMs was performed for subsequent grafting of another type of thiol molecule on the scratched regions [Wadu-Mesthrige99]. Topographical structures can also be created by thermomechanical writing using a heated atomic force microscopy (AFM) tip for locally melting a polymer substrate [Mamin92]. Direct local deposition of a foreign substance on a surface is done by dip-pen nanolithography (DPN), where capillary forces transport molecules or particles from an AFM tip to the substrate. DPN was first demonstrated by Piner et al. [Piner99] and has been extended to a variety of materials, including biomolecules [Agarwal03, Lim03] and gold nanoparticles (AuNPs) [Wang08]. By combining DPN with an electrochemical approach, Li et al. designed polythiophene nanowires on semiconducting or insulating substrates [Li01]. A review on DPN can be found in [Ginger04]. Tip-induced nanoelectrochemical patterning was also shown on SAMs, where only the molecular head groups could locally be altered by biasing a conductive tip, yielding patterns of hydrophilic and hydrophobic regions [Liu04]. Tip-biasing is further used for local oxidation of semiconductors [Snow94, Bo02, Dorn02], for creating ferroelectric domains in piezoelectrically active materials such as lithium niobate [Rodriguez05], for local etching of metal surfaces [Kirchner01] or for the structuring of graphite [Park07a] or graphene [Giesbers08].

Electric fields have shown to be a promising option to guide the assembly process, due to their long-range nature and their capability for contactless, rapid and parallel manipulation of particles or molecules. Barry and Jacobs [Barry06] as well as Kim et al. [Kim06] both showed how addressable areas, used as ‘nanoscopic electrostatic lenses’, designed by resist patterns with openings to a silicon substrate, serve as templates to direct charged nanoparticles and ions from the gas phase into the openings. (Di)electrophoretic forces are used for parallel manipulation of small particles, such as in electrodeposition [VanderBiest99] or for the alignment of carbon nanotubes [Yamamoto98, Krupke03]. In Xerography, the attraction of charged toner particles towards light-generated charge patterns is driven by (di)electrophoretic forces as well [Mort89]. First xerography-like experiments at the microscale were performed by Feder already in 1976 [Feder76].
Carbon particles were attached to electron-beam written charge patterns on Teflon foils, achieving a resolution in the micrometer range.

Patterns of local surface charge can be created by using conductive stamps [Jacobs01, Barry05], focused ion and electron beams [Fudouzi01, Fudouzi02a] or SPM-based techniques [Mesquida02b, Naujoks05c, Tzeng06, Seemann07a]. For the charge storing materials used as substrates, thin films of polymers [Jacobs01, Mesquida02b, Blanco08, Knorr09] or semiconductors [Palaria06, Tzeng06] have been used to a large extent. Deposition of the particles or molecules onto the charged patterns has been achieved by various routes: Nanoparticles could be directly deposited from the gas phase [Jacobs01, Krinke03, Krinke02, Barry05]. From the liquid phase, nonpolar oils were primarily used as the solvent carrying the particles or molecules either in suspended [Fudouzi02b, Fudouzi02a, Tzeng06, Ressier09] or in emulsified [Mesquida01, Naujoks05c, Naujoks06] form. The reason for nonpolar instead of polar solvents is that in the nonpolar liquid the surface charges are likely to have a higher stability. In a polar solvent the issue of charge stability is more challenging, probably because the charge is trapped at the surface, rather than in the bulk of the material. Nevertheless, Cao et al. were the first to show that microspheres can be deposited from polar ethanol-based suspensions onto local surface charges as well [Cao05].

Electric fields have several advantages that make them particularly suited for directing particle or molecule assembly: they can easily be generated in air as well as in liquids. Their field strength can be varied and the polarity can be switched, which is of great use for the selective deposition of charged particles or molecules. Furthermore, in polar solvents the colloidal chemistry provides a solid basis for understanding and tuning the electric properties of colloidal dispersions.

1.2 Motivation and outline of the thesis

The precise and effective assembly of particles and molecules on surfaces at the nanoscale is a fundamental requirement to integrate them into functional devices. Electrostatic fields have shown to be a promising option to guide particle assembly, due to their long-range nature and their capability to attract many objects in parallel. Local surface charges trapped in electret layers may serve as templates for particle or molecule assembly.

Nanoscale objects have been selectively positioned on surfaces using such
xerography-like processes. However, in most cases, particle or molecule deposition was achieved from the gas phase or from a nonpolar solvent. Only one experimental result achieved from a polar solvent is known to us, showing the deposition of 200 nm sulfonate-modified polystyrene (PS) spheres suspended in ethanol [Cao05]. Though electrostatic-field directed deposition of particles or molecules suspended in polar solvents seems promising due to several reasons: There is a huge availability of many kinds of particles and molecules forming stable suspensions in polar solution. Thus, the attachment of particles or molecules from polar suspensions onto local surface charges promises the capability to create nanostructures of a wide range of materials in a similar way, using the same method. Furthermore, the distribution of electric charges in polar suspensions is well-characterized and described in colloidal science by terms such as the electric double layer, the Debye length, the zeta potential or the DLVO theory.

The main goal of this thesis is to explore selective particle and molecule deposition onto local surface charges from polar suspensions. The method - so-called nanoxerography - is schematically illustrated in Figure 1.1. In a first step, patterns of local surface charges are written into a thin electret layer by applying voltage pulses of defined height and length to a conductive AFM tip (Figure 1.1a). In a subsequent development step, the charged sample is immersed into the suspension containing the particles or molecules, which are electrostatically attracted to the previously defined surface locations due to their surface charge (Figure 1.1b). After rinsing and drying, the particles or molecules are attached to the charge pattern and reproduce the structure defined in (a) (Figure 1.1c).

Besides gaining a basic understanding of the process itself, one possible application of this method for creating functional structures of particles is to be investigated, too. Patterns of gold nanoparticles may be used as catalytic site to grow structures of silicon nanowires.

This method has the great advantage over mechanical manipulation that the particles assemble without intervention of an operator and thereby without the usually encountered problems of AFM-based, mechanical manipulation.

This thesis is structured into four main parts:

- Chapter 2 gives a general overview of the charge writing process, including experimental details. In the results part, different electret materials are compared regarding their tendency of charge decay under certain environ-
Introduction

- As an introduction to chapter 3, fundamental properties of electrical charges in polar media and colloidal suspensions are explained. Results obtained from nanoxerography of polystyrene microspheres, multi-walled carbon nanotubes (MWCNTs), single-walled carbon nanotubes (SWCNTs), C_{60} fullerenes and AuNPs are then presented. The results are structured according to the different examined parameters influencing particle deposition.

- Chapter 4 contains a brief introduction to and results of silicon nanowires grown from nanoxerography-assembled AuNP patterns serving as catalytic site. A necessary intermediate step for nanowire growth is the vertical transfer of the AuNP structures from the PMMA surface onto underlying SiO_{2} by thermal decomposition of PMMA.

- In chapter 5, first attempts of the selective deposition of ionic macromolecules such as the polyelectrolytes poly(styrene sulfonate) (PSS) and poly(allylamine hydrochloride) (PAH) from aqueous solutions, by using positively charged patterns written into PMMA as templates, are presented.

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Figure 1.1: Scheme of nanoxerography process. (a) Charge writing: Surface charges are written into an electret layer by applying voltage pulses between a conductive AFM tip and the sample. (b) Development: The sample is immersed in a suspension containing the particles to be electrostatically deposited. (c) Particle attachment. After rinsing and drying the sample, the particles are firmly attached to the predefined pattern.
Chapter 2

Charge Writing

This chapter addresses the first process step of nanoxerography, the local injection of surface charges into electrets by using AFM. The first sections comprise basics of electret materials as well as an introduction to and recent advances in AFM-based charge writing. In the following results part, charge patterns written into different electret materials are compared regarding their tendency of charge decay under certain environmental conditions. High stability of trapped charges is an essential requirement for the selective particle or molecule deposition from suspension.

2.1 Electrets

Nanoxerography starts with the injection of charges into a thin layer of a charge storing material, a so-called electret. An electret is defined as a piece of dielectric material exhibiting a quasi-permanent electric charge ([Sessler87], p.1). Quasi-permanent means that the time constant for charge decay is much longer than the time period of study. An electret not covered by metal electrodes produces an external electric field as long as either its polarization or its trapped, real charges do not compensate each other everywhere in the dielectric. According to these two possibilities, electrets are generally classified into piezo- or ferroelectric materials and real-charge electrets. AFM-based charge writing belongs to the methods for forming real-charge electrets, on which we will focus in the following. Real charges generally comprise trapped positive and negative carriers, often positioned at or near the dielectric surface.

Charge carriers can be injected into the dielectric by various means, by contact electrification, corona charging, electron and ion beam, or they can be generated within the dielectric by light, radiation or heat ([Sessler87], p.20). Diverse
electrical charging technologies make use of electrets being employed in equipment such as laser printers or copy machines for xerographic printing [Mort89, Schein92], electret microphones or gas filters [Kressmann96], electrospinning [Frenot03] or electrostatic filtration [Moshkin97]. Today’s electret research especially deals with thin-film electrets, such as thin polymer layers or silicon-based multilayer systems [Kressmann96].

From the physical point of view, surface and volume charges in electrets are stored in trapping levels located in the large band gap of more than 4 eV between conduction and valence bands, leading to the very small conductivity at ambient temperature ([Sessler87], p.55). Both electron and hole traps are present in general. From the chemical point of view, trap sites can in principle be due to a number of structural anomalies, such as impurities, defects of the monomeric units, chain irregularities, and imperfections of the crystallites ([Sessler87], p.54).

However, while fundamental electrostatic concepts are well established for metals and semiconductors, there is still a lack of agreement on certain basic topics concerning insulators [Schein07]. It is currently debated, for instance, whether or when the charge carriers trapped in electrets are of the nature of ions or free electrons, respectively. In 2008, McCarty and Whitesides hypothesized that contact electrification directing the self-assembly of PS microspheres is mainly due to partition of hydroxide ions from water adsorbed between the contacting surfaces [McCarty08]. Knorr et al. systematically studied charging of various amorphous polymer films by AFM-based charge writing and found the threshold voltages for charge trapping correlating with the water affinities of the polymers, leading to the conclusion that surface near accumulation of aqueous ions takes place during the charging process [Knorr09]. Liu and Bard in contrast recently demonstrated triboelectric charging by free electrons of poly(tetrafluoroethylene) (PTFE) upon rubbing with poly(methyl methacrylate) PMMA [Liu08].

Either way, electret charging is limited by internal and external breakdown whenever the charges produce fields of sufficient magnitude. The occurrence of internal breakdown effects primarily depends on the dielectric strength of the material. For polymers for instance, the dielectric strength is of the order of MV cm$^{-1}$.

In this study local charge injection was investigated on thin films of PMMA on p-doped silicon. Figure 2.1 depicts the chemical structure of PMMA. PMMA is known to have excellent charge storage capabilities. Whereas the typical dielec-
tric strength of PMMA is approximately $E \approx 0.3 \text{ MV cm}^{-1}$, increased dielectric strength of up to $E \approx 1.1 \text{ MV cm}^{-1}$ was measured for isotactic PMMA isomers [Park07b]. Assuming a charge layer of planar density

$$\sigma = \varepsilon \cdot E$$

on the electret surface, maximum charge densities of

$$\sigma \approx 0.6 \cdot 10^{-7} \text{ C cm}^{-1} \quad \text{typical PMMA}$$
$$\sigma \approx 2.2 \cdot 10^{-7} \text{ C cm}^{-1} \quad \text{isotactic PMMA isomer}$$

can be reached for an approximate permittivity of $\varepsilon \approx 2 \cdot 10^{-11} \text{ C V}^{-1} \text{ m}^{-1}$ for PMMA. These charge densities correspond to about

- $60 \times 60$ typical PMMA
- $120 \times 120$ isotactic PMMA isomer

elementary charges per $\mu \text{m}^2$, respectively. Besides high charge densities, PMMA especially shows advantageous properties in terms of charge stability in ambient as well as upon exposure to liquids. Moreover, thin layers of PMMA can easily be produced by spin-coating, and can later on be removed by thermal decomposition or plasma oxidation.

![Figure 2.1: Chemical structure of PMMA](image)

### 2.2 AFM-based charge writing

#### 2.2.1 Introduction

The idea to derive advantage from the highly sensitive probe actuation available in scanning probe instruments not only for surface characterization, but also
for surface manipulation, came soon after the invention of the STM by Binnig and Rohrer in 1981. Today, scanning probe-based nanofabrication techniques include purely mechanical nano-machining, such as scratching and grafting [Wadu-Mesthrige99], dip-pen nanolithography [Piner99], localized electrochemistry, such as oxidation of semiconductors [Snow94] or self-assembled monolayers [Liu04], thermomechanical [Vettiger02] and thermoelectric [Lyuksyutov03] indentation of polymers, or local charge trapping in electret materials, as discussed in this thesis.

Already in 1976, Feder performed charge writing in PTFE foils using an electron beam, achieving electric structures of about 10 µm resolution [Feder76]. The first investigations on high-resolution charge writing using a scanning probe tip were conducted by Stern and Terris [Stern88, Terris90]. They deposited local charges in PMMA using etched Ni tips, and showed that the sign of the charge depends on the polarity of the voltage pulse applied during charge writing. A promising novelty further consisted in the small size of the charge patterns created, being in the range of 2 µm lateral width. Based on these results, one of the first motivations for performing AFM-based charge writing was the potential applicability to high-density data storage using charge dots as data bits. Barrett and Quate demonstrated storage and fast readout techniques for 256 kilobits of information on (120 µm)² area (or 11.5 Gbit/inch², respectively) on a nitride-oxide-silicon (NOS, Si₃N₄-SiO₂-Si) substrate [Barrett92].

In 1998, Wright and Chetwynd suggested that trapped charges might also be used to promote and guide assembly processes [Wright98]. In first successful experiments, silica and gold particles emulsified in a nonpolar solvent were electrostatically attracted and attached to charge patterns written into thin fluorocarbon (FC) films [Mesquida01, Mesquida02c]. Since those early investigations, nanoxerographic printing was shown for various kinds of particles and molecules, including metal nanoparticles [Mesquida02c, Barry05, Tzeng06], proteins [Naujoks04], polymer microspheres [Cao05, Seemann07b], carbon nanotubes [Seemann07a, Seemann07b] and fullerene molecules [Seemann07a].

Whereas long charge decay times of the order of years are necessary for data storage, high charge stability upon exposure to the development medium - be it a particle plasma, a nonpolar or polar solvent - is required for directed assembly. A fascinating fact concerning both applications is that, different to magnetic storage techniques where the finite size of magnetic domains usually limits the
resolution, there is no a priori physical restriction of the size of the charge patterns. The smallest charge pattern theoretically consists of a single elementary charge at a fixed position. Of course, factors such as diffusion and recombination of the charge carriers leading to decay of the charge patterns, as well as the dielectric strength of the material, set their limits regarding the minimal size and maximal resolution of the charge patterns.

2.2.2 Materials

The most considered dielectrics for AFM-based charge writing are thin films of polymers and oxides, with layer thicknesses ranging from a few nanometers to several hundred micrometers.

PTFE and related fluorocarbon-based materials, PMMA and PS are amongst the most widely used polymers. Favorable characteristics are their good charge storage capabilities [Sessler87] and that these materials can easily be produced by spin-coating or gas phase deposition methods. Mesquida systematically investigated AFM-based charge writing on layers of PTFE-like fluorocarbon films deposited by plasma-enhanced chemical vapor deposition [Mesquida02b, Mesquida02a]. Charge patterns of positive and negative sign, with a resolution of 100 nm in the best case and 200 nm on average could be created using highly-doped Si AFM tips. Dependence of charge writing on the film thickness and the impact of humidity on written charge patterns were further characterized in these contributions. Already in 1992, charge dots as small as 70 nm could be created in PMMA, demonstrating first promising characteristics of PMMA for charge writing [Schoenenberger92]. Especially for PMMA [Jacobs01, Ressier08] and PS [Blanco08] high stability of surface charge patterns upon exposure to polar solvents was further reported.

SiO$_2$ is the most often investigated oxide for charge writing, mainly because of its universal applicability in micro- and nanotechnology. Sufficient and stable charge trapping though requires an oxide layer of at least 100 nm thickness [Wright98]. A drawback of SiO$_2$ with regard to trapped surface charges is its hydrophilicity, which leads to adsorption of ambient water causing a high lateral surface conductivity [Olthuis92]. Surface charge decay could be reduced considerably by coating the SiO$_2$ with hexamethyl disilazane (HMDS) [Palaria06]. Promising substrates in terms of charge pattern resolution are NOS and oxide-nitride-oxide-silicon (ONOS, SiO$_2$-Si$_3$N$_4$-SiO$_2$-Si) layers [Wright98]. NOS ele-
trets were amongst the first materials investigated for AFM-based charge writing [Barrett91, Barrett92]. Tzeng et al. demonstrated the creation of high-resolution charge patterns using AFM tips with carbon nanotubes attached [Tzeng02]. Both charge writing and surface potential imaging could be accomplished with these high-aspect-ratio tips on 4 nm thin NOS layers in high-vacuum. A pattern resolution of 50 nm was achieved with an imaging resolution of 5 nm.

2.2.3 Charge writing procedure

Charge patterns are written by applying voltage pulses between a conductive AFM tip and the conductive backside of the sample while scanning over the surface (Fig. 2.2). Charge writing is most often performed in AFM tapping mode with z-feedback turned on [Mesquida02b, Naujoks05c, Blanco07]. The voltage pulses applied between the conductive tip and the sample usually are of a longer period than the oscillation period of the cantilever, to guarantee that the tip is touching the surface several times during one voltage pulse. Mesquida showed that voltage pulse lengths in the range or shorter than the oscillation period lead to unreproducible results [Mesquida02a]. This observation let us suggest that the charges are locally trapped in the electret due to contact electrification, whereas ‘contact’ refers to the short time interval during a whole tapping period where the tip is closest to the surface. Mesquida further demonstrated that longer voltage pulses do not lead to a higher amount of charge transferred, leading to the conclusion that the entire charge transfer takes place within the first microseconds, or the first tip-sample contacts respectively [Mesquida02a]. During these first tip-sample contacts, the electric field which is applied during the voltage pulse bends the cantilever towards the sample leading to charge transfer. Once the charges are trapped, the cantilever most likely bends back due to electrostatic repulsion, and further charge transfer is inhibited.

In the ideal AFM-based charge writing procedure, pattern generation exclusively consists in the local creation of net surface and volume charges, and does not induce any topographical modifications (Fig. 2.3). However, because of the short distance between tip and conductive back-electrode, the electric breakdown field strength of the electret is easily reached, even at bias voltages below 100 V. Tapping mode combined with voltage pulse amplitudes up to \( \approx 70 \text{ V} \) were often used [Mesquida02b, Naujoks05c, Blanco07, Seemann07a] and appear to be reliable for obtaining reproducible charge patterns without undesired topographical features. In the case of polymer electrets, these settings avoid any mass
transport of the polymer during AFM charging. In contrast, electric breakdown is provoked in so-called AFM-assisted electrostatic nanolithography (AFM-EN) to create defined nanoscale features in polymer surfaces due to mass transport [Lyuksyutov03]. By permanently biasing the tip and writing in contact mode, joule heating is generated under the tip and a localized mass transport of softened polymer liquid occurs within the highly non-uniform electric field. At even higher voltage or current flow, Lyuksyutov et al. observed ablation of polymer material, forming holes at the centre of the raised features, spreading outward with further current increase [Lyuksyutov03].

Inorganic electrets have the tendency towards local oxidation when a voltage is applied between a conductive AFM tip and the surface. The degree of oxidation is essentially influenced by the water film covering the surface. Nanostructuring by means of local oxidation is therefore accomplished under high humidity, and has been shown to be a promising tool for the fabrication of quantum structures [Snow94, Dorn02]. In AFM-based charge writing in contrast, surface oxidation is an undesired effect and may be avoided by a dry atmosphere or by vacuum conditions [Tzeng06].
2.3 Charge pattern characterization by Kelvin Probe Force Microscopy

A great advantage of AFM-based charge writing is that the written charge patterns can be characterized in-situ using Kelvin probe force microscopy (KFM). KFM was introduced by Nonnenmacher [Nonnenmacher91], and is meanwhile a standard function implemented in many commercial AFMs. The technique allows for quantitative measurements of local surface potentials on all kinds of materials. It is often applied for dopant profiling in semiconductors [Kikukawa95] or for detecting material contrast [Jacobs97, Sugimura04], and was also used for studying potential changes on biological samples [Knapp02] or the orientation of organic thin films [Fujihira99].

The KFM measurement principle is based on a lift mode strategy: Each scan line is traced twice. After recording the topography in a tapping mode scan, the tip is lifted, and performs the KFM scan at a constant lift height above the sample surface (Figure 2.4). This way, the influence of short-range, non-electrostatic force contributions such as van-der-Waals forces on the measured surface potential is minimized. The lift mode allows for a quasi-simultaneous measurement of
surface potential and topography with minimal crosstalk.

**Figure 2.4: Principle of KFM measurements.** The topography is acquired in tapping mode during a first pass. In a subsequent second pass, the tip is lifted to a constant height (usually 5 - 30 nm) above the surface to measure the surface potential. The Kelvin feedback control adjusts the offset voltage $U_{DC}$ so that $F_C^\omega = 0$.

For the KFM scan, the tip is electrically excited at its resonance frequency $\omega$, by an AC voltage

$$U(t) = U_{AC} \cos(\omega t) + U_{DC}$$

with amplitude $U_{AC}$ and DC offset $U_{DC}$. The tip-sample system basically represents a capacitor $C$ with potential difference

$$U_C = U(t) - \Phi_S$$

wherein $\Phi_S$ is the surface potential to be measured. A potential difference $U_C$ applied to the capacitor leads to an attractive force, $F_C^\omega$, between tip and sample, which can be derived from the electrostatic energy

$$W = \frac{1}{2} CU_C^2$$

stored in the capacitive system. The force $F_C^\omega$ is the gradient of $W$

$$|F_C^\omega| = \left| \frac{\partial W}{\partial z} \right| = \frac{1}{2} \left| \frac{\partial C}{\partial h} \right| U_C^2$$

reduced to the z-component because of its rotational symmetry. The height $h$ denotes the tip-sample distance. According to the convention that attractive forces
are negative, we define
\[ F_C = \frac{1}{2} \frac{\partial C}{\partial h} U_C^2. \]  
(2.5)

Inserting equations (2.1) and (2.2) into (2.5) results in
\[ F_C = \frac{1}{2} \frac{\partial C}{\partial h} \left( U_{AC}^2 \cos^2(\omega t) + (U_{DC} - \Phi_S)^2 \right) + \frac{\partial C}{\partial h} U_{AC} (U_{DC} - \Phi_S) \cos(\omega t). \]  
(2.6)

KFM works as a nulling technique: The \( \omega \)-component of \( F_C \)
\[ F_C^\omega = \frac{\partial C}{\partial h} U_{AC} (U_{DC} - \Phi_S) \cos(\omega t) \]  
(2.7)

is detected by a lock-in amplifier and the Kelvin mode feedback adjusts the offset voltage, \( U_{DC} \), so that \( F_C^\omega = 0 \), leading to \( U_{DC} = \Phi_S \). Under experimental conditions, the tip has its own potential \( \Phi_T \) depending on the tip material, and the Kelvin signal \( U_{DC} \) corresponds to the contact potential difference \( \Phi_T - \Phi_S \).

A challenge in KFM measurements is that, due to the long range of electric forces, the lateral resolution and accuracy of KFM is limited by the finite geometry of the AFM tip. The electrostatic interaction zone between tip and sample is considerably larger compared to the small interaction zone of van-der-Waals forces in topographic AFM measurements. Hence the surface potential measured by KFM is a weighted average of the potential at the tip location and the surrounding potential distribution: Jacobs and Stemmer [Jacobs99] showed that the total force acting on the tip at a particular point over the sample surface is influenced by different sample regions and represented by mutual tip-sample capacitances, \( C_i \) (Figure 2.5). The measured KFM potential is then a weighted average over all potential areas, wherein the mutual capacitance derivatives, \( C'_i = \frac{\partial C_i}{\partial z} \), are the weighting factors:
\[ U_{DC} = \frac{\sum_{i=1}^{n} C'_i \Phi_i}{\sum_{i=1}^{n} C'_i}. \]  
(2.8)

Small features in the surface potential accordingly appear larger and their measured potentials appear smaller than they are in reality.

Based on numerical simulations using the multiple multipole method and experiments with surface potential features of known geometry, Jacobs further demonstrated that the surface potential measured by KFM strongly depends on the tip geometry and also on the tip sample distance [Jacobs98]. A point-like potential feature due to a point charge at or just below the sample surface, for instance, would appear as 50 to 100 nm large structure in the KFM image [Jacobs98].
Figure 2.5: Influence of the finite tip geometry on KFM measurements. Areas of different surface potentials $\Phi_1$ and $\Phi_2$ contribute to the tip-sample force and lead to an averaged measured surface potential.

It is consequently difficult to use KFM to determine the actual physical dimensions of written charge patterns at length scales below 100 nm. Questions concerning the number of trapped elementary charges together with their exact location both in lateral direction as well as in depth are still challenging to answer.

### 2.4 Charge decay in AFM-written charge patterns

Electrets are known for trapping charges with long-time stability up to years ([Sessler87], p.67). However, certain conditions such as high temperatures, high humidity or exposure to liquids can lead to fast and severe charge decay.

There are several reasons of possible charge decay in electrets, which are usually classified into external and internal charge decay ([Sessler87], p.66). External charge decay is due to neutralization of surface charges, which can be caused by the adsorption of counterions from the surrounding medium or by charge loss due to its electrical conductivity. Internal charge decay is caused by the small but non-zero electrical conductivity of the electret material and by diffusion of charge carriers. Excess charges are subject to drifts caused by their own fields. While surface charges are primarily affected by external decay, volume charges are mainly affected by internal decay (Figure 2.6).

One can suggest that material properties of the electret, such as the number, location and energy level of the trapping sites essentially influence the ratio of
Figure 2.6: Charge decay in electrets. External charge decay occurs due to ion adsorption from the surroundings and influence of the electrical conductivity of the surrounding medium, and primarily affects surface charges. Internal charge decay occurs due to ohmic drift and thermal diffusion, and primarily affects volume charges.

surface versus volume traps of a written charge pattern. In other words, while one type of electret traps charges primarily at or directly below the surface, another type of electret may reveal trapping sites much deeper in the electret. Such differences would have crucial impact on the external charge decay, affected by environmental conditions such as high humidity or exposure to liquids, and local surface charge-directed assembly of particles and molecules from polar solution would require electret materials that

- trap charges sufficiently deep, but
- still provide high lateral resolution of the charge patterns, to enable in turn high lateral resolution of the final particle patterns.

However, besides these basics and guesses few concrete facts are known about the responsible mechanisms for charge dissipation in electrets, making the choice of a favorable material not straightforward. The dominating idea is that charges in insulator surfaces disappear due to surface conductance [Rezende09], but, as we mentioned in section 2.1, the nature of the charge carrying species - whether they are ions or free electrons - and with it their mobilities are still a controversial issue [Schein07, McCarty08, Liu08]. Moreover, characterizing the surface conductance is not trivial because even hydrophobic polymer surfaces in ambient
air of 20%-70% relative humidity are coated with layers of water that can reach a few nanometers in thickness, but are in turn hardly continuous due to dewetting events [Lee03, Lee04].

Albeit the sparse background knowledge various publications report on empiric studies on charge retention in electrets. The available publications primarily focus on only one electret of interest at a time, making a comparison between the most considered materials for charge writing, such as PMMA, PTFE and related FC-layers, PS, SiO\textsubscript{2} or NOS, difficult. A brief comparative investigation on charge retention times upon (i) exposure to ultrahigh quality (UHQ) water and (ii) during AFM scanning using a conductive tip on (1) PMMA, (2) PTFE-like fluorocarbon layers and (3) SiO\textsubscript{2} is added in section 2.7.

Relatively high charge stability in high humidity or upon exposure to water was found throughout the contributions for PMMA. For charge patterns created by electrical microcontact printing, Jacobs et al. documented a surface potential decrease of 83% after 30 min exposure of a positively charged pattern to ionized water [Jacobs01]. In addition, the patterns appeared not to diffuse laterally during immersion. In ambient laboratory air of 55% relative humidity, a charge decay between 45% for lower (≈ 200 mV) and 80% for higher (≈ 1 V) created surface potentials of both polarities was recorded 24 h after charge writing by Ressier et al. [Ressier08]. A charge decay of about 80% in PTFE-like electrets was reported by Mesquida after only 8 h in similar conditions [Mesquida02a], whereas the charges were found to completely dissipate in SiO\textsubscript{2} electrets after only 70 min [Palaria06].

Charge patterns written into PTFE-like FC-layers [Mesquida02a] as well as SiO\textsubscript{2}, even when covered by a hydrophobic HMDS layer [Palaria06], did not withstand immersion in ultra-pure water at all. Comparatively good charge storing capabilities upon exposure to water, in contrast, have recently been shown for PS films, with a charge decay of only 20% after a brief immersion of 20 sec in UHQ water [Blanco08].

2.5 Experimental details

2.5.1 Sample preparation

Due to the excellent charge storage properties, including relatively high stability upon exposure to polar liquids, PMMA layers were used as electret substrates. P-doped Si wafers served as conductive support. The samples were of the following
two types:

- $\approx 150$ nm thick PMMA layers, spin-coated onto p-doped silicon at 3500 rpm (Chemat Technology, Spin-Coater KW-4A, Northridge CA, USA) from a 3.5% solution of PMMA ($M_w = 350$ kDa) in toluene. These silicon wafers contained only a thin surface layer of native oxide.

- $\approx 50$ nm thick PMMA layers, spin-coated at 3500 rpm from a 1% solution of PMMA in toluene onto p-doped silicon wafers covered with 200 nm thermally grown $\text{SiO}_2$. The $\text{SiO}_2$ layer was a prerequisite for the nanowire growth performed in a vapor-liquid-solid (VLS) process (chapter 4).

Both sample types were subsequently baked on a hotplate at 180 °C for 3 min.

2.5.2 Technical setup and charge writing details

Charge writing, KFM and topography measurements were performed with a NanoScope Multimode AFM equipped with a NanoScope IIIa Controller (Digital Instruments Veeco Metrology Group, Santa Barbara, CA, USA). A necessary condition for charge writing as well as KFM is the use of conductive AFM tips. Two types of highly doped Si-cantilevers served throughout all experiments ((1) Nanosensors, Neuchatel, Switzerland, type PPP-NCHR-W (2) MikroMasch, Estonia, type NSC15/No Al), both with an electrical resistivity of $\rho = 0.001-0.002 \, \Omega \, \text{cm}$ and a tip radius of $a < 10$ nm.

Charge writing was performed by applying voltage pulses of defined height and length to the cantilever using a custom-built pulse generator connected between tip and grounded sample mount. The pulse length was kept at 1-2 ms at a repetition frequency of 100 Hz, and the pulse height varied between 15 V and 70 V, according to the local surface potential difference to be created. By switching the connection between tip and sample mount, both positive and negative charge patterns could be written. Charge writing was carried out in tapping mode with $z$-feedback turned on.

Three different kinds of typical charge patterns were used to study directed assembly of particles and molecules (Figure 2.7). To determine the general selectivity of the deposition process, large-scale cross patterns were written onto 40 x 40 $\mu m^2$ areas (Figure 2.7a). As the internal lithography mode showed too much drift and hysteresis for larger scanning areas, these larger patterns were
simply generated by turning the voltage pulse generator on and off manually during normal scanning. Two rectangles were consecutively written by rotation of the scanning direction by 90°. Line patterns primarily served to characterize surface potential-dependent deposition behavior (Figure 2.7b). To this end, graded series of charge lines of 20 µm length and 1-1.5 µm spacing were created by decreasing the applied voltage pulse amplitudes in 3 V or 5 V steps. The charge lines were written at a tip-drawing velocity of 1-2 µm s$^{-1}$. Small-scale charge dot arrays with pitches between 250 nm and 2 µm finally were used to investigate deposition of single or small numbers of particles per charge dot, as well as the general influence of polarization forces on particle deposition (Figure 2.7c). The dot arrays were written with a charging time of 1 ms at the dot position and a repositioning velocity of 10 µm s$^{-1}$. For the line and dot patterns the tip motion was determined by the internal lithography mode of the Nanoscope software.

2.6 Reproducibility of charge writing

We did not perform systematic studies on the reproducibility of the charge writing procedure. However we observed that the most obvious impact on charge writing reproducibility had the AFM tip used. A sudden loss of charge writing capability of a particular tip could be explained by local oxidation of the tip material due to the current flow. A substantial oxide layer at the tip apex would lead to a too high contact resistance and to blocked charge transfer. It was reported that doped Si tips, as employed in our studies, are considered better than metal-coated tips because the latter can show abrasion of the metal layer during charge writing [Naujoks05b]. We further suggest that charge writing reproducibility is substantially limited when using broken or blunt tips, or tips with attached dirt or particles. We observed, for instance, that a tip shape, such as a broken 'double tip', was reproduced in doubled charge pattern features.

Hence high reproducibility was usually achieved within one run of charge pattern creation using an undisturbed tip. After writing several charge patterns or during intermediate particle imaging, a loss or change in charge writing ability of the tip used could occur.

The effect of an oxidized tip is not as pronounced in the KFM measurements because KFM is measuring potential or force, respectively, while only minute current flow occurs during capacitance charging. Broken or blunt tips have higher impact on the surface potential measurements due to the strong influence of the
Figure 2.7: Typical charge patterns written into PMMA for studying selective particle and molecule deposition. KFM (left) and topography (right) images of large-scale cross patterns (a), series of lines of decreasing surface potential (b) and high-density dot arrays (c). Z-scales: (a) 5.8 V, 26 nm (b) 2.4 V, 11 nm (c) 1.5 V, inset 530 mV at an offset of +500 mV with respect to the main image, 7 nm.
2.7 Charge decay measurements

A prerequisite for nanoxerography is that the charge patterns written into the electret surface remain sufficiently stable during particle or molecule deposition. Even though various publications report on charge retention in high humidity or upon exposure to polar liquids, there exists no study directly comparing different electret materials. In this section, we compare three of the most considered electret candidates for nanoxerography regarding their tendency for external charge decay of AFM-written charge patterns, i.e.:

1. PMMA; 50 nm thick layers, spin-coated onto p-doped silicon covered with 200 nm thick thermally grown SiO$_2$, as described in the experimental section.

2. PTFE-related FC-layers; 300 nm thick, produced by plasma-enhanced chemical vapor deposition (PECVD) from C$_4$F$_8$ precursor gas in a Deep Reactive Ion Etching (DRIE) set-up, on p-doped silicon wafers [Naujoks05a].

3. SiO$_2$; 200 nm thick, thermally grown on p-doped silicon.

In first experiments (section 2.7.1), charge patterns are characterized before and after 5 sec of immersion in UHQ water, simulating conditions similar to our later nanoxerography experiments. In a second series of experiments (section 2.7.2), charge patterns are repetitively imaged by KFM in ambient air. Due to continuous tapping mode scanning, charge decay occurs during the short contact times between the charged locations and the conductive AFM tip. Charges trapped right at or very close to the surface are being ‘collected back’ by the AFM tip. Even though this procedure has no direct relevance for nanoxerography, it allows for recording slower and stepwise charge decay, and may help to visualize further influencing factors regarding external charge decay in the different electret substrates.

We restrict our investigations to positively charged patterns written into the electrets because charge patterns of positive rather than negative polarity are playing the major role for particle and molecule deposition in the following experiments.

2.7.1 Charge decay upon exposure to aqueous solution

On all substrates, a series of ten positively charged lines with decreasing surface potential were written by applying pulse amplitudes of 50 V (line 1) down to
26 V (line 10) in 3 V steps. The surface potential difference determined by KFM ranged between $\Delta V = 4.8$ V (line 1) and $\Delta V = 0.8$ V (line 10) for PMMA (Fig.2.8a), $\Delta V = 4.0$ V (line 1) and $\Delta V = 0.2$ V (line 10) for the FC-layer and $\Delta V = 4.2$ V (line 1) and $\Delta V = 0.3$ V (line 10) for SiO$_2$. After charge writing and KFM imaging, the samples were immersed for 5 sec in UHQ water and dried in an air stream. The second KFM characterization was then performed immediately.

![Figure 2.8: Charge decay in PMMA upon 5 sec exposure to UHQ water. KFM images before (a) and after (b) sample immersion. Scale bars: 1.5 µm. (c) Comparison of profiles across the charge lines reveal a charge decay in the range of 78-86%](image)

On PMMA, the line patterns were still clearly recognizable after exposure, though with a decay of the peak surface potential of 78-86%. On the FC-layer as well as on SiO$_2$ however, complete neutralization of the charge patterns occurred, rendering identification of the charge patterns impossible. These KFM images are
not illustrated.

### 2.7.2 Charge decay during tapping mode scanning

Again, charge patterns of positively charged lines were created as described in the foregoing section 2.7.1. After charge writing, the charge patterns were continuously scanned ten times in KFM thereby acquiring topography (first pass, tapping mode) and surface potential (second pass, lift mode). A scanning area of $25 \times 25 \ \mu \text{m}^2$, a scanning line frequency of 2 Hz, 256 lines per frame and a lift height for KFM of 5 nm were set during all measurements.

Figures 2.9a (PMMA), 2.9b (FC-layer) and 2.9c (SiO$_2$) display cross sections of the line patterns after the first, fifth and tenth scan. An obvious observation comparing the three substrates is that the charge patterns written into PMMA show far higher stability than those written into fluorocarbon and SiO$_2$. In PMMA, decay of the peak surface potentials was 3-16% after ten scans. A peak surface potential drop of about 40-60% was found for fluorocarbon and about 20-40% for SiO$_2$. A striking difference between fluorocarbon and SiO$_2$ can further be observed regarding loss in lateral resolution. While lateral spreading of trapped charges is substantial in SiO$_2$, the lateral resolution in fluorocarbon is maintained during scanning. An explanation can be found in the higher hydrophilicity of SiO$_2$ compared to the hydrophobic fluorocarbon. Water condensation occurs at the hydrophilic surface and promotes lateral charge migration due to the electrical conductivity of the water film [Olthuis92].

We conclude that PMMA is the most favorable substrate out of the three candidates tested for charge writing regarding charge pattern stability.
Figure 2.9: Charge decay in line patterns written into different electret substrates during tapping mode scanning. Profiles across the charge lines written into PMMA (a), FC-layers (b) and SiO$_2$ (c) were recorded during the first, fifth and tenth scan. The charge patterns written into PMMA show clearly the smallest charge loss.
Chapter 3

Selective particle deposition

This chapter contains a substantial part of the experimental results achieved in this thesis. They show how AFM-based nanoxerography is applied to a variety of materials, including polystyrene microspheres, different kinds of carbon nanotubes, fullerene molecules and gold nanoparticles. In the following, if generally mentioned, these ‘nano objects’ will be combined into the term ‘particles’. The goal of the experiments was to understand and progressively develop the particle deposition process.

The chapter is divided into four parts: As an introduction, nanoxerography from gas phase, nonpolar and polar liquids is compared and discussed. In a second part, fundamental properties of electrical charges in polar media and colloidal suspensions are explained, which are essential to describe the interactions between substrate surface and solvent as well as solvent and suspended particles. Some preliminary considerations concerning the requirements for electrostatic field-directed particle deposition can be taken from these basics. A third part contains the experimental details, i.e. the composition of the different suspensions and the origin of the surface charges in these suspensions, and the development procedure. Finally, the experimental results are structured according to the different parameters examined that have an impact on the particle deposition characteristics.

3.1 Nanoxerography from gas phase, nonpolar and polar liquids

A key challenge in nanoxerography is the exposure of the written charge patterns to the development medium. While the surface charges show long term stability
in ambient, charge decay can emerge much faster in contact to a plasma or to liquids. Mandatory for successful selective particle attachment onto the charge patterns is that particle attraction occurs faster than the charge patterns dissipate.

The particles can principally be deposited either from the gas or from the liquid phase. Gas phase means that the samples containing the charge patterns are dipped into a dry powder, or, to provide more reproducible conditions, exposed to a particle gas, generated in a tube furnace. Gas phase deposition was so far primarily shown on charge patterns created by charge stamping, with a minimal feature size of the stamping electrodes of 50 nm [Barry05]. The created particle assemblies show a high reproducibility and selectivity throughout the contributions [Jacobs01, Jacobs02, Barry03a, Barry03b, Kang04, Barry05, Cao05]. More differentiated investigations, for example on the influence of the surface potential or the particle concentration in the gas have however not been published. A typical result of directed particle assembly from gas onto a charge line pattern, achieved by Barry et al. [Barry05], is illustrated in Figure 3.1a. The main motivations why the research efforts in this thesis are focused on liquid rather than gas phase deposition are the following: Deposition from liquid phase presents a simple dip-and-dry process with no need for demanding equipment, and further seems more suited for the deposition of molecules such as biomolecules or polyelectrolytes. Moreover, it is our speculation that deposition from liquids has high potential for the creation of high-density particle patterns. In a stable suspension, the particles are already in close proximity to the attachment sites, so more uniform and accurate particle deposition may be a consequence. Furthermore, colloidal chemistry is a field where profound knowledge for understanding the electric properties of suspensions is available, and at the same time a huge technological versatility is provided. This may allow one to chemically tune suspensions, by involving surfactants or by pH-adjustments, for instance, until they fulfill the requirements for appropriate particle deposition onto local surface charges.

In liquids, one possibility to prevent charge patterns from fast dissipation is to transfer the particles to be deposited into a nonpolar solvent. In 2001, Mesquida et al. demonstrated nanoxerography as a simple dip-and-dry process by development of surface charge patterns in a water-in-oil emulsion containing silica beads encapsulated in the emulsion droplets [Mesquida01]. Emulsion droplets constitute perfect containers to transport any water-soluble material to the defined surface spots. This makes them well-suited for the creation of bioassays, as the biomolecules can be kept in their buffer solutions during the whole deposition process. Promising results were obtained on site-directed assembly of
Figure 3.1: Typical nanoxerography patterns achieved from gas phase and non-polar media. (a) Gas phase deposition of unoxidized silver nanoparticles onto charge lines, demonstrated by Barry et al. [Barry05]. (b) Deposition of gold nanoparticles encapsulated in water droplets emulsified in FC-77, a nonpolar oil, reported by Mesquida et al. [Mesquida02c]. Emulsion droplets of different sizes attached to the charged lines.

layered biomolecular structures [Naujoks06] and on deposition of different antibodies into multifunctional microarrays [Blanco07], for instance. However, a disadvantage of this emulsion-based approach is that the achievable resolution is determined by the emulsion droplet size, together with the fact that water-in-oil emulsions are challenging to stabilize. Hence, emulsion droplets of nanometer up to micrometer size usually coexist in the emulsion (see Figure 3.1b). An approach based on nonpolar suspensions instead of emulsions was demonstrated by Tzeng et al. [Tzeng06]. Gold nanoparticles were directly suspended in a nonpolar toluene solvent via a stabilizing tetraoctylammonium bromide (TOAB) sur-
factant and deposited onto negatively charged patterns written into a NOS substrate using AFM. These structures show a high definition and a resolution down to 30 nm.

However, the usage of nonpolar development media principally bears the difficulty that the concentration of ions is naturally very low. Because electrostatic charges are a key factor regarding suspension stability, stable dispersions in nonpolar liquids are often far more difficult to achieve than in their polar counterparts. Accordingly, many commercial dispersions of nanoparticles and molecules with potential applications in nanodevices are based on polar solvents. Electrostatic stabilization of polar colloidal dispersions is well researched and described by the DLVO theory (see section 3.2.4). Furthermore, a sufficient surface charge on the particles, either originating from the adsorption of ions or the dissociation of surface groups, is often guaranteed by involving surfactants or ligands (see section 3.2.4), or covalently bound functional surface groups. The challenging issues in polar media remain the screening of the electric field (see section 3.2.2) and the substantial charge decay in the electret. It is very likely that these factors limit the applicability of nanoxerography to weakly ionic solvents.

3.2 Electrical charges in polar media

The following four subsections give a brief overview on important characteristics and terms in colloidal chemistry which are relevant for nanoxerography. They include the electric double layer, the Debye length, the zeta potential, the topic of surfactants and ligands and the DLVO theory.

3.2.1 Electric double layer

In polar solvents, like water or alcohols, most dispersed particles and substrate surfaces are electrically charged. The whole liquid system must be electrically neutral, meaning that an equivalent number of counterions are present in the solvent surrounding the particles and surfaces. The layer of counterions surrounding a charged particle or substrate surface is called the electric double layer. Thus, due to the charge compensation of the surrounding ions, the electrostatic field originating from a charged particle or substrate surface is completely screened outside the electric double layer (Figure 3.2).
Figure 3.2: Schematic illustration of the electric double layer surrounding charged particles and substrate surfaces in polar media. An example of two negatively charged particles and a positively charged surface in suspension. Ions are loosely distributed around the charged particles and the substrate surface due to electrostatic attraction, leading to a completely screened electric field outside the double layers.

### 3.2.2 Debye length

From the mathematical point of view, the structure of the electric double layer, meaning the concentration of counterions as a function of distance from the surface of the particle, is described by the Poisson-Boltzmann equation [Verwey48]. For a planar surface, or a spherical particle with core radius \(a\) respectively, an exact solution of the Poisson-Boltzmann equation is provided by the Gouy-Chapman model [Gouy10, Chapman13]. The model is only valid for small potentials but any electrolyte [Morrison02], and leads to the following distribution of the electrical potential \(\Phi\) outside the surface as a function of the distance \(x\) from the surface, or the distance \(r\) from the center of the sphere, respectively:

\[
\Phi(x) = \Phi_0 e^{-\kappa x} \quad (3.1)
\]

for a planar surface and

\[
\Phi(a) = \Phi_0 \frac{a}{\kappa} e^{-\kappa(r-a)} \quad (3.2)
\]
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for a spherical particle, where

\[
\kappa^2 = \frac{2000 \cdot N_A^2 e^2 \cdot I}{\epsilon \epsilon_0 \cdot RT}.
\]  

(3.3)

The term \( \kappa \) has units of reciprocal length, and \( 1/\kappa \) is the characteristic length or the ‘thickness’ of the electric double layer, known as the Debye length. \( \Phi_0 \) is the surface potential, \( N_A \) Avogadro’s constant, \( e \) the elementary charge, \( I \) the ionic strength of the solution, \( \epsilon \) the dielectric constant of the medium, \( \epsilon_0 \) the permittivity of free space, \( R \) the gas constant and \( T \) the temperature.

For the experiments discussed in this thesis, mainly three qualitative properties described by the formulas (3.1), (3.2) and (3.3) are of relevance:

- The electrostatic field in the polar solvent declines exponentially with distance from the charged surface.

- The magnitude of the Debye length depends solely on the properties of the liquid, such as the ionic strength, the permittivity of the solution and the temperature, and not on any property of the surface such as its charge or potential.

- An increased Debye length can be due to (a) a decreased ionic strength (Figure 3.3) (b) an increased temperature or (c) an increased relative permittivity of the solution.

For ultrapure water at pH 7, the Debye length is approximately 1 \( \mu \)m. However, in laboratory atmosphere, absorption of CO\(_2\) can lead to a decrease in pH, and the Debye length can be substantially reduced to 200-300 nm [Thormann08, Sharma09]. Water of salt concentrations of 0.01 mM, 0.1 mM or 1 mM has Debye lengths of about 100 nm, 30 nm or 10 nm, respectively. Isopropanol (\( \epsilon \approx 20 \)) has a relative permittivity of approximately a fourth than that of water (\( \epsilon \approx 80 \)) and therefore a Debye length which is about half that of water, assuming identical salt concentrations. However, in pure isopropanol or ethanol (\( \epsilon \approx 25 \)), a lower ion concentration and hence a larger Debye length can be expected compared to ultrapure water, due to the lower polarity of these media. Based on theoretical considerations, Philipse and Koenderink estimated the Debye length of pure ethanol of the order of \( \kappa^{-1} = 5 \mu \)m as an upper limit [Philipse03]. Ionic contaminations and counterions reduce this value under laboratory conditions, of course.
An important fact for nanoxerography is that the Debye length in water- and alcohol-based suspensions is in the nano- to micrometer range, and hence in a similar order of magnitude than the diameters of the dispersed particles to be deposited. Because the electrostatic field is screened outside the double layer surrounding the surface charges trapped in the electret, so that particle attraction takes only place within, a sufficiently thick double layer is a crucial requirement for a successful application of nanoxerography combined with polar suspensions.

### 3.2.3 Zeta potential

The inner structure of the electric double layer can be separated into two regions (Figure 3.4): an inner region is composed of counterions strongly attached to the surface. These ions are carried with the particle when it moves with respect to the surrounding medium. The surface charges themselves can originate from adsorbed ions, dissociated surface groups or, in the case of charge writing, trapped surface charges. This inner layer is called Stern layer. The outer, ‘Diffuse layer’ contains the remaining ions within the electric double layer. These counterions are distributed according to a balance between their thermal motion and the forces of electrical attraction [Morrison02].
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Figure 3.4: Zeta potential. Primarily negative counter-ions attach strongly to the positively charged particle surface, and move with the particle when the particle moves with respect to the surrounding medium. This region within the plane of shear is the Stern layer, and the potential at the plane of shear is the zeta potential. The Diffuse layer outside the plane of shear contains more loosely bound ions.

The Stern layer (separated by a dotted line in Figure 3.4) is defined as the region within the plane of shear, and the electric potential at the plane of shear is called the zeta potential. Even though the zeta potential, $\zeta$, is not exactly equal to the surface potential, it is often a potential of practical interest and use. While the real surface potential is difficult to measure, a number of methods exist to record the zeta potential of a colloidal dispersion. Most common are electrophoretic techniques, such as laser Doppler velocimetry (LDV) or phase-angle light scattering. A basic, but for our experiments essential information that can be directly derived from zeta potential measurements is whether the electrical charge on a dispersed particle or a substrate surface is positive or negative.

3.2.4 Surfactants and ligands for stabilizing colloidal dispersions

Surfactants

A surfactant (a contraction of the term surface-active agent) is a chemical substance which is ideally present at low concentration in a system, and has the property of adsorbing onto the surfaces of the system. The surfactant thereby alters to a marked degree the surface free energies of those surfaces. Surfactants have
a characteristic molecular structure consisting of two structural groups. While one group has a high affinity for the surface, the other group has a high affinity for the solvent. This so-called amphipathic structure of the surfactant therefore causes not only concentration of the surfactant at the surface and reduction of the surface tension of the solvent, but also orientation of the molecule at the surface. In a polar solvent such as water, the group attaching to the surface is of hydrophobic nature and often consists of a long-chain hydrocarbon residue. The group oriented towards the solvent is hydrophilic, either with an ionic (ionic surfactants) or a polar (nonionic surfactants) head group.

**Ligands**

Ligands are surfactant-related chemical substances with amphipathic structure. Ligands bind to a central metal to form a coordination complex. The bonding between metal and ligand generally involves formal donation of one or more of the ligand’s electrons and can range from covalent to ionic.

Surfactants and ligands play a crucial role in colloidal dispersions where they are used to enable and enhance dispersion stability. The attached surfactant usually alters the surface charge and accordingly the zeta potential of a particle dispersed in a solvent. The surface charge of a particle in turn can be an essential factor regarding dispersion stability. Without the addition of a surfactant to a particle-solvent system, especially particles with hydrophobic surfaces tend to aggregate and settle out of the suspension.

**Stabilization of colloidal dispersions**

Colloidal dispersions can be divided into two major groups regarding their mode of stabilization: Steric stabilization is obtained by solvation of the colloids, including all degrees of interaction from mere physical wetting to the formation of adherent thick layers of polymer molecules. Electrostatic stabilization comprises electrostatic repulsion between the particles, arising from ions that are either adsorbed by or dissolved from the particle surface [Morrison02]. The zeta potential is often used as an index of the magnitude of electrostatic interaction between colloidal particles. Nanoparticles with a zeta potential less than -15 mV or more than 15 mV are expected to be stable from electrostatic considerations [Hiemenz97], whereas particles with zeta potentials between -15 and 15 mV can still be stable if they are stabilized sterically.
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The dispersions under investigation in our thesis are (1) PS spheres and multi-walled carbon nanotubes, both functionalized with carboxylic surface groups, (2) single-walled carbon nanotubes and fullerenes stabilized by the nonionic surfactants Synperonic NP10 and Triton X-100, respectively, and (3) gold colloid stabilized by a citrate ligand. A detailed overview will be given in section 3.3.1 and is depicted in Figure 3.5. The solvents used are either pure UHQ water or isopropyl alcohol (IPA).

Electrostatic stabilization obviously dominates for the carboxyl functionalized particles, where the carboxyl surface groups establish a negative surface charge on the particles by dissociation into COO$^-$ and H$^+$. Zeta potential measurements revealed values around -50 to -60 mV for 60-100 nm COOH-polystyrene spheres suspended in UHQ water in the 5-12 pH range [Liu09]. Likewise, the gold colloid is expected to be stabilized primarily by electrostatic interactions imparted by the citrate ligand, with similar zeta potential values around -50 to -60 mV in the 5-10 pH range [Aroca06]. For the surfactant-stabilized SWCNTs and fullerenes the situation is less apparent. White et al. measured a zeta potential of -23 mV on Triton X-100-wrapped SWCNTs suspended in deionized water [White07]. Due to the high chemical similarity between Triton X-100 and Synperonic NP10 (chemical structures in Figure 3.5) a similar value can be assumed for Synperonic NP10. From this perspective one cannot exclude that electrostatic effects play at least a partial role for stabilization. In general it is suggested that non-ionic surfactants stabilize nanoparticles and nanotubes in solution either primarily by steric repulsion [Napper83] or by a combination of electrostatic and steric effects [Romero-Cano98], known as electrosteric stabilization. Because of the higher relevance in our case we briefly focus a bit more on electrostatic stabilization in the following section.

DLVO theory

Electrostatic stabilization of colloidal dispersions is generally described and calculated by the DLVO theory. The DLVO theory quantitatively explains the balance between attractive and repulsive interactions of the dispersed particles. It was independently formulated by B. V. Derjaguin and L. Landau in 1941 in the U.S.S.R. and by E. J. W. Verwey and J. Th. G. Overbeek in 1948 in the Netherlands, and is accordingly denoted by the term ‘DLVO’. The basic idea behind the theory is that the stability of a dispersion is determined by the sum of attractive and repulsive forces between individual, suspended particles. The mutual attraction of
particles is a consequence of the van der Waals forces, while the mutual repulsion of particles is a consequence of the interaction of the electric double layers surrounding each particle. Consequentially, to disperse the particles, the repulsive interactions must be increased to the point where they overcome the attractive interactions; to aggregate the particles, the reverse must be done.

In nanoxerography, we suggest that surfactants and ligands fulfill a twofold function: First, they enable stable suspension of particles to be deposited, irrespective of electrostatic or steric effects dominating stabilization. We assume that high suspension stability is favorable for regular and reproducible particle attachment. Second, the surfactants and ligands attached to the particle surfaces may be the ‘carriers’ of the surface charges responsible for electrostatic attraction of the particles to the written charge patterns.

3.2.5 Requirements for electrostatic particle attraction to locally trapped surface charges in polar media

Based on the aforementioned properties of trapped charges in electrets (chapter 2) and of ion distributions in polar media (sections 3.2.1 to 3.2.4), we summarize a number of conditions that presumably must be met for successful particle attraction in nanoxerography:

- The charge pattern must be sufficiently stable during particle attachment.
- A suspended particle is only attracted to the charge pattern when the electric double layers of the particle and the charged surface interpenetrate. In other words, the electric double layer, or the Debye length respectively, has to be sufficiently thick to provide a sufficient volume within particle attachment can take place.
- This further implies that solvents of low ionic strength and of low polarity might be favorable in order to keep the double layers surrounding the particle and substrate surface as thick as possible.
- Because of the small volume available for particle attraction - different to nanoxerography from nonpolar solvents - we suggest that a stable suspension is at least advantageous, if not strictly required, to guarantee for an adequate reproducibility of the final particle patterns.
3.3 Experimental details

3.3.1 Overview of suspensions

Nanoxerography was applied to five kinds of particles, including:

- Carboxylate functionalized polystyrene microspheres
  (50 nm and 100 nm nominal diameter)

- Carboxylate functionalized multi-walled carbon nanotubes
  (COOH-MWCNTs, 10 nm nominal diameter)

- Single-walled carbon nanotubes (SWCNTs, 1-2 nm nominal diameter)

- $\text{C}_{60}$ fullerenes ($\approx 1$ nm diameter)

- Gold colloid (5 nm nominal diameter)

The particles were suspended in IPA (Fluka, art. no. 59300, $\geq 99.8\%$) or in UHQ water (18 M$\Omega$-cm resistivity). From the dispersion point of view, the particles investigated can be classified into three groups (Figure 3.5):

(a) PS microspheres and functionalized MWCNTs form a stable suspension due to their carboxylate surface groups (-COOH). These functional groups are covalently, and thus irreversibly bound to the particles.

(b) Pristine SWCNTs and fullerenes are, due to their completely apolar surface chemistry, not directly suspendable in polar solvents. The lack of electrostatic repulsion forces leads to immediate attraction of the tubes or fullerenes to each other, ending up in growing clusters and fast coagulation. Stable suspensions of theses particles are hence achieved by the addition of a surfactant. In our experiments, we used the nonionic surfactants Syneronic NP10 (poly(ethylene glycol) nonylphenyl ether) for SWCNTs and Triton X-100 (poly(ethylene glycol)tert-octylphenyl ether) for the fullerenes to achieve stable suspensions in water. Nonionic rather than ionic surfactants (such as sodium dodecyl sulfate (SDS) for instance, an ionic surfactant very often used for SWCNT dispersions) were used due to the lower ionic strength resulting in the solvent.

(c) Similar to pristine carbon nanotubes and fullerenes, gold nanoparticles do not form stable suspensions in polar solvents without the assistance of functional surface groups. A widely used approach to disperse gold nanoparticles in an aqueous solvent is via a citrate ligand [Turkevich53].
### Figure 3.5: Schematic overview of particle suspensions.

The suspensions used are all based on an alcohol or aqueous solvent and can be classified into three groups: (a) PS microspheres and MWCNTs can be directly suspended due to their carboxyl surface groups. (b) SWCNTs and C_{60} fullerenes form stable suspensions via the attachment of nonionic surfactants to their surfaces. (c) Gold nanoparticles are stabilized in aqueous solution due to a citrate ligand.

A shared characteristic of all suspensions is that the particles exhibit a negative surface charge when dispersed in the polar solvent. The following subsections describe the detailed preparation of the suspensions and explain the origin of the negative charging.
Selective particle deposition

Carboxylate functionalized polystyrene microspheres

The purchased stock solutions of carboxylate polystyrene microspheres of 50 nm and 100 nm diameter (Polyscience Inc., Warrington, USA, art. no. 16661 and 16662) were diluted in pure water, pure IPA or mixed IPA/water solvents at dilution ratios of 1:20 (100 nm beads) and 1:50 (50 nm beads). Before development, the dispersions were sonicated in an ultrasonic cleaning bath (Branson Ultrasonic Bath, model 1210, Branson Ultrasonics) during 5 min. The negative surface charge on the microspheres arises from dissociation of carboxylic surface groups into COO$^-$ and H$^+$. 

Carboxylate functionalized MWCNTs

For the COOH-MWCNT experiments we used commercially available carboxylate functionalized multi-walled carbon nanotubes (Nanocyl S.A., Sambreville, Belgium, art. no. 3101) with a nominal diameter of 10 nm and lengths between 100 nm and 10 $\mu$m. The carboxylic surface groups are supposed to be linked to the nanotube at defect sites, distributed over the sidewalls and ends of the tube. The nanotubes were directly suspended in pure IPA or pure water solvents with a concentration of 0.2 mg/ml, if not otherwise mentioned, and sonicated using a high power ultrasonic probe (Branson Digital Sonifier, model 450, Branson Ultrasonics) for 10 min at a power level of 40 W, while keeping the dispersion in an ice-water bath. Dissociation of carboxylic surface groups leads to the negative surface charge on the nanotubes, equivalent to the PS microspheres.

Single-walled carbon nanotubes

SWCNTs (purchased from Cheap Tubes Inc., Brattleboro, VT, nominal diameter 1-2 nm) were dispersed in UHQ water containing 1-5 wt% Synperonic NP10 (Sigma-Aldrich). A stable dispersion was achieved by ultrasonication for 10 min using the Branson ultrasonic probe at a power level of 40 W, while keeping the dispersion in an ice-water bath. After sonication, the suspension was centrifuged at 75000g for 4h to separate the bundles, amorphous carbon, and residual catalytic material from the single tubes. The upper 90% of the supernatant was decanted for use. The resulting nanotube suspensions had a typical mass concentration of 20-25 mg/l. In some experiments, nanotube deposition from dispersions achieved by mere ultrasonication but no centrifugation was studied. If not otherwise mentioned, however, the centrifuged dispersions containing 5 wt% surfactant were used.
Compared to the PS sphere and MWCNT suspensions, the reason for a negative surface charge on pristine SWCNTs when suspended via a nonionic surfactant is less apparent. White et al. measured for Triton X-100-wrapped SWCNTs in UHQ water a negative zeta potential of -23 mV [White07]. Hence a negative zeta potential of Synperonic NP10-wrapped tubes is an obvious guess regarding the high chemical similarity between Triton X-100 and Synperonic NP10. Furthermore, we indeed suggest that the negative surface charge on the nanotubes arises from the Synperonic NP10 surfactant, which attaches to the nanotubes with its hydrophobic part (a nine-carbon alkyl chain linked to a benzene ring), exposing the polar head group (a poly(ethylene oxide)(PEO) chain, ∼ 10 units) to the aqueous solution. The benzene ring increases the binding of the surfactant to the nanotubes [Islam03]. The PEO chain is nonionic, though it is highly polar and known to solubilize metal cations [Cowie89]. The tendency of PEO to complex metal cations is attributed to ion-dipole interactions, arising between the metal ion and the free electron pairs of the oxygen atoms of the PEO chain. The polarity of the C-O bonds leads to local dipoles in the PEO molecule: electrons are pulled toward the oxygen atoms, inducing negative partial charges. These negative partial charges enable the PEO to form complexes with positive ions. In a polar environment, such as in water, the PEO molecules acquire a helical conformation with the hydrophilic oxygen atoms facing outside of the molecular chain toward the solution and the hydrophobic ethylene groups embedded inside of the molecule [Sui07]. We assume this mechanism is responsible for Coulomb attraction of SWCNTs in nanoxerography (section 3.4.1). The negative partial charges located at the oxygen atoms of the PEO chains face toward the water and can thus interact with positive trapped charges in the electret.

C$_{60}$ fullerenes

A stable suspension of C$_{60}$ aggregates was prepared by adding 10 wt% of the nonionic surfactant Triton X-100, which is nearly identical to Synperonic NP10; the two surfactants only differ by the length of the alkyl chain attached to the benzene group (Figure 3.5b). The C$_{60}$ suspension in UHQ water and Triton X-100 was achieved by a similar procedure as described by Beeby et al. [Beeby94]. In brief, 0.5 mg of C$_{60}$ (Sigma-Aldrich) was dissolved as a molecular solution in 2 ml of toluene. A concentrate of C$_{60}$ in surfactant was prepared by mixing the C$_{60}$ toluene solution with 0.5 g of pure Triton X-100 (Sigma-Aldrich) and subsequent evaporation of the toluene. The resulting transparent orange-colored suspension was further diluted with 5 ml of UHQ water under mild sonication. The final
Selective particle deposition

suspension contained 0.5 mg of C\textsubscript{60} in 5 ml of UHQ water with 10 wt\% of Triton X-100 surfactant. Again, we suggest that the surfactant is responsible for the negative charge on the fullerene aggregates, due to the same reason as explained for SWCNTs.

**Colloidal gold**

The colloidal gold suspension purchased from British Biocell International (5 nm nominal diameter, type GC5) was diluted 1:1 in UHQ water and stored in the refrigerator. The charge patterns were developed in this 4 °C cold suspension without further treatment. The negative surface charge imparted to the AuNPs is due to the strongly adsorbed citrate ions. In polar solvents, the OH-groups tend to dissociate into O\textsuperscript{-} and H\textsuperscript{+} (Figure 3.5c).

All used suspensions were kept in a refrigerator at 4 °C, and the charge patterns were developed in these 4 °C cold suspensions. All suspensions revealed stabilities up to weeks or even months.

### 3.3.2 Development

For charge pattern development, the sample was immersed in ca. 1 ml of suspension by means of pipetting the suspension onto the sample. Times of sample immersion in the particle suspension were usually between 5-10 sec. Following, the sample was directly rinsed in fresh IPA, without intermediate drying of the sample surface. IPA appeared a better suited rinsing solvent than water, because of easier wetting of the PMMA surface due to its lower surface tension. Sample rinsing usually lasted further 5-10 sec. After rinsing, the sample was dried in an air stream.

### 3.4 Results

#### 3.4.1 Coulomb attraction and pattern selectivity

For all dispersions, first experiments were performed on charge patterns consisting of positively as well as negatively charged regions, to identify whether particle deposition is dominated by Coulomb or by dipolar forces. Two such experimental results, one of SWCNTs and one of 5 nm AuNPs, are shown in Figures 3.6 and 3.7, respectively. Figures 3.6a and 3.6b display the surface potential (KFM)
and topography (AFM tapping mode) of a charge pattern consisting of five positively and five negatively charged parallel lines after sample development in the aqueous surfactant-based SWCNT suspension, rinsing and drying. The topography image shows that the carbon nanotubes clearly reproduce the charge patterns on the positively charged lines, forming well-defined stripes of nanotubes. The negatively charged lines in contrast as well as the background remain free of nanotubes. The result leads us to the assumption that the nanotubes carry a net negative surface charge and are attracted by means of Coulomb interaction. Since the negatively charged patterns yielded no attachment of nanotubes, dielectric attraction can be excluded as the predominant driving force.

![Figure 3.6](image_url)

**Figure 3.6: Coulomb attraction of SWCNTs to a pattern of five positively and five negatively charged lines.** (a) KFM image of the line pattern after development. Z-scale: -170 mV to +230 mV (400 mV range). (b) AFM topography image after development. The nanotubes deposit as clearly defined stripes exclusively onto the five positively charged lines. Z-scale: 11 nm. Scale bars: 2 µm.

An identical conclusion can be drawn for the citrate-stabilized AuNPs, as illustrated in Figure 3.7. A charge pattern consisting of positively and negatively charged "ETH" letters was recorded in KFM (a,c) and AFM tapping mode (b,d) immediately after charge writing and before development (a,b), and after development (c,d). Again, the AuNPs deposit exclusively onto the positively charged dots, whereas no specific attachment on the negatively charge dots can be observed.
The same experimental result, i.e. electrostatic attraction of the suspended particles exclusively onto positively charged patterns, was found for all other investigated suspensions, providing evidence that the deposition process is driven by Coulomb force in all suspensions discussed in this chapter, as listed in the experimental details section 3.3.

For nanoxerographic deposition of particles onto PMMA substrates from non-polar emulsions rather than polar suspensions, it was found that, in contrast
to our results, dipolar forces rather than Coulomb forces were dominating the attraction of the emulsion droplets towards the trapped surface charges [Naujoks05c]. However, the charge distributions in polar and nonpolar liquids are completely different. In a water-in-oil emulsion, the emulsified water droplets carry a positive surface charge, and the PMMA exhibits a positive surface potential, for instance. Nevertheless, the different results emphasize that pattern resolution and definition in nanoxerography is generally expected to depend on the balance of Coulomb and dipolar forces.

A second conclusion can be drawn from these first experiments: The particle patterns are of excellent selectivity, meaning that virtually no particles attach to the background around the pattern. The high selectivity presumably arises from the PMMA background acquiring a negative zeta potential when immersed into aqueous and alcohol-based solutions [Fa05]. The negative zeta potential apparently leads to repulsion of the negatively charged particles from the pristine PMMA surface.

The KFM images in Figure 3.7 further illustrate the stability of the charge patterns upon exposure to the AuNP suspension (5 sec), IPA rinsing (10 sec) and sample drying. The charge patterns are still clearly defined after immersion, though with a decay over 90%. The slightly higher charge decay compared to the exposure of positively charged patterns to pure UHQ water for 5 sec (78-86%, as was reported in section 2.6.1) can have several reasons, such as the two-step development-and-rinsing procedure, the higher ionic content of the AuNP suspension compared to UHQ water, or the fact that the positively charged patterns are covered by deposited AuNPs.

### 3.4.2 Influence of surface potential

To analyze the impact of the surface potential on particle arrangement, we investigated particle deposition onto line patterns consisting of a series of ten positively charged lines with surface potentials decreasing from line to line. A KFM image of such a typical charge pattern acquired immediately after charge writing is illustrated in Figure 3.8a. AFM topography images recorded after sample development show the achieved particle patterns of SWCNTs (Figure 3.8b and insets in Figure 3.9a,b), fullerene clusters (Figure 3.8c and insets in Figure 3.9c,d) and 5 nm AuNPs (Figure 3.8d and insets in Figure 3.9e,f). An obvious observation is that the width of the lines covered with particles decreases with decreasing
Figure 3.8: Influence of surface potential on particle deposition. SWCNTs, C$_{60}$-fullerenes and 5 nm AuNPs selectively deposited onto a pattern of ten parallel lines of decreasing surface potential. (a) Surface potential of a typical charge pattern, imaged by KFM immediately after charge writing. (b,c,d) AFM topography images of the SWCNT (b), C$_{60}$ (c) and AuNP (d) patterns after development. The indicated insets are displayed in Figure 3.9. Z-scales: (a) 6.3 V, (b) 12 nm, (c) 8 nm, (d) 19 nm. Scale bars: 1 µm.

Surface potential on all patterns. At a certain surface potential, the line width is reduced to a single string of particles, or a straight line of aligned tubes in the case of SWCNTs, see lines 9 and 10 on the SWCNT pattern (Figure 3.9b), line 8 on the C$_{60}$s (Figure 3.9d) and line 8 on the AuNP pattern (Figure 3.9f). The sur-
Figure 3.9: Insets of Figure 3.8. AFM topography images of SWCNTs (a,b), fullerene clusters (c,d) and 5 nm AuNPs (e,f). The inset in (b) indicates an individual SWCNT, the inset in (d) two small fullerene clusters. Z-scales: (a,b) 8 nm, (c,d) 6 nm, (e,f) 25 nm. Scale bars: 1 µm.

face potential of these lines, still considering the value recorded immediately after charge writing, was found to be around $\Delta V = 0.5-0.9$ V for all three suspensions. The broader stripes of higher surface potentials are homogeneously covered by nanotubes, fullerene clusters or AuNPs, respectively, and show a well-defined line width over their entire lengths. No or only sparse attachment of particles oc-
Selective particle deposition

curs on lines with lower surface potentials, suggesting the existence of a threshold surface potential for particle attraction in the aforementioned range of $\Delta V = 0.5-0.9$ V. Similar results, i.e. surface potential-dependent line widths of the particle deposits, were likewise achieved for carboxylate PS beads and carboxylate MWCNTs. According patterns of MWCNTs are illustrated in Figure 3.16, section 3.4.7, where the influence of the particle concentration in suspension was studied additionally.

Based on these experimental results, we can conclude that the magnitude of the surface potential generally provides strong process control over the achieved particle patterns.

An explanation for this surface potential-dependent line width of the particle patterns could be that the charge carriers diffuse laterally within the electret due to repulsion, as soon as a certain charge density is reached. Higher voltage amplitudes applied during charge writing inject more charges, leading to a wider lateral distribution of trapped charges than lower voltage amplitudes. Evidence for such behavior is found by observing that the charge patterns indeed exhibit local charge densities close to the maximum charge density in PMMA, as defined by the dielectric strength. Assuming a planar layer of charges on the PMMA surface and the corresponding counter charges at the interface between the p-doped silicon substrate and the electret, the latter consisting of

(a) 150 nm PMMA
(b) 200 nm SiO$_2$ and 50 nm PMMA

for the two substrates investigated (described in section 2.5.1), we calculate the charge density $\sigma$ via a simple parallel-plate capacitor model [Sessler87, Barry05] with one (a) or two (b) dielectrics, respectively, by

(a)

$$\sigma_{(a)} = \frac{\varepsilon_{\text{PMMA}} \cdot \Delta V}{d_{\text{PMMA(a)}}}$$

(b)

$$\sigma_{(b)} = \Delta V \cdot \left( \frac{d_{\text{PMMA(b)}}}{\varepsilon_{\text{PMMA}}} + \frac{d_{\text{SiO}_2}}{\varepsilon_{\text{SiO}_2}} \right)^{-1}.$$  

$\varepsilon_{\text{PMMA}} (\approx 2 \cdot 10^{-11} \text{ C V}^{-1} \text{ m}^{-1})$ and $\varepsilon_{\text{SiO}_2} (\approx 3.5 \cdot 10^{-11} \text{ C V}^{-1} \text{ m}^{-1})$ are the permittivities of PMMA and SiO$_2$, respectively, $d_{\text{PMMA(a)}}$ (150 nm), $d_{\text{PMMA(b)}}$ (50 nm) and
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d_{SiO_2} (200 nm) the respective layer thicknesses and \( \Delta V \) the voltage drop across the electret. A typical maximum surface potential change (line 1) recorded by KFM is \( \Delta V = 4 \) V. Due to the impact of the tip geometry and scan height on the KFM measurement, an approximately 2 times higher real value of \( \Delta V \) can be expected for surface potential features in the 300-400 nm size range [Jacobs98]. Hence, for \( \Delta V_{real} \approx 8 \) V, we obtain estimated charge densities of

(a) \( \sigma_{(a)} \approx 1.1 \cdot 10^{-3} \) C m\(^{-2}\)

(b) \( \sigma_{(b)} \approx 0.97 \cdot 10^{-3} \) C m\(^{-2}\).

The maximum charge density of PMMA in comparison, based on a dielectric strength of \( E_{PMMA} \approx 30 - 50 \) MV m\(^{-1}\), results in a charge density of

\[ \sigma = \epsilon_{PMMA}E_{PMMA} \approx 0.6 - 1 \cdot 10^{-3} \) C m\(^{-2}\).\]

The following subsection and the next section (3.4.3) discuss two particular aspects of the particle patterns illustrated in Figures 3.8, 3.9:

**Surface potential-dependent line widths and heights analyzed for a 5 nm AuNP pattern**

Figure 3.10 shows again the deposition of 5 nm AuNPs onto the same graded series of 10 positively charged lines as in Figure 3.8d. The local surface potential determined by KFM decreases from \( \Delta V = 3.9 \) V (line 1) down to \( \Delta V = 0.25 \) V (line 10) with respect to the background (Figure 3.10a). After KFM characterization, the sample was developed in the colloidal suspension, rinsed, dried and imaged in tapping mode (Figure 3.10b). Figure 3.10c illustrates averaged surface potential (dashed) and topography (solid) profiles calculated along the charge lines (Figure 3.10a) and AuNP deposits (Figure 3.10b), respectively. An obvious observation on the two profiles is that the gold structures are (i) centered on the peak potential and (ii) less wide than the surface potential measured by KFM. The full width at half maximum (FWHM) of the AuNP deposits ranges from 330 nm (3.9 V, line 1) to 50 nm (0.4 V, line 9), the values not corrected for tip radius. As explained in section 2.3, based on [Jacobs98], the surface potential measured by KFM is a weighted average of the potential at the tip location and the surrounding potential distribution and further depends on the tip geometry. Hence the charge patterns are likely to be narrower. Whereas the magnitude of the surface potential determines the width of the AuNP deposits, it has much less influence...
Figure 3.10: AuNPs selectively deposited onto a pattern of 10 parallel lines. (a) KFM image acquired immediately after charge writing. The values indicate the peak surface potential of the line with reference to the background. (b) AFM topography image of the AuNP pattern after development. Z-scale: 19 nm. (c) Profiles illustrating average topography (solid) and surface potential (dashed) across the line structures. The FWHM values of the AuNP deposits, averaged along the lines and not corrected for tip radius, range between 330 nm (line 1) and 50 nm (line 9). Scale bars: 1 µm.
on their density, as can be derived from the similar height values of lines 1 to 7. The densely covered lines 1-7 in Figure 3.10b all have an average height of $\approx 8$ nm, slightly higher than the nominal diameter of the AuNPs (5 nm). Some stacking can be discerned in the higher magnification images (Figures 3.9e, f). We further suggest that remained citrate compounds have additional influence on the height value. Lines 8 to 10 exhibit decreasing height values due to increasingly discontinuous particle attachment.

### 3.4.3 Differences in deposition density and pattern definition

Comparison of the patterns of SWCNTs (Figure 3.8b, insets in Figures 3.9a,b), fullerene molecules (Figure 3.8c, insets in Figures 3.9c,d) and AuNPs (Figure 3.8d, insets in Figures 3.9e,f) reveals that the AuNPs deposit more close-packed onto the charge lines than the SWCNTs and fullerene clusters, leading to a clearly higher pattern definition of the AuNP pattern. We attribute this effect to the involved stabilizing agents, i.e. the citrate ligand (AuNPs) and the surfactants Synperonic NP10 (SWCNTs) and Triton X-100 ($C_{60}$ clusters). First of all, a far lower concentration of citric acid (<0.02%) is present in the gold colloid, compared to the surfactant concentrations (5 wt% Synperonic NP10 and 10 wt% Triton X-100) in the SWCNT and fullerene suspensions, respectively. Moreover, the surfactant concentrations used are well above the so-called critical micelle concentrations (CMC) of Synperonic NP10 and Triton X-100, the CMC in both cases being around 0.015 wt% [White07]. Hence, it is very likely that different and not well-defined shapes of surfactant micelles are present both in the suspension as well as formed on the surface of the nanotubes and $C_{60}$ clusters. Experiments with nanotubes where the rinsing step was skipped, as will be shown and discussed in section 3.4.6, revealed up to 70 nm thick surfactant coatings, hindering high-density deposition.

### 3.4.4 Towards single particle accuracy and networks of individual SWCNTs

Based on the high pattern definition and the sensitive control provided by the local surface potential, experienced on the larger line patterns as presented in the foregoing section 3.4.2, the creation of finer patterns such as the assembly of individual or small numbers of particles into arrays or the creation of SWCNT networks was investigated.
Individual 100 nm PS spheres deposited onto separated charge dots

The positioning of single beads was investigated on an array of 2 \( \mu \)m-separated charge dots written into the PMMA substrate. Such an array of positive charge dots is shown in the KFM image in Figure 3.11a, where each dot was generated by a single 70 V voltage pulse. Figure 3.11b shows the topography of the same area recorded after development in a 50%/50% IPA/UHQ-water suspension containing 100 nm diameter carboxylate PS beads. The image reveals that the charge dot array was completely reproduced by beads trapped on the single dots. Mainly single beads are attached to the charge dots (Figure 3.11b and inset), with some pairs being present. The result can be seen as a first approach proving the capability of nanoxerography to guide single nanoscale objects to desired locations.

High-density gold nanoparticle arrays

In this section, investigations on the creation of even finer patterns such as the assembly of individual 5 nm AuNPs into arrays are presented. Figure 3.12a shows the KFM image of a typical array of positive charges with a pitch of \( \approx 250 \) nm. Figures 3.12b and 3.12c document the selective and very accurate attachment of AuNPs to two such dot arrays differing in the amount of charge injected. Both charge patterns were written onto the same substrate and developed simultaneously, as described in the experimental section. Single particles and small clusters assemble in the center of the charge dots. Histogram analysis of the number of particles assembled per charge dot (add-ons to Figures 3.12b and 3.12c) reveals deposition patterns that depend on the surface potential. For a surface potential of \( \Delta V = 0.5 \) V above background (Figure 3.12b) charge dots predominantly attract one particle and 95% of the dots (evaluated over a 16 x 16 array) are covered by 1 or 2 particles. For a surface potential of \( \Delta V = 0.8 \) V above background (Figure 3.12c) the particle distribution gets wider, on average 3 particles assemble per dot and 90% of the dots are covered by 2, 3 or 4 particles.

SWCNTs forming networks and curved geometries

Although carbon nanotubes are known to have considerable potential as key components in future nanotechnological devices, such as field-effect transistors [Bachtold01] or sensors [Kong00, Stampfer07], the integration of individual carbon nanotubes into devices still presents a challenging issue. Current approaches include catalyst-pattern-directed growth [Fan99], electric-field-induced alignment [Yamamoto98, Krupke03], flow cell methods [Xin04], and alignment based on
Figure 3.11: Attachment of single 100 nm carboxylate polystyrene beads onto positive charge dots from an IPA/UHQ-water suspensions onto PMMA. (a) Surface potential of charge dot array imaged in KFM directly after charge writing. Z-scale: 2 V. (b) AFM topography images of the same area after development. The deposited beads completely reproduce the charge template. The profile plot illustrates two single beads attached to the charge template on individual charge dots. Z-scale: 100 nm. Scale bars: 2 µm.

self-assembled monolayers [Im06]. However, the applicability is often limited to high temperature conditions or only one available direction of alignment. The advantage of nanoxerography may be that flexible geometries of nanotube structures can be created on surfaces under normal laboratory conditions.

Based on the observation that SWCNTs individually align along charge lines of $\Delta V = 0.5-0.9$ V surface potential (section 3.4.2), we explored the creation of small nanotube networks. The attachment of CNTs to two different geometries, a
Figure 3.12: High-density AuNP arrays. (a) Surface potential of a typical charge dot array with ≈ 250 nm lateral dot intervals, imaged by KFM immediately after charge writing. Z-scale: 530 mV. (b) and (c) AFM topography images of AuNPs attached to charge dot arrays with an initial peak surface potential of $\Delta V = 0.5$ V (b) and $\Delta V = 0.8$ V (c) above the background. Z-scale: 16 nm. Histogram insets illustrate particle density per charge dot, evaluated over a 16 x 16 dot array. Scale bars: 500 nm.
straight network and a sine-shaped pattern, is illustrated in Figure 3.13.

**Figure 3.13:** Small CNT networks assembled from individual SWCNTs and SWCNT bundles. (a) The straight perpendicular nanotube network shows locations of crossing nanotubes (A), nanotube interconnections along straight lines (B), but also interrupts (C). The insert illustrates the profile across a well-aligned SWCNT. Z-scale: 6 nm. (b) The sine-shaped pattern features regions of CNTs well aligned to the pattern (A), as well as regions where nanotubes shear out of the intended directions (B). The inset is a profile plot across a SWCNT bundle of 4.1 nm diameter and an individual SWCNT. Z-scale: 11 nm. Scale bars: 1.5 µm.

The suspension for the rectangular network shown in Figure 3.13a was prepared as described in the experimental section, including centrifugation. The nanotube deposition was achieved in one development step. The rectangular network is predominantly composed of lines of one single SWCNT or one SWCNT bundle in width. At some nodes, nanotubes or nanotube bundles are deposited onto each other, forming a right angle crossing (locations (A) in Figure 3.13a). At other locations, nanotubes or nanotube bundles appear to form interconnections along straight lines (B). Apparently, the negative charge on the nanotubes is too weak to completely prevent nanotube deposition onto already deposited nanotubes. Nevertheless, to build an intact complete SWCNT network, further improvement would be needed to overcome the number of interrupts (C). Depositing the perpendicular tube lines in two sequential process steps may be a possibility to further improve pattern reproduction.
The suspension used for the development of the sinusoidal pattern shown in Figure 3.13b was prepared by dispersing 1 mg of raw nanotube material in a 10 ml solution of 5 wt% Synperonic NP10 surfactant. After sonication, the ice-cooled suspension was used immediately, without further centrifugation. Hence, the fraction of long nanotubes is higher in these suspensions, though they also contain more bundles and entangled nanotubes than the centrifuged ones. As the sinusoidal pattern emphasizes, the nanoxerography method is capable of attaching SWCNTs to curved geometries to a certain extent.

The sine pattern features regions where the charge pattern is clearly reproduced (location A), as well as regions where nanotubes shear out of the intended direction of alignment (B). While single CNTs may be easily aligned on the pattern via the electrostatic forces from the charge patterns, a substantially higher force seems to be required to overcome the stiffness of nanotube bundles. A related, interesting study on bending of carbon nanotubes by Zou et al. showed the assembly of SWCNTs bent into rings of different diameters down to 200 nm and estimated the interaction energy between tube and substrate required for nanotube bending [Zou07].

From the results presented in this section we conclude that the magnitude of the surface potential provides a high degree of process control that has not been reported before.

### 3.4.5 Influence of surfactant concentration and centrifugation on SWCNT deposition characteristics

SWCNTs are unique nanoscale components, known to exhibit excellent mechanical, electrical, thermal and optical properties, thus offering potential promise for diverse novel applications. Although much progress has been made in the handling of SWCNTs, a widely recognized bottleneck towards application still presents the purity and dispersion of SWCNTs. While chemical functionalization has been found to deteriorate the intrinsic properties of SWCNTs [Garg98], physical approaches using surfactants have proven capable of debundling SWCNT bundles and stabilizing individual tubes while maintaining the SWCNT integrity [O’Connell02]. A full understanding of the fundamental mechanisms for dispersing carbon nanotubes with surfactants is still lacking. Moreover, the desired consistency of a SWCNT dispersion often depends on the final application. While
high-density deposition of SWCNT material may be the task for bulk applications such as SWCNT thin films of high conductivity [Ng08], for instance, individually dispersed tubes of a certain length are required to build up devices where individual SWCNT act as core components, such as in SWCNT transistors [Bachtold01].

In our experiments, various dispersions of Synperonic NP10-wrapped SWCNTs were under investigation for nanoxerographic patterning. The main differences were the amount of surfactant used, as well as whether centrifugation was involved or not. The two examples shown in Figure 3.14a,b (first example) and Figure 3.14c,d (second example) give an idea of different deposition characteristics of SWCNTs onto charge patterns, dependent on these two criteria.

**Surfactant concentration**

Figure 3.14a,b are two AFM topography images of SWCNTs attached to identical charge patterns, consisting of a zig-zag-shaped positively charged line and a sine-shaped positively charged line, well recognizable especially in Figure 3.14a where the charge pattern is precisely reproduced by small SWCNT deposits. The SWCNT suspensions contained 1 wt% Synperonic NP10 surfactant in the case of Figure 3.14a and 5 wt% in the case of Figure 3.14b. They were prepared by dispersing 1 mg of raw nanotube material in a 10 ml solution of 1 wt% or 5 wt% surfactant, respectively, by ultrasonication for 10 min using an ultrasonic probe at a power level of 40 W, while keeping the dispersion in an ice-water bath.

Whereas primarily single tubes and tube bundles aligned along the charged lines in Figure 3.14b - with some larger bundles and longer tubes shearing out of the intended direction of alignment - the charged lines in Figure 3.14a are precisely reproduced by much shorter tubes. It is very likely that 1 wt% yields a suspension with (i) longer and thicker, maybe entangled bundles of tubes, as well as (ii) individually and uniformly suspended, very short tubes. Whereas the short tubes are deposited, the larger bundles are too large to disperse uniformly, and if not in close proximity to the charge pattern, are not attracted. 5 wt% in contrast seems in our case the ideal amount of surfactant to achieve a stable suspension primarily consisting of individually suspended, long tubes or thin tube bundles.
Figure 3.14: Influence of surfactant concentration and centrifugation on SWCNT deposition. (a,b) AFM topography images of SWCNTs, dispersed in 1 wt% (a) and a 5 wt% (b) Synperonic NP10, deposited onto a charge pattern consisting of a zig-zag-shaped positively charged line and a sine-shaped positively charged line. (c,d) AFM topography images of SWCNTs dispersed in 5 wt% Synperonic NP10 by mere ultrasonication (c) or ultrasonication and subsequent centrifugation (d), respectively, deposited onto a typical charge line pattern as reported previously. Z-scales: (a) 15 nm, (b) 10 nm, (c) 20 nm, (d) 10 nm. Scale bars: 2 µm.

Centrifugation

Figure 3.14c,d show SWCNTs deposited onto a charge pattern consisting of a series of charge lines of decreasing surface potential, similar to the charge patterns...
Results

reported earlier in this chapter, in section 3.4.2. The two resulting SWCNT patterns illustratively reveal different consistencies of the involved dispersions. Both dispersions contained 5 wt% of Synperonic NP10. The dispersion used in Figure 3.14c was prepared by 1 mg of raw SWCNTs directly dispersed in 10 ml UHQ water with 5 wt% of surfactant by ultrasonication for 10 min using the ultrasonic probe. This dispersion was identical to the dispersion in Figure 3.14b. The initial preparation steps for the dispersion used in Figure 3.14d were the same as in (c). Subsequently, the dispersion was centrifuged at 75 000g for 4h, and the 90% of the supernatant was decanted for use.

Hence, while the dispersion for Figure 3.14c contained besides individually dispersed tubes a substantial portion of thin, but entangled tube bundles, primarily single tubes and small, not entangled SWCNT bundles were present in the dispersion of Figure 3.14d.

The results elucidate that the dispersion and the achieved pattern quality are unavoidably accompanying each other. As the improvement of SWCNT dispersions is an own extensive research field and was not the main task in our studies, one can suggest that ‘real’, connected networks of individual SWCNT may be assembled by nanoxerography once the dispersion quality allows therefor.

3.4.6 Removal of SWCNT-attached surfactant

Regarding devices built of nanotubes, like nanotube transistors, it is a known issue that surfactant residues can influence the carbon nanotube device characteristics [Li06]. In this context, we show in this section that most of the Synperonic NP10 surfactant is washed away during generous rinsing of the sample in IPA after development, as images before rinsing (Figures 3.15a and 3.15b) and after rinsing (Figures 3.15c and 3.15d) illustrate. Again, ten parallel charge lines were written with decreasing AFM tip voltage, resulting in lines with decreasing surface potential peaks between $\Delta V = 2.3$ V and $\Delta V = 0.5$ V. A stable nanotube dispersion was achieved by sonicating 1 mg of raw nanotube material in a 10 ml solution of 0.3 wt% Synperonic NP10 surfactant for 10 min. After sample development in the ice-cold suspension for 30 s, the sample was immediately dried in an air stream, without rinsing. The charge patterns are weakly recognizable in the KFM image, with maximal surface potential values of approximately $\Delta V = 12$ mV (Figure 3.15a). However, the pattern is visible in the topography image: surfactant-nanotube agglomerates in the range of 70 nm in height line up atop the charge pattern. Vibrations of the cantilever while scanning over the sample
are a hint for a soft material. An increased background roughness and a weak contrast in surface potential suggest that the sample is completely covered by a thick surfactant layer.

**Figure 3.15:** Selective attachment of carbon nanotubes before and after rinsing the sample in IPA. All four images show the same section. KFM (a) and topography image (b) before rinsing. The sample is completely covered by a layer of surfactant. The insert illustrates the profile across a surfactant structure. KFM (c) and topography image (d) after rinsing. The inserts are profile plots across a SWCNT bundle of 9.4 nm diameter and an individual SWCNT. Z-scales: (a) 27 mV, (b) 81 nm, (c) 192 mV, (d) 7 nm. Scale bars: 3 µm.

In a second step, the analyzed sample was generously rinsed in IPA for 30 s and dried again in an air stream. The nanotube pattern can now clearly be re-
solved on the PMMA surface, similar to the images obtained after deposition, rinsing and drying. Regarding the increased surface potential difference of $\Delta V \leq 60$ mV in the KFM image (Figure 3.15c), it seems that the surfactant layer was mostly washed away. The AFM topography image (Figure 3.15d) shows the typical background structure of PMMA with a roughness in the range of 1 nm. The carbon nanotubes on the patterns have heights of 1-2 nm for single tubes and up to 10 nm for nanotube bundles, indicating that most of the surfactant was removed by the IPA rinsing.

Due to the chemical similarity of Synperonic NP10 and Triton X-100, we expect Triton X-100 to be removed from the sample by the IPA rinsing procedure to a similar extent as demonstrated for Synperonic NP10. However, we have still not verified that our samples are completely free of residual surfactant molecules after rinsing, so this issue would need further investigation.

### 3.4.7 Additional observations

#### Influence of particle concentration in suspension

The particle concentration in suspension obviously has an influence on the deposition characteristics of the particles. Tuning the particle concentration was found to be fundamental to achieve an ideal pattern definition for all examined suspensions. Lower concentrations than the ‘ideal’ generally led to a lower deposition density and less uniform attachment on the predefined charge patterns. For ‘too high’ concentrations, a reasonable charge pattern reproduction, but a loss in selectivity due to an increased number of particles distributed over the background was usually detected.

Figure 3.16 illustrates an example of COOH-MWCNTs deposited onto positively charged lines from IPA suspensions containing 0.02 mg/ml (a), 0.2 mg/ml (b) and 2.0 mg/ml (c) nanotubes. Ten charge lines of decreasing surface potential served as charge templates again. For the highest dilution (Figure 3.16a), only sparse nanotube attachment and only on the lines of higher surface potential occurred, providing evidence that a certain concentration is needed to obtain continuous stripes and strings of tubes down to surface potentials of $\Delta V = 0.5-0.9$ V, as was observed in section 3.4.2 for SWCNTs, fullerene clusters and AuNPs. Such is the case for the ‘ideal’ concentration of 0.2 mg/ml (Figure 3.16b), where the tube deposits are stripes of decreasing width, reduced to a single string of tubes.
Selective particle deposition at line 9 ($\Delta V = 0.91$ V). Although the charge pattern is clearly reproduced by nanotubes deposited from 2.0 mg/ml, apparently more tube material deposited onto the charge lines as well as in the background around the pattern and between the lines make these structures appear more fuzzy.

![Figure 3.16: Influence of MWCNT concentration in suspension on deposition characteristics.](image)

**Figure 3.16: Influence of MWCNT concentration in suspension on deposition characteristics.** AFM topography images of COOH-MWCNTs deposited onto ten positively charged lines of decreasing surface potential from IPA suspensions containing 0.02 mg/ml (a), 0.2 mg/ml (b) and 2.0 mg/ml nanotubes. Z-scales: 15 nm. Scale bars: 2 $\mu$m.

**Influence of suspension temperature**

Based on our experimental results, we assume that the suspension temperature generally constitutes an important factor influencing pattern definition. Denser and more regular deposition was achieved when using ice-cold suspensions rather than solutions kept at room temperature. The improvement can be explained by reduced kinetic energy and correspondingly reduced Brownian motion in the solvent.

The diffusion of particles due to Brownian motion is described by the diffusion coefficient $D$, which is for spherical particles of radius $R$ according to the Stokes-Einstein relation.
\[ D = \frac{k_B T}{6\pi \eta R}. \]  

\( k_B \) is Boltzmann’s constant, \( T \) is the temperature and \( \eta \) the dynamic viscosity of the solvent. The average distance \( d \) that a particle covers in time \( t \) is [Hiemenz97]

\[ d = \sqrt{6Dt}. \]

Thus, assuming spherical particles of diameters between 2 and 100 nm as an approximation for our dispersions and IPA (\( \eta \approx 3.9 \text{ mPa}\cdot\text{s at 4 °C}, \eta \approx 2.0 \text{ mPa}\cdot\text{s at 25 °C} \)) and water (\( \eta \approx 1.5 \text{ mPa}\cdot\text{s at 4 °C}, \eta \approx 0.9 \text{ mPa}\cdot\text{s at 25 °C} \)) as solvents, the particles diffuse within 1 sec over a distance of

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<th>IPA 2 nm</th>
<th>IPA 100 nm</th>
<th>water 2 nm</th>
<th>water 100 nm</th>
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<tr>
<td>4 °C</td>
<td>17.6 µm</td>
<td>2.5 µm</td>
<td>28.5 µm</td>
<td>4.0 µm</td>
</tr>
<tr>
<td>25 °C</td>
<td>25.6 µm</td>
<td>3.6 µm</td>
<td>38.1 µm</td>
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Notably, different to the Debye length - which is in an ideal case around 1 µm in water and 5 µm in IPA, as was discussed in section 3.2.2 - the diffusion distances (covered per sec) are larger in water than in IPA.

The diffusion velocities further indicate that lower suspension temperatures are particularly important for small particle diameters.

**Impact of double layer thickness**

When investigating nanoxerographic printing of 50 nm and 100 nm PS beads from water, IPA and mixtures of water/IPA suspensions, we observed different deposition behavior that presumably can be explained by the impact of the double layer thickness. The charge patterns used were positively charged large-scale cross patterns of high surface potential differences in the range of \( \Delta V = 6-10 \text{ V} \). While selective particle deposition onto the charge patterns occurred for 50 nm PS spheres suspended in pure water, no selective deposition at all could be found for 100 nm, suspended in pure water as well. From pure IPA suspensions in contrast, both particle diameters yielded selective attachment to the charge patterns. It was found that the threshold regarding selective particle attachment of 100 nm PS beads was in the range of 40%/60% IPA/water solvent mixtures.
The results make sense regarding the Debye length being expected to be larger in IPA than in water. For the smaller fullerenes, nanotubes and AuNPs, no limitations imparted by the double layer thickness could be observed. However, the phenomena mentioned for the bigger particles show that nanoxerography may come to its limits for solvents of higher ionic strength as well as particles of increased diameter. As one consequence, improving a suspension by pH adjustments, which always entails an increase in ionic strength, is challenging.

Reproducibility of particle deposition

Systematic reproducibility studies have not been performed in this thesis. Still we observed within a pattern or within several patterns on the same sample and developed in the same run a generally high reproducibility regarding the reproduction of the charge patterns by the deposited particles. From this point of view one can state that positive charge patterns written into PMMA substrates, which acquire a negative zeta potential in the employed solvents, present effective electrostatic templates for the directed assembly of particles. For independent development runs, unexpected experimental results occurred occasionally. Unexpected can best be characterized by means of shifts to the left or to the right within Figure 3.16, illustrating the influence of concentration on deposition behavior. In other words, it was most often observed that an ideal concentration led either to only sparse deposition or to ample deposition with increased background coverage.

Though, the reproducibility was still high enough to systematically study the influence of the surface potential and the creation of single-particle assemblies, the influence of the amount of surfactant, centrifugation or the particle concentration in suspension.

We assume that reproducibility is primarily limited by the simple and manually performed immersion, rinsing and drying procedures, providing relatively low process control. It can be expected that, due to the wide range of forces acting on the particles in such plain ‘beaker chemistry’, undesired attachment of particles in the uncharged background as well as undesired detachment of particles already deposited on charge patterns easily occurs. Remedy could for example be found in microfluidic-like setups or similar setups as used for forming colloidal crystals to stabilize the process environment during development.
Chapter 4

PMMA removal and catalysis of silicon nanowires from assembled gold nanoparticle structures

Single and high-density nanoparticle structures are, as aforementioned, desired for many applications in nanotechnology, including bio assays [Jensen07] and biosensors [Staedler07, Sannomiya09], molecular electronics [Dadosh05], nano optics [deWaele07] or catalytic processes [Schmid08]. However, in addition to accurate positioning an essential requirement for a wide applicability is that the particles retain functionality during the assembly process which in turn must be compatible with later process steps. We show in this chapter, on the example of AuNP line patterns, how the structures assembled on the thin PMMA electret layer can be transferred vertically down onto the underlying SiO$_2$ substrate (Figure 4.1a,b). Vertical transfer of structures assembled by nanoxerography broadens the range of applicable substrate materials much beyond electrets. In addition, we demonstrate retained catalytic activity of the AuNPs by growing silicon nanowires (SiNWs) from the transferred line structures (Figure 4.1c).

4.1 Experimental details

PMMA removal

Thermal decomposition of 50 nm thick PMMA layers was accomplished by oxidation in air at 700-800 °C. To this end, the sample was placed onto a ceramic plate heated from underneath by a gas burner. The procedure lasted ca. 1 min, and was stopped as soon as the surface color changed to that of pristine SiO$_2$, 

PMMA removal and catalysis of SiNWs from assembled AuNP structures

(a) (b) (c)

Figure 4.1: Scheme illustrating PMMA removal and SiNW growth. (a) AuNP patterns created by nanoxerography. (b) The 50 nm thick PMMA layer is removed by oxidation in air, leading to vertical transfer of the AuNP patterns onto the underlying SiO$_2$ substrate. (c) SiNWs are grown from the AuNPs serving as catalytic sites in a VLS process.

indicating complete PMMA removal.

Silicon nanowire growth

SiNWs were grown in a vapor-liquid-solid (VLS) process in a low pressure chemical vapor deposition (LPCVD) hot wall quartz tube furnace. Silane (SiH$_4$) was used as Si source diluted in Hydrogen (H$_2$) in a 1:4 mixture. The total gas pressure was 5 mbar and the gas flow was 250 ccm in combination with nitrogen (N$_2$) for the purge cycles. The process temperature ranged between 450$^\circ$C and 500$^\circ$C. The structures were metal coated for scanning electron microscopy (SEM) inspection with 2 nm Pt-Pd.

4.2 Results

Vertical transfer is accomplished by thermal decomposition of the PMMA electret layer in ambient air at 700-800$^\circ$C, as described in the experimental details section above. Thermal oxidation of PMMA requires temperatures of 300-400$^\circ$C [Kashiwagi86] and citrate is decomposing at even lower temperatures. Hence we assume that the line structures transferred onto the SiO$_2$ surface primarily consist of gold nanocrystals. AFM topography images before (Figure 4.2a) and after decomposition (Figure 4.2b) of the 50 nm thick PMMA layer document that the line structures are preserved during oxidation. The simple thermal decomposition of the PMMA layer results in some loss of pattern selectivity and fidelity, as indicated by a higher number of particles distributed over the background and a
Results

Figure 4.2: PMMA removal by oxidation in air for subsequent SiNW growth. (a,b) AFM topography of the AuNP line patterns before (a) and after (b) thermal decomposition of the 50 nm thick PMMA layer. (c,d) Profile plots across the line patterns in (a) and (b) illustrate a decrease in height and broadening of the particle lines upon vertical transfer. Z-scales: 10 nm. Scale bars: 500 nm.

slight line broadening accompanied by line heights decreasing from 10-12 nm to 6-8 nm (Figures 4.2c and 4.2d).

Silicon nanowires are subsequently grown in a VLS process, using the AuNP lines as catalytic sites. The VLS process described in the experimental section below is based on a widely known protocol introduced by Wagner and Ellis in 1964 [Wagner64] that involves Au particles as catalysts for the anisotropic crystal growth. The applied growth protocol was optimized for AuNPs larger than 5 nm, with highest yield for 40 nm particles. Yet Figures 4.3a,b clearly demonstrate that almost all 5 nm AuNPs initiated nanowire growth, indicating the undisturbed functionality of the deposited AuNPs for the VLS process. Samples containing line patterns of 40 nm AuNPs, kept in the same VLS run as the 5 nm structures shown in Figures 4.3a,b were completely overgrown by nanowires, catalyzed from AuNPs loosely distributed over the background (Figures 4.3c,d). The line patterns were impossible to relocalize on these samples. Nanowires appearing thicker and longer in Figure 4.3a,b might have grown from larger AuNP clusters fused together during elevated process temperatures. 5 nm AuNPs start melting in the temperature range of 800°C [Buffat76].

The obtained results, in their current state of progress, merely present a proof of principle, documenting a possible route of electret removal as well as a first
Figure 4.3: SiNW grown from line patterns of AuNPs. The catalytic activity of the AuNPs is preserved during nanoxerography and subsequent vertical transfer to the SiO$_2$ substrate by thermal decomposition of the PMMA electret layer. (a,b) SEM images of SiNWs grown by a VLS process from the 5 nm AuNP line patterns, vertically transferred onto the SiO$_2$ substrate. (b) Zoom into the section marked in (a). (c,d) SEM images of SiNWs grown during the same VLS process as in (a,b) from 40 nm AuNP line patterns, demonstrating higher yield for the larger AuNPs. The line patterns could not be relocalized on the sample overgrown by nanowires. (d) Zoom into the section marked in (c). Scale bars: (a,b) 500 nm, (c) 10 µm, (d) 4 µm.

catalytic use of nanoxerography-assembled nanoparticle patterns. However, in the context of process control achieved in silicon nanowire growth from gold nanoparticles, our approach does not keep up with already established methods such as epitaxial nanowire growth from gold clusters [Schubert04] or evaporated gold disks [Schmid08].

The results presented in this chapter were achieved in cooperation with Joerg Albuschies (Biologically oriented materials group, ETH Zurich), who performed the VLS growth process and did the SEM imaging.
Chapter 5

Selective deposition of polyelectrolytes

In chapter 3, nanoxerography was demonstrated on particles and molecules forming stable suspensions due to covalently bound surface groups, or attached surfactants or ligands, whose net or partial charges turned out to be responsible for electrostatic attraction onto the charge patterns as well. However, nanoxerography might further be investigated as a tool for direct patterning of ionic molecules, yielding patterned molecular layers.

In this chapter first attempts of nanoxerography-based selective attachment of polyelectrolytes are presented and discussed. A general, brief introduction into polyelectrolytes and multilayer thin films is first given as a background.

5.1 Polyelectrolytes and multilayer thin films

Polyelectrolytes are polymers whose repeating units bear an electrolyte group. These groups dissociate in polar solution, leading to net charges in the molecular chains. Polyelectrolytes can be divided into weak and strong types. Whereas a strong polyelectrolyte dissociates completely in solution for most reasonable pH values, a weak polyelectrolyte is most often partially dissociated, and their fractional charge can be modified by changing the solution pH, counterion concentration, or ionic strength. Polyelectrolytes are commonly present in soft matter systems, where, due to their charged molecular chains, they play a key role in determining structure, stability and the interactions of the molecular assemblies. They are for example used to modify flow and stability properties of aqueous solutions and gels, as thickeners, emulsifiers, conditioners or flocculants. Many
biological molecules, such as polypeptides and DNA, are polyelectrolytes as well.

Polyelectrolytes belong to the most important components for the formation of new types of materials known as multilayer thin films. By the so-called Layer-by-layer (LbL) deposition technique, introduced by Decher in 1991 [Decher91], multilayer thin films are built up by the adsorption of a single species in each adsorption step, yielding a multilayer thin film after a defined layer deposition sequence. In the LbL deposition of pure polyelectrolyte multilayers (PEMs), a suitable growth substrate with a certain surface charge is dipped back and forth between dilute baths of positively and negatively charged polyelectrolyte solutions [Decher97]. During each dip a thin film of polyelectrolyte is adsorbed and the surface charge is reversed, allowing the gradual and controlled build-up of electrostatically cross-linked films of polycation-polyanion layers. The technique allows for a thickness control of such films down to the single nanometer scale.

However, the general term of multilayer thin films is a wider concept. Besides polyelectrolytes, various multilayer composites are used for the build-up of multilayers, including colloids [Hattori01], biomacromolecules [Elbert99, Lang99] or inorganic compounds [Ito01, Lutkenhaus07]. Furthermore, there are many interaction types that have been used successfully for multilayer deposition, including donor-acceptor interaction [Shimazaki01], hydrogen bonding [Hao00], covalent bonds [Fang97] or specific recognition [He94].

Of course it is attractive to create order not only along the layer normal but also within the plane of the film. Lateral structuring of polyelectrolyte multilayer systems at the micro- or nanoscale opens new opportunities for the application of conducting and conjugated polymers as electronic and optical devices, for instance. Examples are polymer light-emitting diodes (LEDs) [Ho00], patterned conducting polymer films [Smith06] or organic thin film transistors [Stricker07]. In a more immediate context, polyelectrolyte patterns can be used as templates for further material deposition, such as colloids [Kim07] or biomaterials [Yoo08].

Various approaches targeting lateral structuring of polyelectrolyte surfaces via directed assembly are based on self-assembled monolayers. Microcontact printing often serves as the patterning tool to define alternating regions on the substrate that allow or resist the deposition of charged polymers. Regions for deposition are for example designed by carboxylic acid, sulfonate or amino functionalized monolayer surfaces, whereas ethylene glycol (EG) functionalized surfaces discourage polyanion deposition [Clark97a, Clark97b, Papra01, Alvarez09].
Preliminary considerations

The EG system provides excellent prevention of both polyanion and polycation adsorption over several adsorption cycles, and thus allows to build up multilayer thin films exclusively on the predefined, non-EG-coated regions.

5.2 Preliminary considerations

In our experiments we explore the possibility to use charge patterns written into electrets for the selective deposition of polyelectrolytes. The idea of nanoxerography-based creation of polyelectrolyte patterns presents a simple and fast approach, and based on the general concept of electrostatic attraction or repulsion, may have the potential to be applied to a broad range of polyelectrolytes in a similar way. An obvious challenge however presents the non-permanent patterning. In contrast to the SAM-based templates, the trapped charges decay during the immersion in the polyelectrolyte solution. The fact that the ionic strength in polyelectrolyte solutions is, due to the polyelectrolytes themselves, far higher than in the particle and molecule dispersions discussed in chapter 3, may present a further difficulty for the implementation of this approach.

As a starting point, we choose PMMA as electret, mainly because of its so far successful use for nanoxerographic patterning from polar media. Although pretreated and thus either positively [Decher92] or negatively [Cho01] charged SiO$_2$ surfaces are the most common substrates for the build-up of PEMs, polymers including PMMA were also reported to be suited for polyelectrolyte deposition [Delcorte97]. On the uncharged polymer support, the adsorption of the first polyanion or polycation layer is due to polar or to hydrophobic interactions, respectively. We investigate the selective deposition of the anionic poly(styrene sulfonate) (PSS) and the cationic poly(allylamine hydrochloride) (PAH). Figure 5.1 depicts the chemical structures of PSS and PAH. PSS/PAH multilayer systems belong to the most extensively researched PEMs. The strong polyanion PSS remains fully charged throughout a large pH range. PAH is a weak polyelectrolyte whose allyl hydrochloride group can be charged positively at low and medium pH values. A high pH leads to the dissociation of H$^+$ ions and the formation of an uncharged amine group. The acid dissociation constant ($pK_a$) of PAH in bulk solution is around pH 10 [Yoo98].

The films are typically deposited from adsorbate concentrations of several milligrams per milliliter [Decher92, Smith04, An06]. These concentrations are higher than that required to reach the plateau of the adsorption isotherm, but the
Selective deposition of polyelectrolytes

excess ensures that the solutions do not become depleted during the fabrication of films composed of several hundred layers [Decher03]. Typical dipping times for consecutively alternating adsorption of polyelectrolyte layers are 15 to 30 minutes per layer [Yoo98, Smith04, Poptoshev04]. The solutions are usually used at room temperature, and after each layer adsorption the samples are usually rinsed with UHQ water. As a variation of polyelectrolyte adsorption by dipping of the substrate in the solution, the application of layers was further demonstrated by the use of spin-coaters by Cho [Cho01] and Chiarelli [Chiarelli01]. Spin-coating allows for faster consecutively alternating adsorption and has the advantage that only small amounts of liquids are needed.

![Chemical structures of PSS (polyanion, left) and PAH (polycation, right).](image)

Figure 5.1: Chemical structures of PSS (polyanion, left) and PAH (polycation, right).

According to these polyelectrolyte deposition procedures described in literature, we perform our first experiments with similar solution concentrations between 5 mg/ml to 200 mg/ml of polyelectrolytes dissolved in UHQ water at room temperature. As a start, we use the solutions without pH-adjustments. Because of the expected charge decay of the charge patterns during immersion, we choose shorter immersion times of about 5 sec. In addition to sample rinsing in UHQ water, we study sample rinsing in IPA because it proved useful for particle and molecule deposition, due to easier wetting of the PMMA surface, as described and discussed in chapter 3. However, as neither PSS nor PAH dissolve well in IPA, coagulation of the polyelectrolytes can be anticipated.

Because PMMA exhibits a negative zeta potential in aqueous suspension, two scenario of polyelectrolyte patterning seem most reliable:
(1) A polyanion (e.g. PSS) may be attracted by and selectively attached onto positive charge patterns, yielding high selectivity due to repulsion from the pristine PMMA surface, as schematically illustrated in Figure 5.2c.

(2) A polycation (e.g. PAH) may cover the pristine PMMA surface except for positively charged regions preventing attachment, as schematically illustrated in Figure 5.2d.

Figure 5.2: Scheme of polyelectrolyte deposition. (a) Charge writing. (b) Immersion of the charge pattern in an aqueous solution containing polyelectrolytes. (c) Polyanions selectively attach to the positively charged regions. (d) Polycations adsorb to the PMMA surface except for the positively charged regions.

5.3 Experimental details

The selectivity of polyelectrolyte deposition was investigated on large-scale cross patterns, written onto 40 x 40 µm² areas. The charge patterns were created on 150 nm thick PMMA substrates and were of high surface potential differences in the range of $\Delta V = 6$-$10$ V, measured by KFM immediately after charge writing.

Selective deposition of PSS

The solutions of PSS (Sigma-Aldrich, $M_w = 70$ 000) in UHQ water had concentrations of 5 mg/ml, 100 mg/ml and 200 mg/ml and were ultrasonicated using an ultrasonic probe (Branson Digital Sonifier, model 450, Branson Ultrasonics) at a power level of 40 W for 2 min before development. The charge pattern was developed in the resulting solution at room temperature for 5 sec, subsequently rinsed with UHQ water or with IPA, and dried in an air stream.
Selective deposition of PAH

Instead of pristine PAH, a modified fluorescent version, poly(flourescein isothiocyanate allylamine hydrochloride) (PAH-FITC, Sigma-Aldrich, poly(allylamine hydrochloride) : fluorescein isothiocyanate = 50 : 1, $M_w \approx 56\,000$) was used. The fluorescent marker allowed for light-microscopy (LM)-based characterization besides topography and surface potential measurements in AFM tapping mode and KFM, respectively. PAH-FITC was dissolved in UHQ water at concentrations of 0.05 mg/ml and 5 mg/ml by ultrasonication for 2 min, as mentioned above for PSS. The solutions have a pH of 6-7, implicating a positive charge of the polymer chains [Yoo98]. Following development for 5 sec in the PAH-FITC solution at room temperature, the sample was rinsed in UHQ water or in IPA and dried in an air stream.

Light microscopy

Green fluorescence images were taken using a Nikon Eclipse E800 microscope, an NA 0.5/20x objective and a Retiga 2000R CCD camera. Integration times of the CCD camera were between 8 sec and 20 sec.

5.4 Results

5.4.1 Selective deposition of PSS

Only few experiments were performed to explore the selective deposition of PSS onto positively charged patterns written into PMMA. One of the experimental results in which selectivity could be observed, at least to a certain extent, is illustrated in Figure 5.3.

The initial surface potential difference between cross pattern and background, measured in KFM immediately after charge writing, was $\Delta V = 8\text{-}10\ V$ (variations for the different regions such as cross center (10 V) and cross bars (8 V)). The charge pattern was developed for 5 sec in a 200 mg/ml PSS-solution, rinsed in IPA, and dried in an air stream. Due to the IPA rinsing, the PSS adsorbed on the PMMA in the form of clusters rather than a flat covering, as visible in the topography image in Figure 5.3b. Pattern selectivity is weakly recognizable by a slightly higher cluster concentration and an increased number of bigger clusters on the positively charged cross area than in the background. After the development procedure, a surface potential difference of the cross pattern of $\Delta V = 400\text{-}500\ mV$
Figure 5.3: Selective deposition of PSS. KFM (a) and simultaneous topography (b) image of PSS deposited onto a positively charged cross pattern. Only weak selectivity can be discerned in the topography image. The PSS deposits in the form of clusters because of sample rinsing in IPA after immersion in the PSS solution. Z-scales: (a) 1.0 V (b) 24 nm. Scale bars: 8 µm.

remained (Figure 5.3a), corresponding to a charge decay of 95%.

Besides the weak pattern selectivity in this experiment, a low degree of reproducibility over all achieved experimental results was observed. Several experimental runs investigated with solution concentrations between 5 mg/ml and 200 mg/ml and subsequent IPA rinsing led to PSS clusters non-selectively distributed over the PMMA surface with a substantially higher cluster density than shown in Figure 5.3b, despite equal or lower PSS concentrations.

UHQ instead of IPA rinsing prevented PSS clustering and led to a lower resulting surface roughness of ≈ 1-2 nm, similar to that of pristine PMMA. However, any topographical pattern selectivity could be detected for these charge patterns, immersed in PSS solution and rinsed with UHQ water.

The results reveal that the pristine PMMA surface seems not repellent enough to completely prevent PSS adsorption. Furthermore, the electrostatic forces emerging from the charged regions are either too weak or too fast depleted to allow for dense adsorption of PSS. Regarding reproducibility, we suggest that the short immersion time and the simple development and rinsing procedures present the main challenges prohibiting constant and homogenous PSS adsorption. This is-
Selective deposition of polyelectrolytes

Selective deposition of PAH-FITC

Figure 5.4 shows KFM (5.4a,c) and simultaneous topography (5.4b,d) images of PAH-FITC adsorbed on a PMMA surface except for the positively charged cross pattern which prevented adsorption to a large extent. For PAH-FITC adsorption, the charge pattern was developed for 5 sec in a 5 mg/mL PAH-FITC solution, rinsed in IPA, and dried in an air stream. As a consequence of the IPA rinsing, the PAH-FITC-covered background around the charge pattern does not consist of a comprehensive layer of PAH-FITC, but rather of small clusters of \( \approx 5-30 \) nm size, as can be derived from the inset profile plot in Figure 5.4d. The higher magnification image (Figure 5.4d) further reveals that pattern selectivity is clearly existent, however not ideal, as the positively charged regions seem not completely free of deposited material. Especially in the KFM image (Figure 5.4c), it can be seen that the slightly darker spots representing small PAH-FITC clusters are randomly distributed over the charged area, deposited in the square-shaped gaps of the charge pattern as well as on the positively charged diagonal lines (see indicated circle in Figure 5.4c).

The fluorescence image in Figure 5.5 illustrates the same cross pattern as shown in Figure 5.4. The clearly resolved cross pattern is marked with (a). The scratches, marked with (b), are large-scale identifiers to retrieve the charge pattern location in the AFM after sample immersion. Impurities of the PMMA surface, appearing in bright fluorescence, are marked with (c). An interesting observation concerning the PAH-FITC-covered background is that there exist different regions of different amount of adsorbed PAH-FITC, some of the most pronounced marked with (d), (e) and (f). Close to the PMMA impurities, such as in (f), for example, the drying direction after IPA rinsing is clearly discernible. The variations demonstrate the limitations of the simple dip-and-dry-approach, providing only limited possibilities for constant and homogeneous development conditions.

The observation helps explaining the limited reproducibility of the selective PAH-FITC adsorption. Experiments with identical parameters - i.e. 5 mg/ml PAH-FITC solution, 5 sec of development, IPA rinsing and air stream drying - led to both patterns of excellent selectivity as well as obviously reduced selectivity.
Figure 5.4: Selective deposition of PAH-FITC (5 mg/ml). KFM (a,c) and simultaneous topography (b,d) images of PAH-FITC predominantly adsorbed on the background around the positively charged cross pattern. PAH-FITC adsorbs as clusters of \( \approx 5-30 \text{ nm} \) size (profile plot inset in (d)) due to IPA rinsing. Still, selectivity is not fully pronounced as small clusters of PAH-FITC deposit on the positively charged area as well ((d) and indicated circle in (c)). Z-scales: (a) 0.9 V (b) 25 nm (c) 0.5 V (d) 42 nm. Scale bars: (a,b) 5 \( \mu \text{m} \) (c,d) 1 \( \mu \text{m} \).

Two such contrary examples are shown in Figure 5.6a,b and Figure 5.6c,d. Visible in the KFM and simultaneous topography image in Figure 5.6a,b, small PAH clusters exclusively deposit onto the non-charged areas, reproducing the charge pattern even at the small scale by filling the square-shaped gaps (insets in Figures 5.6a,b), whereas the positively charged diagonal lines remain completely free of adsorbed PAH. In Figure 5.6c,d, in contrast, the background as well as the charge pattern are densely covered by PAH clusters, though selective deposition can still be discerned. In the corresponding fluorescence image (inset in Figure 5.6d), the
Selective deposition of polyelectrolytes

Figure 5.5: Selective deposition of PAH-FITC (5 mg/ml). Fluorescence image of the same cross pattern as illustrated in Figure 5.4. Marks: (a) cross pattern (b) large-scale scratches used as identifiers (c) PMMA impurities (d,e,f) areas illustrating different amounts of adsorbed PAH-FITC. Integration time: 8 sec. Scale bar: 40 µm.

cross-shaped pattern is even clearly recognizable. The brightness contrast between cross pattern and the dark large-scale scratches however confirms that the cross pattern area is not free of PAH deposits.

With identical PAH-concentration (5 mg/ml) but (i) UHQ instead of IPA rinsing and (ii) no rinsing but direct drying, no selectivity at all, neither in the fluorescence images nor in the AFM images, could be detected. Only with drastically reduced PAH-FITC concentrations such as 0.05 mg/ml, the cross patterns could be weakly recognized in the fluorescence image, as shown in Figure 5.7. The higher integration time (20 sec), compared to the fluorescence images in Figures 5.5 and 5.6d (inset) (8 sec) indicates a thinner layer of PAH-FITC. Additionally, the brightness contrast between the cross pattern and the large-scale scratch again let assume that the cross pattern area is to a certain extent covered by PAH-FITC. The corresponding topography, as shown in the AFM topography image in Figure 5.7c is a flat surface of ≈ 1-2 nm roughness. No topographical structures can be found that indicate a correlation to the charge pattern visible in the KFM image in Figure 5.7b.
Figure 5.6: Two examples of PAH-FITC adsorption (5 mg/ml) demonstrating differences in selectivity. (1) KFM (a) and topography (b) image of PAH-FITC adsorbed on PMMA except for positively charged regions, yielding high pattern selectivity. The small PAH-FITC clusters reproduce the charge pattern even at a small scale by depositing into the square-shaped gaps (see insets). (2) KFM (c) and topography (d) image of PAH-FITC adsorbed on PMMA with poor pattern selectivity. Although PAH-FITC clusters are covering both background and cross pattern, the pattern is still clearly recognizable in the fluorescence image (inset in (d)). Z-scales: (a) 280 mV (inset 190 mV) (b) 7 nm (c) 600 mV (d) 21 nm, integration time: 8 sec. Scale bars: (a,b) 3 µm, (c,d) 4 µm (LM 40 µm).

The reason for the differences in selectivity dependent on the rinsing solvent might be found in the different surface tensions of IPA and aqueous media. Water has a surface tension of 73.1 dynes/cm, while IPA has a much lower surface
Figure 5.7: Selective deposition of PAH-FITC (0.05 mg/ml) and subsequent UHQ rinsing. (a) The cross pattern is weakly recognizable in the fluorescence image, see arrow. Integration time: 20 sec. (b,c) KFM and simultaneous topography image of the cross pattern shown in (a). No topographical structures can be detected that indicate a correlation to the charge pattern. Z-scales: (b) 300 mV (c) 8 nm. Scale bars: (a) 40 µm, (b,c) 3 µm.

tension of 21.7 dynes/cm. A consequence of the lower surface tension is easier wetting and easier removal of a liquid from a surface due to weaker capillary forces caused by the evaporating liquid. For the same reason, IPA is extensively used to dry substrates (e.g. wafers) after DI water rinsing, because of its ability to displace water at a surface and its ease of removal from the surface.

5.4.3 Conclusion

Positive charge patterns written into PMMA can in principle be used for both selective deposition of PSS onto the charge patterns as well as selective adsorption of PAH-FITC on PMMA except for the charged patterns. We suggest, however, that the most fundamental challenge presents the non-permanent patterning due to charge pattern depletion during immersion in the polyelectrolyte solution.

The ‘electrostatic contrast’ between charged and non-charged regions seems overall too weak, in most cases leading to deposition of polyelectrolytes onto both regions, albeit with different deposition densities. Huge differences in selectivity could be observed for different rinsing solvents, such as IPA in contrast to UHQ water. Due to weaker capillary forces, the polyelectrolyte solutions were easier removed from the PMMA surface by IPA rinsing, resulting in a generally higher selectivity. UHQ rinsing led to an additional covering of both patterned and non-patterned regions due to the higher capillary drag forces of the evap-
orating water. Hence, IPA rinsing may help as a visualizing approach. Due to polyelectrolyte coagulation and clustering however, it is not a realistic option for a final polyelectrolyte patterning technique.

An idea for improvement that has not yet been implemented is spin-coating instead of immersion [Cho01, Chiarelli01], as it allows for fast polyelectrolyte adsorption.
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Chapter 6
Conclusions and Outlook

Nanofabrication such as the creation of defined arrangements of particles and molecules on solid surfaces presents a key issue in nanotechnology, and besides diverse strategies currently researched, directed assembly of nanoscale objects from the liquid phase by using electrostatic templates is one promising option.

The main focus of this thesis was to explore the possibilities to precisely direct the assembly of particles and molecules from polar media onto electret surfaces by created, local electrostatic fields, a method called nanoxerography. Nanoxerography is a maskless process consisting of two steps: In a first step, patterns of local surface charges are written into a thin electret layer by applying voltage pulses between a conductive AFM tip and the sample. In a subsequent development step, these charge patterns act as templates for the selective deposition of the particles or molecules.

The choice of the electret material for nanoxerography in polar solvents is not trivial. The major requirements are the capability for high-resolution charge writing and that generated patterns of charges trapped in the electret surface remain sufficiently stable during development of the sample in the polar solution containing the particles or molecules to be deposited. Because even the fundamental mechanisms of charge trapping in electrets such as thin films of amorphous polymers or semiconductors are still researched and debated, primarily empiric studies give hints for suitable substrates. A dielectric often used for SPM-based charge writing and for nanoxerography is PMMA. Charge dots as small as 70 nm written into PMMA were already demonstrated in 1992 [Schoenenberger92]. Several studies further document relatively high charge stability of trapped surface charges in high relative humidity or upon exposure to ultrapure water [Jacobs01, Ressier08]. Due to the lack of comparative studies in literature, we showed for three of the most considered materials for nanoxerography, PMMA, PTFE-like
FC-layers and SiO$_2$, that PMMA reveals clearly best charge retention characteristics upon exposure to UHQ water and during AFM-scanning in ambient air using a conductive tip.

We investigated nanoxerographic printing of diverse nanoscale objects dispersed in either UHQ water or IPA, i.e. 50 nm and 100 nm COOH-PS spheres, COOH-MWCNTs of 10 nm nominal diameter, SWCNTs stabilized in water by the nonionic surfactant Synperonic NP10, C$_{60}$ molecules Triton X-100-stabilized in water, and 5 nm AuNPs stabilized in water by a citrate ligand. Deposition characteristics on charge patterns consisting of positively as well as negatively charged parts evidenced that Coulomb rather than dipolar forces are dominating particle attraction, since the positively charge patterns were well reproduced by attached particles, while negatively charged patterns remained free of deposited material. The negative charge on the particles originates either from dissociation of surface groups (PS spheres, COOH-MWCNTs, AuNPs) or local dipoles in the polar head groups of the surfactants (SWCNTs, C$_{60}$).

We demonstrated that varying the amount of injected charge and hence the surface potential allows one to control the line width of the assembled structures, the approximate number of particles deposited per charge dot and even to induce alignment of individual and thin bundles of SWCNTs along straight and curved charge lines. This way, we succeeded in assembling arrays of PS spheres and AuNPs with pitches between 250 nm and 2 $\mu$m and in creating small networks of SWCNTs. An explanation for the surface potential-dependent deposition characteristics could be that higher voltage amplitudes applied during charge writing lead to a wider lateral distribution of trapped charges than lower voltage amplitudes, due to repulsion. Evidence for such behavior was found by observing that the charge patterns indeed exhibit local charge densities close to the maximum charge density in PMMA, as defined by the dielectric strength. Furthermore, we observed differences in pattern definition imparted by the stabilizing agents. While voluminous wrappings of the nonionic surfactants Synperonic NP10 and Triton X-100 appeared to inhibit dense deposition of SWCNTs and C$_{60}$ clusters, for instance, the small citrate ligand permitted the assembly of 5 nm AuNPs into densely packed layers with high pattern definition. The quality of the SWCNT dispersions, such as different amount of surfactant and dispersion treatment such as ultrasonication and centrifugation, as well as the particle concentration in suspension in general, had additional influence on deposition behavior.

In addition to accurate positioning, an essential requirement for applicability is that the nanoscale objects retain their functionality during the assembly process.
which in turn must be compatible with later process steps. We showed on the example of 5 nm AuNP line patterns, how the structures assembled on the thin PMMA electret layer could be transferred vertically down onto the underlying \( \text{SiO}_2 \) substrate by thermal decomposition of PMMA. The simple approach for PMMA removal might be further improved by applying established but more elaborate techniques such as plasma decomposition [Kraus07]. Subsequently, we demonstrated retained catalytic activity of the AuNPs by growing SiNWs in a VLS process from the transferred line structures.

Electrostatic field-directed assembly of nanoparticles, nanotubes and \( \text{C}_{60} \) molecules succeeded due to the ‘encapsulation’ or surface functionalization of the nanoscale objects, be it by covalently bound surface groups, surfactants or ligands. However, besides ‘encapsulated’ nanoscale objects the question arises whether nanoxerography can further be used for the direct patterning of ionic molecules. By these means, first attempts of selective deposition of the polyelectrolytes PSS and PAH-FITC, dissolved in water, by using 40 \( \times \) 40 \( \mu \text{m}^2 \) large positively charged cross patterns as templates were undertaken. These first experiments revealed general pattern selectivity for both PSS and PAH-FITC deposited onto PMMA, however to a partly weak extent. For further improvement of this approach, rendering it a useful alternative to existing methods primarily based on SAMs [Clark97b], further exploring the mechanisms limiting selectivity is needed. The main bottlenecks and subjects of investigation could be the non-permanent patterning, the limited process control of the simple rinse-and-dry procedures or the strong screening of the charge patterns due to the high ionic strength of the polyelectrolyte solution.

In our thesis we demonstrated that nanoxerography can be used to assemble various kinds of nanoscale objects dispersed in polar media into nanoscale structures on solid surfaces. The obtained results constitute a proof-of-principle of the developed tool. On its basis, we can expect that the approach is similarly applicable to a variety of further nanoscale objects. Arraying of ferritin molecules that could open new possibilities for growing ordered structures of SWCNTs from ferritin-based iron catalyst, known to yield narrow diameter distributions [Durrer08, Durrer09], is one possible application example. Interesting candidates could also be nanowires and nanorods, as they attract increasing interest as building blocks throughout a wide range of nanotechnology applications. It is also conceivable to extend the approach to a sequential technique for assembling structures consisting of different kinds of particles or molecules.
Conclusions and Outlook

We suppose that considerable potential for further improving pattern resolution and definition is provided by the choice of substrates and dispersions involved. As substrates, nanocrystalline or granular materials could be an option. On nanocrystalline SnO$_2$ surfaces, Wilks et al. injected electrons into individual 8 nm SnO$_2$ nanocrystals by STM and showed that the spatial resolution of the resulting charge dots is limited by the size of tip and particle [Wilks04]. In another, granular substrate, Decossas et al. demonstrated charge trapping in Si nanocrystals embedded in SiO$_2$ and the detection of the number of injected charges in ultrahigh vacuum AFM [Decossas05]. Regarding the dispersions, taking full advantage of tuning dispersions on the basis of colloidal science might lead to much ‘better’ dispersions than were used in this thesis. In colloidal systems, we expect that (1) covalently bound, small surface groups or small surface-active agents, permitting high-density deposition, (2) low ionic strength of the solvent and (3) high surface potential of the colloid are among the major, favorable properties.

Finally, the speed of AFM-based nanoxerography is primarily limited by the serial charge writing process with writing velocities in the $\mu$m/s range. Alternatively using either conductive stamps or polymer stamps inducing contact electrification would have the advantage that extended and complex charge patterns could be created in one step. One such a charge-stamping based nanoxerography approach is presented in Appendix A, with already established strategies discussed in the introduction. We suggest that especially charge pattern generation by means of pure contact electrification upon contact of insulating materials such as polymers, combined with our process of subsequently assembling nanoscale objects from polar suspensions, could comprise a simple and promising method. This approach would facilitate the nanoxerography setup as the need for conductive electrodes and externally applied voltage is eliminated. An open question would be how surface potentials of different amplitudes could be created. Surface potential contrasts up to $\approx 1$ V detected in KFM on electrets after micro-contact stamping with surface-functionalized PDMS stamps were recently shown by Jacobs et al. [Jacobs07].
Appendix A

Charge stamping-based nanoxerography

In 2001, Jacobs et al. invented a parallel high-resolution charge patterning concept and demonstrated high resolution nanoxerographic printing from a powder [Jacobs01]. Due to the parallel approach, charge stamping, also denoted as electrical microcontact printing (e-µCP), allows for a crucial speed-up in charge pattern generation compared to AFM-based charge writing. Considering a reasonably fast scanning-probe based system, capable of writing charge dot arrays with a pitch of 500 nm at a speed of 100 kHz, more than an hour is still required to pattern an area of 1 cm². By a stamp, the same is done in a couple of seconds.

The first stamps were made of polydimethylsiloxane (PDMS), with a patterned surface rendered electrically conducting by thermal evaporation of 7 nm Cr (as a promotion layer) and 80 nm of Au onto the PDMS [Jacobs01]. With these stamps, areas as large as 1 cm² could be patterned with features as small as 150 nm. However, the combination of a ‘stiff’ gold film evaporated on an elastic PDMS stamp often leads to cracks in the gold layer [Kang04]. Furthermore, gold evaporated on PDMS exhibits disadvantage properties such as weak adhesion due to solvents leaking out of PDMS, and due to the low surface energy of PDMS [Lim06], easily leading to undesired material transfer of the gold film to the electret surface during stamping. Cao et al. [Cao05] made a ‘virtue out of necessity’ and removed the gold film on the contact areas of the stamp beforehand by a process related to micro- or nanotransfer printing [Bernard98, Loo02]. The remaining stamps still had conducting sidewalls of \( \approx 40 \) nm thickness that allowed for the creation of charge lines with a lateral width of \( \approx 300 \) nm recorded in KFM. Barry et al. [Barry05] fabricated small features (50 nm) for charge stamp-
ing by phase-shift photolithography [Odom02] and reactive-ion etching of a 10 \( \mu \text{m} \) thick n-doped silicon wafer. The thin wafer was mounted onto a thicker (500 \( \mu \text{m} \)) silicon wafer via a 5 mm layer of PDMS in-between, which served as flexible support for the thin silicon electrode during charge stamping.

In this appendix a charge stamping approach based on a conductive polymer (elastosil LR 3162 by Wacker) used as stamp material is described. LR 3162 is less elastic and more coarse-grained than PDMS, hence the feature sizes of the fabricated stamps do not reach the nanometer scale, but are in the range of tens of micrometers. Nevertheless, the conductive polymer-based stamps present a robust, fast and easily implementable possibility for creating micrometer-sized charge patterns in electrets (Figure A.1a), which can be used for subsequent microxerographic printing (Figure A.1b,c). Further investigations in the choice of the conductive polymer material may yield a promising alternative to the current approaches.

![Figure A.1: Scheme of charge stamping-based nanoxerography.](image)

**Figure A.1: Scheme of charge stamping-based nanoxerography.** (a) Charge stamping: Surface charges are stamped into PMMA by applying a voltage pulse between a patterned, soft conductive electrode and the sample. (b) Development: The sample is immersed in a suspension containing particles to be deposited. (c) Particle assembly. After rinsing and drying the sample, the particles are firmly attached to the predefined pattern.

### A.1 Experimental details

The polymer stamps were fabricated by soft lithography. A master made of SU-8, a negative photoresist extensively used in soft lithography, served as reusable casting mold.
PMMA films spin-coated onto indium tin oxide (ITO)-coated glass slides served as electrets. ITO instead of p-doped silicon was used as conductive support because the transparency of ITO allowed for optical inspection of the stamp-PMMA contact from the backside.

**SU-8 master**

The SU-8 master was fabricated by photolithography. To this end, glass slides were first dehydrated by heating them at 200 °C for 5 min on a hotplate. SU-8 5 (negative photoresist, microchem, Newton MA, USA) was then spin-coated onto the glass slides at 1600 rpm (Chemat Technology, Spin-Coater KW-4A, Northridge CA, USA), resulting in a film thickness of ≈10 µm. The photoresist was subsequently soft-baked for 2 min at 65 °C and 5 min at 95 °C in an oven (Binder, Tuttlingen, Germany). The structures were then exposed for 55 sec with UV-light emitting lamps (Heeb Elektro AG, Kuesnacht, Switzerland). The exposure mask was designed in CorelDraw and printed onto transparent foils with a printing resolution of 3800 dpi. After a post exposure bake for 1 min at 65 °C and 2 min at 95 °C in the oven, the structures were developed for 2 min (mr-Dev 600, micro resist technology, Berlin, Germany) and rinsed in IPA. For further cross-linking, the master was finally hard-baked for 15 min at 200 °C.

**Polymer stamp**

The polymer stamps were fabricated by replica molding. The two components, elastosil LR 3162 A and B (Wacker Ltd., Stuttgart, Germany) were mixed at a 1:1 ratio and poured onto the master. The stamps were baked for 3 min at 200 °C, and the cured stamp could then be peeled off the master immediately. The LR 3162 elastosil has a resistivity of ≈11 Ω·cm.

**Substrate**

A 3.5% solution of PMMA (M_w = 350 kDa) in toluene was spin-coated at 3500 rpm onto ITO-coated glass, resulting in a PMMA film thickness of ≈150 nm. The samples were subsequently baked on a hotplate at 180 °C for 3 min.

**Charge stamping**

To generate patterns of trapped charges, we placed the conductive polymer stamp on top of the PMMA without added pressure, and applied a voltage of 30-60 V
between the backside of the stamp and the ITO for 5 sec. After turning off the applied potential, we removed the stamp by hand.

A.2 Results

An overexposure of the SU-8 photoresist led to a not complete removal of the SU-8 on the non-exposed regions and thus to structures less deep than the SU-8 layer thickness. This was intended and favorable because the LR 3162 elastosil showed strong adhesion on glass, while it could be easily removed from SU-8. The resulting, casted polymer stamps consisted of line structures of 15-20 µm lateral width in intervals of 60 µm, but only ≈ 1 µm in depth (Figure A.2a,b). The weak edge definition (as visible in the profile plot add-on to Figure A.2a) was already present in the exposure mask (no image shown) and an effect of the limited printing resolution of 3800 dpi.

Despite the flat topography, however, the line structures of the stamp appeared clearly pronounced when imaged in light microscopy (Figure A.2b) and provided stable line contacts when brought in contact to the PMMA substrate. Figure A.2c shows the KFM image of a charge pattern stamped into PMMA, achieved by applying 30 V between stamp and ITO for 5 sec. The profile plot illustrates the high edge definition of the generated charge lines with a surface potential difference of almost 2 V against background.

The charge line patterns clearly defined in the KFM image were reproduced by deposited, fluorescent 100 nm COOH-PS beads or SWCNT (primarily bundles) with high fidelity, as the two examples in Figure A.3 show. The apparent smears through the densely covered PS sphere lines, visible in the green fluorescence image (Figure A.3a) are probably due to excessive air stream drying. The SWCNTs deposited onto the positively charged lines with high selectivity. However, the deposition density is not sufficient to form continuous stripes of SWCNT material, capable of conducting electric current, for instance.

Further investigations

The amplitude of the applied voltage required to create a certain surface potential difference crucially depends on the stamp properties such as its thickness and conductivity. Here, a monitoring of the current flow per area during stamping could provide helpful intermediate information to estimate the amount of
Figure A.2: Conductive elastosil stamp and charge pattern. AFM topography (a) and LM (b) image of the elastosil stamp surface. The lines are ≈ 1 µm in height, as the profile plot displays. (c) KFM image of a charge pattern created in PMMA by charge stamping. The profile plot reveals higher edge definition for the charge patterns than for the stamp features. Scale bars: (a) 20 µm, (b) 120 µm, (c) 20 µm.
trapped charge, or the created surface potential respectively, independent of the stamp geometry and material used.

Further investigations that seem promising to us could be done on charge stamping without applied voltage, but pure contact electrification, as was mentioned already in the outlook part in chapter 6. It is conceivable that sufficient charge can be trapped in an electret upon contact with another insulating material such as a polymer. Jacobs et al. recently showed detected surface potential contrast up to \( \approx 1 \) V in KFM on electrets after microcontact stamping with surface-functionalized PDMS stamps [Jacobs07]. Mere micro- or nanocontact stamping instead of charge writing or charge stamping using conductive electrodes would facilitate the process setup, as no externally applied voltage would be required any more.

The results presented in this appendix were worked out together with David Keller during his Bachelor Thesis.

![Figure A.3: 100 nm COOH-PS spheres and bundles of SWCNTs selectively deposited onto charge lines created by charge stamping in PMMA. The green fluorescence image of COOH-PS spheres (a) and the AFM topography image of SWCNTs (b) reveal reproduction of the stamped charge lines by the particles with high selectivity and preserved edge definition. Z-scale (b): 40 nm.](image)
## Appendix B

### Dispersions

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<th>Particle type</th>
<th>COOH-PS spheres</th>
<th>COOH-PS spheres</th>
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<tr>
<td>Diameter</td>
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<td>Standard Deviation</td>
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<td>Solvent</td>
<td>IPA or UHQ water</td>
<td>IPA or IPA/UHQ water mixtures</td>
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<td>Particles/ml (stock)</td>
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<td>Particles/ml (diluted)</td>
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Supplier: Polyscience Inc., Warrington, USA

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<td>-</td>
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Suppliers: (1) Nanocyl S.A., Sambreville, Belgium  
(2) Cheap Tubes Inc., Brattleboro, VT, USA  
(3) Sigma-Aldrich
### Dispersions

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<th>C₆₀⁽¹⁾</th>
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<td>Standard Deviation</td>
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<tr>
<td>Solvent</td>
<td>UHQ water</td>
<td>UHQ water</td>
</tr>
<tr>
<td>Concentration</td>
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</tr>
<tr>
<td>Particles/ml (stock)</td>
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<td>5 · 10¹³</td>
</tr>
<tr>
<td>Particles/ml (diluted)</td>
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<td>2.5 · 10¹³</td>
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<tr>
<td>Dilution</td>
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<tr>
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<td>GC5</td>
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**Suppliers:**

(1) Sigma-Aldrich

(2) British Biocell International, Cardiff, UK
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Curriculum Vitae

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