Ferroelectric Thin Films for the Manipulation of Interfacial Forces in Aqueous Environments

by

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Dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Department of Mechanical Engineering and Materials Science in the Graduate School of Duke University

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ABSTRACT

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Abstract

Ferroelectric thin films (FETFs) offer a promising new platform for advancing liquid-phase interfacial sensing devices. FETFs are capable of expressing surface charge densities that are an order of magnitude higher than those of traditional charged surfaces in liquid environments (e.g., common oxides, self-assembled monolayers, or electrets). Furthermore, the switchable polarization state of FETFs enables patterning of charge-heterogeneous surfaces whose charge patterns persist over a range of environmental conditions. Integration of FETFs into liquid-phase interfacial sensing devices, however, requires the fabrication of films with nanometer-scale surface roughness, high remnant polarization values, and interfacial stability during prolonged exposure. The objectives of my research were to i) fabricate ferroelectric ultra-smooth lead zirconium titanate (US-PZT) thin films with nanometer-scale surface roughness, ii) establish the interfacial stability of these films after prolonged exposure to aqueous environments, iii) measure the interfacial forces as a function of film polarization and ionic strength, iv) calculate the surface potential of the US-PZT surface using electric double layer (EDL) theory, and v) demonstrate the guided deposition of charged colloidal particles onto locally polarized US-PZT thin films from solution.

I demonstrate the use of ferroelectric US-PZT thin films to manipulate EDL interaction forces in aqueous environments. My work conclusively shows that the
polarization state of US-PZT controls EDL formation and can be used to induce the
guided deposition of charged colloidal particles in solution.

I present a robust fabrication scheme for making ferroelectric US-PZT thin films
from a sol-gel precursor. By optimizing critical thermal processing steps I am able to
minimize the in-plane stress of the film and reliably produce US-PZT thin films on the
wafer-scale with mean surface roughness values of only 2.4 nm over a 25 µm² area. I
then establish US-PZT film stability in water by measuring changes in film topography,
crystallinity, surface chemistry, and electrical properties as a function of exposure
duration. My results show that fabrication of crack-free US-PZT thin film is critical for
long-term film fidelity in aqueous environments. Furthermore, I found no change in film
topography or bulk composition with increasing exposure duration. Prolonged exposure
to aqueous environments, however, gradually oxidizes the surface of the US-PZT wich
results in a decrease in film resistivity and polarization saturation. Next, I used colloidal
probe force microscopy (CPFM) to measure the EDL interaction force as a function of
separation distance between polarized US-PZT thin films and a clean borosilicate probe.
CPFM measurements were performed on oppositely polarized US-PZT thin films, which
expressed either a positive or negative surface charge, and over a range of ionic
strengths. The inner-Helmholtz plane (IHP) potential of the US-PZT was determined by
fitting the CPMF force-separation data to number of EDL models, including; an
analytical EDL model using a constant potential boundary condition with a Stern layer,
a charge regulation EDL model, and a numerical EDL model using the non-linear Poisson-Boltzmann equation. Each model provides good agreement with the experimentally measured and predict high IHP surface potential for the polarized US-PZT thin films in solution. Finally, I demonstrate the use of polarized US-PZT to induce the guided deposition of positively or negatively charged colloidal particles from aqueous environments. I explore the effects of ionic strength, particle size, surface roughness, and pH on particle deposition.

Overall, this work demonstrates, for the first time, that FETFs can be used as a platform to manipulate colloidal particles in aqueous environments. The experimental results demonstrate that the surface charge of the FETF is reduced by charge shielding and perform similarly to traditional, charged surfaces in aqueous environments.
Dedication

To my family.
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sec, 450°C oven pyrolyization for 35 min, and final annealing by RTA at 700°C for 20 sec.

Figure A.2.4: AFM height images in air of single layer PZT thin film fabricated with oven annealing (z scale ±25 nm). Processing conditions for all thin films included a 40 sec spin at 3000 RPM, 90°C hot plate evaporation for 120 sec, 450°C oven pyrolyzation for 35 min, and final annealing at 700°C for 35 min.

Figure A.2.5. High-resolution XPS spectra for (A) Pb 4f and (B) Ti 2p as a function of thermal processing conditions (Table 2.1).

Figure A.3.1: Diagram of the counter ion distribution within the electric double layer above a polarized ferroelectric thin film induced to express a (A) positive surface charge and (B) negative surface charge. The dotted line indicates the boundary between the outer-Helmholtz plane and the diffuse double layer.

Figure A.3.2: Reduced surface potential over a range of ferroelectric charge (β) and (A) a low point of zero charge or (B) a high point of zero charge within a range of ionic strength solutions.

Figure A.3.3: Dimensionless Stern layer charge over a range of ferroelectric charge (β) and (A) a low point of zero charge or (B) a high point of zero charge over a range of ionic strength solutions.

Figure A.3.4: Reduced surface potential in 0.1 mM monovalent strength solution for a range of ferroelectric charge (β) and (A) low point of zero charge and (B) high point of zero charge over a range of pH solutions.

Figure A.3.5: Isoelectric point over a range of ferroelectric charge (β) values for ferroelectric thin films with different point of zero charge values in aqueous environments.

Figure A.3.6: Interaction energy as a function of separation distance between a FETF and a negatively charged oxide surface (ψ=-40 mV, Δ=-0.9) for a range of ferroelectric surface charge densities.
1. Overview

1.1 Motivation

For over twenty years, micro- and nano-scale devices have been advancing medical diagnostics, drug discovery, and environmental sensing applications.\(^1\) A number of researchers have demonstrated how micro-devices can be used for sensing applications including multianalyte immunoassays\(^2\) or protein pore sensors.\(^3\) Device miniaturization requires a variety of tasks, such as mixing and separation, to be performed primarily using interfacial forces.\(^4\) A critical need in the continued development of these devices is the ability to reliably control the interfacial forces with high spatial resolution. In dilute electrolyte solutions, the electric double layer (EDL) interaction force is the longest-range and one of the most important forces for determining colloidal interactions.\(^5\)\(^-\)\(^7\) The EDL interaction force depends on the surface charge density of the interacting entities. Continued development of miniaturized sensing devices, however, requires the development of an easy way to pattern surfaces with high charge densities that persist over a range of solution conditions.

Charged surfaces have typically been created through chemically active surface groups,\(^8\) charge injection,\(^9\) or conductive electrodes.\(^10\) Each of these approaches, however, has inherent short-comings that limit their broad integration with interfacial
sensing devices. For example, chemically active surface groups depend on solution conditions (e.g., ionic strength and pH) and inherently have relatively low surface charge densities.\(^8,11\) Charge injected surfaces are susceptible to charge migration and a gradual loss in surface potential,\(^9,12\) while electrode-based systems require a constant power supply, complex circuitry, and are prone to Faradaic charge loss through electrolysis. Instead, polarized perovskite-based ferroelectric thin films (FETFs) are able to maintain a large, switchable, surface charge density even after the removal of an externally applied electric field.\(^{13,14}\)

The surface charge of a FETF is due to a bi-stable polarization state that is held across the film thickness. The surface charge density maintained by a FETF can be an order of magnitude larger than that achieved by chemical modification and is independent of environmental conditions. Furthermore, the ability to reverse the polarization state of a FETF enables the patterning of positive or negative surface charge without extensive chemical processing or alteration of the surface properties. These advantages motivate the study using FETFs to control interfacial forces in liquid environments.
1.2 Objectives

1.2.1 Fabrication of ultra-smooth ferroelectric lead zirconium titanate thin films (Objective 1)

In Chapter 3 I discuss an optimized fabrication scheme for the generation of ultra-smooth lead zirconium titanate (US-PZT) thin films. Smooth PZT surfaces are essential for the guided deposition of target species from solution. Chapter 3 provides information on the thermal-processing steps that are necessary in the sol-gel fabrication method to produce ferroelectric, US-PZT thin films with a mean surface roughness of only 2.4 nm over a 25 µm² area. I show that US-PZT is achieved by minimizing the in-plane stress of the film, which reduces crack formation and grain size.

1.2.2 Establish US-PZT stability in aqueous environments (Objective 2)

Chapter 4 contains the systematic study of the stability of US-PZT thin films in aqueous environments. Here, I investigate a number of film properties as a function of exposure duration, including topography, surface composition, crystallinity, residual stress, and electrical properties. Exposure durations up to 100 days are studied. The results show that film topography, surface composition, and the Raman spectrum are unchanged with prolonged exposure to aqueous environments. XPS analysis of US-PZT, however, shows that the surface undergoes gradual oxidation with extended exposure.
to Milli-Q grade water. This results in an increase in the mobile charge carrier density and leads to the degradation of film resistivity over time. These results support the conclusion that while the ferroelectric US-PZT thin film is stable in aqueous environments, the oxidation of the surface may produce charge screening at the water-PZT interface.

1.2.3 Measure and model the ferroelectrically-induced EDL interaction force (Objective 3)

Chapter 5 presents the measurement and modeling of the EDL interaction force between a polarized US-PZT thin film and a clean borosilicate probe, using colloidal probe force microscopy (CPFM). CPFM is a versatile technique that directly measures the interaction force as a function of separation distance between two charged surfaces. Using CPFM I study the EDL interaction force between a positively or negatively charged US-PZT and a negatively charged probe over a range of dilute electrolyte solutions. CPFM measurements show that native, non-polarized US-PZT has a positive surface potential in solution. CPFM measurements of polarized US-PZT also show that ferroelectric polarization to a negative or positive surface charge can induce long-range EDL repulsion or attraction to a negatively charged probe, respectively. Force separation approach curves were then fitted to three different EDL interaction force models. First, I modeled the EDL interaction force using an analytical model with a constant-potential
boundary condition and a Stern layer. Next, I fitted the force-separation approach curves using a charge regulation EDL model, and demonstrate good agreement between the force-separation approach curves and a numerical EDL model using the non-linear Poisson-Boltzmann equation. Finally I determine the inner Helmholtz plane (IHP) surface potential of the US-PZT as a function of polarization direction and ionic strength.

1.2.4 Demonstrate the guided deposition of charged particles onto locally polarized US-PZT thin films from solution (Objective 4)

In Chapter 6, the guided deposition of charged colloidal particles from solution onto locally polarized US-PZT is discussed. I demonstrate the deposition of both positively and negatively charged colloidal particles, for a range of conditions, including surface roughness, ionic strength, pH, and particle size. I show that increasing the surface roughness dramatically increases the incidence of non-specific binding, supporting the need for an ultra-smooth interface during guided deposition of colloidal particles from solution.

1.2.5 Conclusions and future work

In Chapter 7, I summarize the salient outcomes of the research and provide a number of suggestions for the future study of guided deposition of charged colloidal
particles onto charge-patterned FETFs in solution. Overall, this research demonstrates for the first time, that FETFs can be used for the guided deposition of particles from solution, and that FETFs have the potential to be employed for interfacial sensing applications.
2. Background

The study of FETFs in aqueous environments requires the understanding of thin film fabrication, interfacial phenomenon, and a variety of characterization tools. Each section is intended to introduce an essential concept or characterization tool, for additional information I refer the reader to the referenced review articles and papers. In each case, I attempt to connect each section with my study of FETFs in solution.

2.1 Ferroelectric Materials

Ferroelectrics are a class of materials that can maintain a reversible, non-zero polarization in the absence of an externally applied electric field. The reversible polarization originates from an asymmetric crystal structure within the material. This asymmetry induces a bi-stable dipole moment within the unit structure of the material. The dipole moments can be aligned across the material by an adequately high external electric field, resulting in charge separation to the opposing surfaces of the film. The reversible alignment of dipole moments gives rise to polarization hysteresis, where the non-linear electric permittivity depends on both the applied electric field and the previous polarization state. Because ferroelectric properties rely on the crystal structure of the material, ferroelectric hysteresis is only observed below a critical temperature, known as the Curie temperature. Cooling a ferroelectric below its Curie
temperature is associated with a reorientation of the crystal lattice structure into one exhibiting ferroelectric behavior. Ferroelectric hysteresis has been demonstrated by both polymers (e.g. poly(vinylidene fluoride) (PDVF) or copolymer poly(vinylidene fluoride-trifluoro-ethylene) (PVDF-TrFE)) and inorganic ceramics (e.g. lithium niobate (LiNbO₃), barium titanate (BaTiO₃), and lead zirconium titanate (PZT)). Compared to polymers, ceramic ferroelectrics typically have higher dielectric constants, higher remnant polarization values, and a lower coercive field. Additionally, ceramic ferroelectrics have better thermal stability and resistance to polarization fatigue. Traditional applications of ferroelectric materials include memory devices and micro-electromechanical systems.

Ferroelectrics hysteresis in ceramic pervoskite materials is a result of a natural asymmetry in the crystalline unit cell structure that results in ion displacement and the formation of a bi-stable dipole moment across each unit cell. For example, lead titanate is a ceramic ferroelectric that exhibits a tetragonal perovskite unit cell structure (Figure 2.1 A). The elongation of the unit cells along b (see Figure 2.1) induces displacement of the titanium ion from the centro-symmetric position, which results in charge separation. The titanium atom, however, is equally stable slightly above or below the centro-symmetric position producing a bi-stable dipole moment across each unit cell. Unit cells are typically organized into domains based on allowed crystallographic orientations and
a uniform polarization direction.\cite{24} One or more of these domains collect into grains, which are separated by an intermediate interruption in crystalline order.\cite{24} Figure 2.1 B depicts the hierarchical structure of ferroelectric PZT over a range of length scales.

![A] A ferroelectric rhombohedral unit cell structure of lead titanate. (B) Depiction of the hierarchical structure of a ceramic perovskite ferroelectric material.

2.1.1 Ferroelectric hysteresis loop

The ferroelectric hysteresis loop is a measure of electric displacement in response to an externally applied electric field. In traditional dielectric materials, the measured polarization is linear in response to an externally applied electric field. Ferroelectric polarization, however, includes both the polarization of the dielectric material and
reversible domain switching within the ferroelectric material. This gives rise to a separation in the polarization versus applied electric field plot, commonly referred to as hysteresis (Figure 2.2).\cite{25} Critical ferroelectric material properties, such as remnant polarization and coercive field, are determined by the ferroelectric hysteresis loop. The remnant polarization of the ferroelectric is determined by the two y-axis intercepts of the hysteresis loop and reflects the charge present at the top and bottom surfaces at zero applied electric field. The coercive field is determined by the two x-axis intercepts of the hysteresis loop and reflects the minimum field required to induce flipping of the ferroelectric polarization state. Additional characteristics of the ferroelectric hysteresis loop include the slope at the coercive field, which correlates with the presence of a dielectric deadlayer,\cite{26} and the polarization saturation, which is the maximum polarization value achieved for a given applied electric field.
There are important differences between bulk ferroelectric materials and FETFs. While both are polar functional materials, FETFs are mechanically constrained along one surface. This lattice binding is associated with additional film stress due to lattice mismatch between the underlying substrate and the FETF.\textsuperscript{[27]} The additional in-plane stress has been shown to cause cracking,\textsuperscript{[28-30]} stripping,\textsuperscript{[31,32]} new phase behavior,\textsuperscript{[33]} increased coercive field,\textsuperscript{[14]} and spontaneous polarization.\textsuperscript{[34]} Fabrication of thin ferroelectric materials, however, reduces the polarizing voltage magnitude necessary to
induce a switching moment. As such, FETF devices require low power and enable their implementation in micro- and nanoscale devices.

Even though a large body of work on FETF properties exists, there are a number of complications that inhibit the widespread use of FETF beyond that of memory applications. These complications include polarization fatigue,\textsuperscript{[35]} time or temperature dependent development of a preferred polarization orientation,\textsuperscript{[36]} dielectric losses,\textsuperscript{[37]} crystalline defect formation,\textsuperscript{[38]} and charge shielding.\textsuperscript{[39]} The two primary contributors to these complications are unit cell defects and internal polarization shielding. Unit cell defects involve oxygen or cation vacancies and holes.\textsuperscript{[40]} Alternatively, internal polarization shielding is possible with film contamination by foreign ions or charge injection.\textsuperscript{[40]} FETF degradation is a key concern to be address prior to the integration of FETF in liquid-phase sensing device development.

In addition to changes in FETF properties, surface charge compensation after polarization can affect interfacial properties of FETFs. Polarization of FETFs in ambient conditions has been shown to result in charge transfer to the surface, often resulting in over-compensation of the bound charges of the FETF dipole moment.\textsuperscript{[41,42]} The concentration of these surface-confined counter ions has been detected with KPFM.\textsuperscript{[42]} As such, the presence and mobility of these surface charges must be considered when introducing polarized FETFs to aqueous environments.
2.2 Fabrication of Ferroelectric Thin Films

While the fabrication of FETFs has long-since-been the focus of research,[43-45] it remains the focus of debate and development. Even now, new ferroelectric materials and fabrication methods are being developed.[46] Methods for fabricating FETF include chemical solution synthesis, ion beam sputtering, magnetron sputtering, pulsed laser deposition, and chemical vapor deposition. Briefly, we will review each method with noted advantages and drawbacks.

Chemical solution synthesis (CSS), including sol-gel synthesis, is one of the most common and simple methods for fabricating FETF. CSS uses a liquid solution that contains the heavy metal precursors necessary to form the FETFs. Typically, the solution is deposited onto the substrate by spin coating. The organic matrix used to stabilize the heavy metal precursors is then burned off during annealing and the FETF is crystallized during final pyrolysis. CSS is a robust method for fabricating FETFs due to the high control over final film composition and lack of specialized equipment. FETF properties fabricated using CSS, however, typically depend on process conditions and can vary greatly if not well characterized.

Sputtering techniques, such as magnetron or ion beam sputtering, is a reliable method for fabrication of ultra-thin FETFs with epitaxial unit structure. Magnetron sputtering uses a Argon plasma to displace atoms from a target for re-deposition onto a
The plasma is ignited using a large, alternating electric field while a bias voltage is applied to accelerate the Ar\(^+\) ions towards the target. Ion beam sputtering, is similar to magnetron sputtering, except that the Ar\(^+\) ions are directionally accelerated at the target from an ion source under high vacuum.\(^{[48]}\) The displaced atoms are then transported and deposited on the substrate. In both sputtering techniques the deposition rate and composition are controlled by the ion flux. Benefits of sputtering include processing at low temperatures, flexible control over film composition, and prevention of plasma damage. Sputtering of FETFs, however, offers poor control over exact film composition, requires specialized equipment, and long processing times.

Pulsed laser deposition (PLD) of FETFs uses a high-powered laser to ablate a target surface for atomic deposition onto a substrate. The high-powered laser instantaneously vaporizes the target material, creating a plasma plume. PLD if performed under high vacuum. PLD offers fine control over crystal nucleation, deposition rates, and flexible film compositions. However, PLD requires highly specialized equipment, requires empirical estimation of final film composition, and the chamber is highly sensitive to contamination. Furthermore, the substrate size is limited by the chamber design and film uniformity decreases quickly beyond the plume diameter.
Chemical vapor deposition (CVD) and metalorganic chemical vapor deposition (MOCVD), uses volatile precursors that react on the substrate surface to produce the desired thin film. CVD is performed under high vacuum and has been used to produce a number of high-quality FETFs.\textsuperscript{[14,45,49]} Deposition rates are controlled by the gas flow rates, chamber temperature, and chamber pressure. CVD offers high control over the film composition, uniform confirmation to substrate features, reliable deposition rates, and scalability. CVD, however, typically involves toxic volatile vapors and byproducts, requires specialized equipment, and costly source chemicals. Furthermore, metalorganics used in MOCVD are pyrophoric, meaning they will ignite if put in contact with air.

\subsection*{2.3 Ferroelectric Lead Zirconium Titanate}

Ferroelectric lead zirconium titnate (PZT) thin films are an inorganic cermic perovskite material comprised of lead titante or lead zirconate unit cells. Ferroelectric lead titante units cells are tetragonal and maintain a titanium atom in the body center position. Alternatively, lead zirconate unit cells are rhomboderal and anti-ferroelectric, meaning the unit cell dipole moments align to produce a zero electric field. Inclusion of lead zirconate into PZT, however, enhances film switching by reducing in-plane stress and coercive field the PZT thin film.\textsuperscript{[24]} The ferroelectric properties of the PZT are
enhanced at the morphotropic phase boundary, which occurs at a relative atomic concentration of 52:48 Zr:Ti.\textsuperscript{[50]}

Figure 2.3 demonstrates the tetragonal unit cell structure of PZT. Interestingly, crystallographic studies show a shift in both the body-centered titanium cation and the neighboring oxygen atoms during polarization.\textsuperscript{[51]} This asymmetry produces a bi-stable dipole moment in the unit cell. Alignment of unit cell dipole moments across the film results in the expression of relatively high surface charge densities.

\textbf{Figure 2.3:} A PZT unit cell with noted polarization direction due to titanium and oxygen ion displacement within the unit cell from the otherwise centro-symmetric position.

\section*{2.4 Polarization Patterning of Ferroelectric Thin Films}

Polarization of a FETF is typically discussed in reference to a capacitance device where a ferroelectric material is sandwiched between two conductive electrodes.\textsuperscript{[52-55]}
Polarization is accomplished after applying a sufficiently high electric field between the top and bottom electrodes.\textsuperscript{[56]} During polarization, the electric displacement vector inside the ferroelectric aligns with the externally applied electric field. This induces unit cell dipole moment alignment across the FETF that propagates charges to the opposing ferroelectric-electrode interfaces.\textsuperscript{[55,57]} After removal of the externally applied electric field the ferroelectric remnant polarization results in an electric field inside the film and induces compensating charges to exist in the top and bottom electrodes.\textsuperscript{[54,58],[52,53]}

The ability to pattern surface charge on the nanometer length scale is a major benefit to integrating FETFs into interfacial sensing devices. Charge patterning, by scanning probe or conductive stamp, is easily achieved by locally applying a sufficiently high electric field across the film.\textsuperscript{[59,60]} During patterning the ferroelectric domain polarization direction aligns parallel to the externally applied electric field, i.e., the polarization direction of the FETF works to negate the externally applied electric field.\textsuperscript{[60]} As such, to induce a FETF with a positive surface charge at the top surface, it is necessary to apply a negative bias voltage to the top electrode, and vice versa.

Polarization patterns can be generated using a serial or parallel process.\textsuperscript{[61]} Nanometer scale serial patterns are typically scribed using a conductive scanning probe microscopy (SPM) tip. Parallel patterns can be fabricated using a conductive stamp. In both cases, contact between the top and bottom electrode is made using a voltage source
and the applied electric field must be greater than the coercive field of the film. Figure 2.4 demonstrates how polarization patterns can be generated using serial or parallel methods and an external voltage source.

Figure 2.4: (A) Serial polarization of a FETF domain using a biased conductive SPM tip, (B) Serial polarization of multiple domains using a biased conductive SPM tip, and (C) Parallel polarization patterning of a polycrystalline FETF using a biased conductive stamp.
2.5 The Ferroelectric-Gas Interface

Although understanding FETF surface properties is important for developing interfacial sensing devices,[62] little is known about how these films interact with gaseous environments. A number of papers present FETFs as a promising platform for gas phase sensing. For example, surface adsorption onto a FETF has been shown to depend on to films’ polarization direction.[63] Furthermore, the FETF polarization direction has been shown to switch after exposure to reactive species.[64] Other papers, however, have shown that exposure of FETFs to a gaseous environment results in the disruption of the interfacial unit cell structure, potentially resulting in negation of the film’s remnant polarization[60,65-67] or the formation of a dielectric dead layer.[68,69] Exposure of FETFs to humid environments can also induce polarization inversion of the film,[70] and repeated polarization switching of FETFs under humid conditions can cause stress-induced cracking and breakdown.[71]

FETF domain orientation has been shown to induce differences in gas-phase adsorption possibly providing a new platform for gas phase sensing and device development. For example, poled lithium niobate causes increased adsorption energy of 2-propanol vapor when compared to propanol adsorption on unpoled samples.[72] Furthermore, increased amounts of methanol vapor adsorb onto positively poled
regions of barium titanate, when compared to unpoled or negatively poled regions of the sample.[63]

In addition to preferential adsorption, polarization orientation can also improve surface reaction rates of gaseous species, possibly replacing high-cost precious metal catalysts.[73-75] Un-polarized barium titanate and strontium titanate thin films were studied in the heterogeneous catalysis of carbon monoxide and hydrogen[76] and it was found that both a ferrocatalytic and a photocatalytic effect increased the surface activation of gaseous species. Moreover, positively poled thin films of lithium niobate lowered the activation energy of carbon monoxide oxidation on surface-confined palladium nanoparticles.[77] Interestingly, no activation energy change was observed with negatively poled lithium niobate surfaces.

The sensitivity of FETFs to reactive gaseous species has also been exploited for chemical sensing. For example, exposure of lead titanate to various partial pressures of oxygen produced the first chemically induced hysteresis loop.[64] In this experiment, controlled changes in oxygen partial pressure caused polarization switching events due to thermodynamically driven surface charge compensation via oxygen vacancies. This switching behavior was verified by density functional theory calculations.

Development of commercial sensing applications, however, is hindered by non-specific binding of other gas phase molecules. For example, the exposure of FETFs to air
results in the non-specific adsorption of both polar and non-polar gases, such as CO₂, H₂, O₂, N₂, and H₂O.[64,76,78,79] Additionally, chemisorption of adsorbed species is directly dependent on the concentration of surface defect sites.[63]

2.6 The Ferroelectric-Liquid Interface

The stability of FETFs in aqueous environments can enable integration with interfacial sensing devices. Recently, the piezoresponsive properties of ceramic FETFs have been harnessed for liquid-phase PFM.[80] Liquid-phase PFM images of 95/5 PZT thin films show clear domain structure and contrast over a range of ionic strengths. Although FETF piezoresponse has been demonstrated in liquid environments, a great deal is still unknown about how liquids interact with or change the interfacial ferroelectric properties. Alignment of barium titantate nanoparticles has also been achieved by application of an externally applied electric field in pure ethanol.[81]

The majority of research on FETF liquid-phase exposure has exploited the photoelectric effect which has been demonstrated on naturally polarized[82] and on patterned FETF surfaces.[83] In this process, UV radiation excites valence band electrons in the FETF into the conduction band, and once mobile, these electrons are susceptible to the internal electric field of polarized FETFs and transported to the positively poled surface of the film. Once at the surface, they induce electrochemical reduction of surface
bound species. A number of transition metals, including Pb, Ni, Fe, Co, Pt, Pd, Rh, Au, and Ag have been deposited onto the surface of FETFs. The possibility of cationic charge shielding was eliminated because metal deposition is isolated to the upward polarized (surface positive) domains. Experiments have been performed in a variety of ionic solutions. More recent work demonstrates and discusses the role of a Stern layer above the polarized ferroelectric domains. Taken together these experiments demonstrate that the internal electric field of polarized FETFs is maintained in aqueous environments.

In situ surface catalysis can be influenced by FETFs. For example, it was shown that polarization direction affects the catalytic efficiency of titanium dioxide nanoparticles confined to the FETF surface. More recently, titanium dioxide nanoparticles on a polarized PZT surface induced the degradation of Rhodamine B in water, thus establishing applications for removal of harmful carcinogens. Alternatively, FETFs have also been used for photo-induced electrolytic breakdown of water into H₂ and O₂ in water. Unfortunately, the generation of reactive hydrogen on PZT resulted in film degradation and an increase in dielectric losses. The prolonged exposure of ferroelectric capacitors to aqueous environments, however, does not alter ferroelectric hysteresis. Alternatively, film regeneration is possible by re-annealing the FETF or cleaning with dilute nitric acid solution.
Despite these insights, a number of important questions still remain unanswered regarding the effect of liquid phase exposure on FETF interfacial properties, including: what is the long-term stability of FETFs in aqueous environments, is the polarization state of FETFs capable of influencing EDL formation, and can the FETF polarization state influence interfacial forces in liquid environments?

2.7 Scanning Probe Microscopy

The scanning probe microscope (SPM) enables the reliable measurement of pico-Newton scale forces with nanometer scale spatial resolution. For detailed information we refer the reader to a number of reviews of scanning probe microscopy. Briefly, the SPM uses the deflection of a laser off the back of a micron-scale cantilever to measure the force applied on the cantilever (Figure 2.5). Over the years, the SPM has enabled a broad range of imaging modes. Here, we review three imaging modes that are used to study ferroelectric interfacial properties: Kelvin force probe microscopy (KPFM), piezoresponse force microscopy (PFM), and colloidal probe force microscopy (CPFM).
2.7.1 Kelvin probe force microscopy

Kelvin probe force microscopy (KPFM) is a non-contact imaging mode that provides high-resolution spatial maps of the surface potential distribution.[99,100] KPFM measures changes in differential capacitance between the tip and the surface due to local changes in surface work function. KPFM imaging uses a two-pass system where each slow-scan line is imaged twice, once in contact and once out of contact (Figure 2.6). Surface topography is captured during the first pass. During the second pass, the tip is raised to a offset distance above the surface (typically 10-50 nm) while a feedback loop is
used to measure surface potential between the probe and the substrate along the slow scan line. During surface potential measurement, an AC bias voltage and a DC bias voltage are applied to the tip and the total force felt by the cantilever is modeled as a parallel plate capacitor (Equation 2.1),

$$F = \frac{1}{2} \frac{\partial C}{\partial z} V^2,$$  \hspace{1cm} (2.1)$$

where \(F\) is the force on the cantilever, \(\frac{\partial C}{\partial z}\) is the change in capacitance with respect to the separation height, and \(V\) is the total potential difference between the cantilever and surface.

The total potential difference between the probe and surface is the sum of the applied AC bias (\(V_{AC}\)), the applied DC bias (\(V_{DC}\)), and the surface potential (\(V_{SP}\)) (Equation 2.2),

$$V = V_{SP} + V_{DC} + V_{AC} \sin (\omega t),$$  \hspace{1cm} (2.2)$$

where \(\omega t\) is the AC drive frequency multiplied by time. To optimize KPFM sensitivity, the AC bias voltage frequency is tuned to be near the free-air resonance frequency of the cantilever. Substituting equation 2.2 into equation 2.1, we find the total force measured by the cantilever during KPFM measurement (Equation 2.3),

$$F = \frac{1}{2} \frac{\partial C}{\partial z} \left( [V_{DC} - V_{SP}] + \frac{1}{2} V_{AC}^2 + 2[(V_{DC} - V_{SP})V_{AC} \sin (\omega t)] - \frac{1}{2} V_{AC}^2 \cos (2\omega t) \right).$$  \hspace{1cm} (2.3)$$

As can be seen, there are three forces acting on the cantilever during KPFM measurement. The first term is static, meaning it does not depend on the AC signal.
being sent to the tip. The second term depends on the AC drive frequency and scales linearly with the voltage difference between the applied bias and the measured surface potential. The third term oscillates at twice the drive frequency and depends on the square of the AC drive bias. By setting the DC bias of the cantilever equal to the surface potential of the sample, the oscillatory force at $\omega$ will be nulled. As such, during KPFM measurement the DC bias is varied through a feedback loop to be equal to the surface potential of the sample. The measured DC bias applied to the cantilever provides an exact map of the sample’s surface potential during imaging.

**Figure 2.6:** Diagram of two-pass imaging method used during KPFM.
The surface potential of polarized FETFs has been well studied using KPFM.\cite{41,58,67,68} The local potential of a FETF is a function of both the film polarization and the presence of surface screening charges.\cite{102,103} During KPFM measurement the measured potential is a result of the surface charge due to polarization, free charge carriers in the film, and surface adsorbates.\cite{104} KPFM imaging in air has shown that screening charges dominate the measured surface potential of the FETF\cite{41,60,105,106} to the point of overcompensation.\cite{55,60,135,145} Figure 2.7 presents the topography of our US-PZT, the applied tip bias during polarization, and the measured KPFM surface potential. Note that the measured surface potential does not correlate with a change in topography.
**Figure 2.7:** (A) US-PZT topography of a 2 x 2 μm area (z height ±10 nm), (B) map of applied tip bias during polarization pattern on US-PZT using ±8 V, (C) KPFM images of US-PZT surface after polarization patterning, and (D) 3D rendering of the measured surface potential. KPFM images were performed in air with a Mikro Masch NSC14 Ti/Pt probe, a 30 nm lift-off tip spacing, and a 3 V tip bias (surface potential z scale of ±0.6V).

### 2.7.2 Piezoresponse force microscopy

Piezoresponse force microscopy (PFM) is a contact mode imaging technique that uses the electromechanical response of the FETF to map the crystallographic orientation and grain structure of surfaces.\[^{60,107}\] PFM induces an electromechanical response in the surface by applying an AC voltage signal through the conductive cantilever into the sample. The AC signal is tuned to the contact resonance of the cantilever and surface.\[^{108}\]
PFM measures the cantilever deflection amplitude and phase to determine the ferroelectric grain structure and orientation (Figure 2.8).

**Figure 2.8**: Schematic of how PFM uses the electromechanical response of the FETF to map the substrate grain structure.

Because PFM is a contact mode imaging technique, it provides a high-resolution map of the local grain orientation. The effect of ferroelectric grain structure on topography explains the similarity between the piezoresponse amplitude image and topographical profile (Figures 2.9 A and 2.9 B). The piezoresponse amplitude is decreased at the grain boundaries because of the loss in crystallinity. The phase of the piezoresponse depends on the polarization orientation of the underlying ferroelectric where a 180° phase shift is observed between an upwards and downwards oriented polarization (Figure 2.9 C). The contact resonance frequency can also change due to changes in the underlying elastic modulus, polarization orientation, and topography. To
maintain contact resonance during scanning, an advanced PFM technique has been
developed called Dual Amplitude Resonance Tracking PFM (DART-PFM). DART-PFM
uses a lock-in amplifier and feedback loop to maintain a contact resonance during
scanning. While DART-PFM improves image quality, it remains purely a qualitative
technique due to topographic cross-talk.[109] Figure 2.9 presents a DART-PFM image of
the polarization patterned US-PZT thin film presented in Figure 2.7 B. Note that, unlike
KPFM, DART-PFM shows a sharp boundary between the oppositely polarized regions.
Additionally, the DART-PFM signal reflects the orientation of the US-PZT thin film,
regardless of screening charges.

![Figure 2.9](image)

**Figure 2.9:** (A) US-PZT topography of a 2 x 2 µm area (z height ±10 nm), (B) DART-PFM
images of amplitude, and (C) phase taken in air with an NT-MDT DCP11 conductive-
diamond coated probe at 0.5 Hz fast-scan frequency, a deflection set point of 0.1 V, and
an initial resonance frequency of ~544 kHz.
2.7.3 Colloidal probe force microscopy

Colloidal probe force microscopy (CPFM) measures the normal component of the interfacial force acting on the cantilever as the colloidal probe (attached to the tip of the cantilever) is brought into contact with, or vicinity of the surface.\[110\] CPFM uses a large colloidal probe, typically with a diameter between 2 and 20 µm, attached to a soft cantilever. Both the cantilever and substrate are typically submerged in a liquid (Figure 2.10). CPFM has been used to measure a variety of interfacial forces, including electric double layer interactions,\[111\] surface viscoelastic behavior,\[112\] and adhesion forces.\[113\] Due to the size of the colloidal probe, lateral resolution is limited, but because the probe diameter can be accurately measured, it provides quantitative force-separation information between surfaces. The ability to produce colloidal probes of different materials or coatings has broadened the field to a number of interfacial sensing techniques. Colloidal probes have been made of silica, rutile TiO$_2$, polystyrene, or have been coated in gold for subsequent functionalization.\[111,114-116\]
The study of EDL interaction between a charged probe and polarized FETF requires meticulously cleaned surfaces and solutions of known ionic strength. Any contamination (e.g., surfactant, dirt, or divalent ions) can dramatically alter or inhibit the detection of overlapping EDLs.\textsuperscript{117} If two clean, like-charged surfaces approaching each other in a dilute electrolyte solution, the local increase in counter-ion concentration produces a repulsing osmotic pressure between the surfaces. To demonstrate this, a clean, borosilicate colloidal probe and silicon dioxide surface were placed in dilute electrolyte solution. Both the borosilicate probe and silicon dioxide surface have a
negative surface charge in aqueous environments. The negative surface charge gives rise to a diffuse cloud of cations above the surface in the solution. As the two surfaces approach each other, the two clouds of cations are force together, increasing the osmotic pressure between the surfaces resulting in the increasing repulsive force with decreasing separation distance. At small enough separation the van der Waals interaction between the two surfaces dominates and induces the observed “snap-in” and interfacial contact. A typical force-separation approach curve between a borosilicate probe and silicon dioxide surface is presented in Figure 2.11. The solid line in Figure 2.11 is the fitting of a theoretical EDL model to the measured force-separation data. Details of the EDL model and curve fitting are covered in section 2.8.
Figure 2.11: Force-separation curve for silica-silica interaction in $10^{-4}$ M KCl. The blue fitting is based on an EDL theory derived using a linearized Poisson-Boltzmann and constant charge boundary conditions ($\Psi_{\text{silica}} = -39$ mV).

Effects of Hydrodynamic Forces in CPFM Measurements

The measurement of interfacial forces as a function of separation distance involves (for sample scanned SPM) the movement of a viscous liquid past a colloidal probe. If the fluid velocity is too large, the hydrodynamic drag can unduly contribute to the measured normal force. The hydrodynamic force can be modeled as Stokes drag on a sphere traveling through a Newtonian fluid (Equation 2.4).

$$F_H = -6\pi \eta U \frac{a^2}{h}$$  \hspace{1cm} (2.4)
where \( \eta \) is the fluid viscosity, \( U \) is the sphere velocity, \( a \) is the sphere radius and \( h \) is the separation distance. Researchers have found, however, that the hydrodynamic drag of a 10 \( \mu \)m diameter colloidal probe is negligible if the probe velocity is less than 400 nm sec\(^{-1} \) in water.\(^{[111,120]} \)

**Effects of Surface Roughness in CPFM Measurements**

Surface roughness of the colloidal probe and the substrate can dramatically effect CPFM measurements. Increased surface roughness can decrease the measured EDL interaction force and make it hard to determine the “snap-in” point.\(^{[121-123]} \) The decrease in EDL interaction force has been attributed to an effective increase in the separation distance between the two surface,\(^{[124]} \) which reduces both the van der Waals\(^{[125]} \) and the electrostatic\(^{[126]} \) contributions to the total interaction force. For accurate measurement of the substrate surface potential it is thus necessary to minimize probe and surface roughness.

**2.8 Electric Double Layer Theory**

Electric double layer theory is used to explain the interaction force as a function of separation distance between two charged plates in a uniform solution. EDL theory has advanced a number of practical applications, including water treatment, filtration,
and colloidal stability. A broad range of materials, including oxides, polymers, and silica-based clays, express a net surface charge in aqueous environments.\cite{111,127,128} The total EDL interaction force, as a function of separation distance between two approaching charged surfaces, is the summation of osmotic, Coulombic, and van der Waals forces. As two surfaces approach each other, the clouds of counter-ions are forced together. If the surfaces are like-charged, the osmotic forces become increasingly repulsive with decreasing separation distance. If the surfaces are oppositely charged, the osmotic force becomes increasingly attractive with decreasing separation distance. The Coulombic force between the surface and the counter-ion cloud is always small and attractive.\cite{129} At small enough separations the van der Waals interaction between the two surfaces dominates and induces surface contact. The sum of these interaction forces produces a net force as a function of separation distance (Figure 2.12).
Figure 2.12: Example plots for the EDL interaction forces as a function of separation distance between two (A) same charge and (B) oppositely charged surfaces in solution.

Typically, an EDL of counter-ions forms in the presence of a charged surface in solution to negate the charge expressed by the surface. The EDL structure typically involves a Stern layer and a diffuse double layer (Figure 2.13). The Stern layer is considered as a sheet of counter-ions that is adsorbed onto the surface which can be modeled as a parallel-plate capacitor between the inner Helmholtz plane (IHP) and the outer-Helmholtz plan (OHP) (Equation 2.5),\textsuperscript{130,131}

$$C = \frac{d\sigma}{d\psi},$$  \hspace{1cm} (2.5)

where $C$ is capacitance, $\sigma$ is the surface charge density, and $\psi$ is the surface potential. The diffuse double layer extends beyond the OHP and is modeled as an exponentially decreasing concentration of counter-ions. The ion concentration of the diffuse double
layer is modeled using the Poisson-Boltzmann equation (Equation 2.6), which is a function of surface potential, ion charge, solution temperature, ion strength, and the dielectric constant of the solution.\footnote{115}

\[ \nabla^2 \psi = -\frac{\rho(x)}{\varepsilon_0 \varepsilon_r} \]

(2.6)

where \( \psi \) is the electrostatic potential, \( \rho(x) \) is the electrostatic charge density, \( \varepsilon_0 \) is the absolute permittivity, and \( \varepsilon_r \) is the relative permittivity. Typically Equation 2.6 is reduced to the Gouy-Chapman model for a plate-plate geometry interacting through a uniform dilute electrolyte solution (Equation 2.7),

\[ \frac{d^2 y}{dz^2} = \kappa^2 \sinh y, \]

(2.7)

where \( y = \frac{q \psi}{k_B T} \) is the dimensionless electrostatic potential, \( q \) is the elementary charge, \( z \) is the ion charge, \( \psi \) is the actual electrostatic potential, \( k_B \) is the Boltzmann constant, \( T \) is the absolute temperature, \( \kappa^{-2} = \left[ \frac{z \varepsilon_0 \varepsilon_r k_B T}{2 n q^2} \right] \) is the Debye screening length for a \( z:z \) electrolyte, and \( n \) is the atomic concentration.

Because the surface potential is a function of an equilibrium ion exchange reaction between the surface and the solution, it depends on the solution ionic strength, pH, and temperature.\footnote{130,132,133} This interdependence in the surface potential and EDL formation provides an field of continued research and debate in colloidal and interface science.
Figure 2.13: EDL structure of a negatively charged surface in dilute electrolyte solution. The line plot models the potential energy distribution across the Stern layer and the diffuse double layer.

Effects of Surface Roughness on EDL Interaction Energy

Increasing the roughness of charged surfaces significantly decreases the overall interaction energy in liquids.\[^{121-123}\] Theoretical models have attributed this to an effective increase in the separation distance between the two surfaces.\[^{124}\] The increase in the separation distance reduces both the van der Waals\[^{125}\] and the electrostatic\[^{126}\] contributions to the total interaction energy. As a result, an increase in surface roughness has been shown to increase particle deposition,\[^{124}\] membrane fouling,\[^{124}\] and flocculation.\[^{134}\]
2.8.1 Derjaguin-Landau-Verwey-Overbeek theory

Derjaguin-Landau-Verwey-Overbeek (DLVO) theory is used to describe the interaction energy between two charged surfaces approaching each other through a uniform dielectric medium.\cite{116,129} The theory assumes the total interaction energy ($W_T$) of two overlapping double layers is the summation of van der Waals ($W_{vdW}$) and electrostatic ($W_{ES}$) energies (equation 2.8).\cite{115,127}

\[ W_T = W_{ES} + W_{vdW}. \] (2.8)

Although simple, DLVO theory has been shown to accurately describe the interaction potential of two surfaces.\cite{95,111,117} The van der Waals interaction energy dominates at small separation distances, on the order of a few nanometers, while the electrostatic interaction energy can dominate over longer separation distances, between a few and a hundred nanometers, depending on the solution ionic strength.\cite{135} The double layer interaction energy is of finite magnitude with a characteristic length that is determined by the surface charge densities and ionic strength of the solution. Because the total interaction energy is geometry dependent, the computational complexity often prohibits the generation of an analytical solution.\cite{136-138} As such, the Derjaguin approximation is often used to estimate the theoretical force as a function of separation.\cite{139,140} The Derjaguin approximation relates the normal force measured for a sphere-sphere or sphere-plate geometry to the interaction energy calculated for a plate-plate geometry. We use the Derjaguin approximation to express the interaction force
between the colloidal probe (modeled as a sphere) and our US-PZT surface (modeled as a flat plate) in terms of a plate-plate interaction energy, which has been shown to be valid for when the inverse Debye length, multiplied by the probe radius, is larger than 10.\cite{141}

**van der Waals Interactions**

A large body of work regarding the interaction forces between molecules has been based on the thesis work of Johannes van der Waals regarding the interaction forces between molecules. Hamaker, Lifshitz, and Casimir extended this work to macroscopic solids through the pairwise summation of forces between molecules.\cite{142,143,144} Their work has been used to explain the short-range interaction of various neutral and conducting surfaces as a function of geometry, separation distance, and Hamaker constant (A).\cite{135,143,144} The Hamaker constant for two different solids interacting through a uniform solution depends on the surface geometries, the dielectric constants, and refractive indices of the materials. Lifshitz theory can be used to estimate the Hamaker constant for different interacting surfaces by the summation over a zero frequency (v=0) and a higher frequency (v>0) contribution (equation 2.9).\cite{135,143,144}

\[
A = A_{v=0} + A_{v>0}.
\]  
(2.9)
Typical values for the Hamaker constant of solid oxide surface interacting through water are on the order $10^{-20}$ Joules.$^{[139,145]}$ The electromagnetic nature of the van der Waals interaction can lead to retardation, or decrease in interaction energy due to the Casimir force, between two neighboring bodies with more than a few nanometers of separation.$^{[129,146]}

**Electrostatic Interactions**

The long-range electrostatic interaction energy results from the force exerted on each surface due to a change in the osmotic pressure.$^{[130-132]}$ The counter ion concentration within the diffuse double layer is calculated by the Poisson-Boltzmann equation. DLVO theory uses a linearized form of the Poisson-Boltzmann equation by applying the assumption that the surface potential is less than the surrounding thermal noise ($\Psi < 25 \text{ mV}$) (equation 2.10).$^{[147]}

$$\frac{d^2\Psi}{dz^2} = \kappa^2 \Psi. \quad (2.10)$$

This linearization assumption allows for the analytical solution of the electrostatic interaction energy between charged surfaces in solution.$^{[137,140,148,149]}$ Solution of the linearized Poisson-Boltzmann equation requires two boundary conditions. The force-separation approach curve can change significantly based on the boundary conditions applied to the surface. Common boundary conditions include constant
charge, constant potential, and charge regulation. The constant potential boundary condition describes the interaction energy between two charged surfaces where the surface potential does not change with separation distance (Equation 2.11),

$$\psi_{surface} = \psi_0.$$  \hspace{1cm} (2.11)

If the interaction force as a function of separation distance can be modeled using a constant potential boundary condition at the surface, then a potential-determining ion is in solution. The potential determining ion is able to reversibly bind to the surface, reducing the surface charge with decreasing separation distance. The constant charge boundary condition describes the interaction energy between two charged surfaces when no potential-determining ion exists in solution. As such, the surface potential can increase dramatically with decreasing separation distance (Equation 2.12),

$$\sigma_{surface} = -\varepsilon_0\varepsilon_r \frac{d\psi}{dz}_{z=0}.$$  \hspace{1cm} (2.12)

The constant potential and constant charge boundary conditions can be considered lower and upper limits to the interaction energy of two surfaces, respectively.\[^{130,145,147}\] Typically, however, the interaction force as a function of separation distance falls in between these that predicted by constant potential and constant charge approximations. In these cases, the charge regulation approximation is used to model the interaction force as a function of separation distance.\[^{130,132,139,140,150,151}\] Equations 2.13 describes the linear charge regulation boundary condition,
\[ \sigma_{\text{surface}} = S - K\Psi, \]  \hspace{1cm} (2.13)

where \( S \) is the surface charge of the isolated surface and \( K \) is the regulation capacitance of the surface. \( K \) is a constant value that is greater than zero. If \( K \) approaches infinity the surface acts similar to a constant potential surface, while if \( K \) approaches zero the surface acts like a constant charge surface.

**Non-linear Poisson-Boltzmann Equation**

Because DLVO theory uses the linearized form of the Poisson-Boltzmann equation, it fails to accurately predict the interaction force between two charged plates at close separation (e.g., tens of nanometers or less). Some have addressed this by using the full, non-linear form of the Poisson-Boltzmann equation (Equation 2.6). In this case, the interaction force as a function of separation distance is determined numerically. For additional information, I refer the reader to the following articles.\[^{138,152,153}\]

**2.9 Guided Deposition of Colloidal Particles**

The study of colloidal deposition is important to a number of practical applications including filtration, separation, and sensing. Most charge-heterogeneous surfaces are fabricated by patterning chemically different regions which undergo an ion exchange processes once in an aqueous environment.\[^{129}\] A number of researchers have
demonstrated the guided deposition of colloidal particles onto chemically modified surfaces such as thiol monolayers,\textsuperscript{154} silanes,\textsuperscript{155} and charge injected surfaces.\textsuperscript{9,156} The most popular method for predicting colloidal deposition onto two-dimensional surfaces is the random sequential adsorption (RSA) model.\textsuperscript{157-159} A number of researchers have expanded on the RSA model to include surface charge heterogeneity with finite dimensions.\textsuperscript{160,161} The RSA model uses Monte-Carlo simulations with a particle-overlap exclusion condition to determine the theoretical particle distribution on the surface. To simulate the particle distribution, a particle is randomly positioned above the surface and brought into contact with the surface assuming a perfect sink boundary condition. If the approaching particle overlaps with the diameter of a previously deposited particle, no deposition occurs. If the approaching particle does not overlap with a previously deposited particle, deposition occurs. This simple model has successfully described the distribution of particles adsorbed onto the surface of charge-heterogeneous surfaces.\textsuperscript{161} To study the kinetics of colloidal particle deposition, it is necessary to include the diffusive and EDL forces imposed on the particle in solution and determined by the transport equation.\textsuperscript{162} Theoretical work has shown that the particle deposition rate strongly depends on both the particles radius and the ionic strength of solution.\textsuperscript{163,164} The contribution of Brownian, diffusive, EDL, and van der Waals forces produce a
distribution of particle deposition rates with respect to particle size and ionic strength.\textsuperscript{165}

\textbf{2.10 X-ray Photoelectron Spectroscopy}

X-ray photoelectron spectroscopy (XPS) is a quantitative tool used to measure the atomic composition and chemical bonding environment of a surface.\textsuperscript{166} XPS measures the kinetic energy of inner-core electrons that were ejected after irradiation with high energy X-rays. The measured kinetic energy is specific to the electron binding energy of a particular atom and it’s binding configuration. XPS measurements are limited to the top few nanometers of a sample.\textsuperscript{167} Peak broadening of high-resolution XPS scans provides information on the chemical bonding structure of a particular element in the sample.\textsuperscript{166} Deconvolution of the spectral envelope is used to determine the chemical structure of the surface. XPS has been used to determine the surface atomic composition and chemical structure for various FETFs.\textsuperscript{168-171}

\textbf{2.11 X-ray Diffraction}

X-ray diffraction (XRD) is a non-destructive measurement technique that can measure the crystal structure and the internal strain of crystalline solids and thin films. XRD uses the elastic scattering of X-rays off of crystal planes within the material.\textsuperscript{172} By
varying the angle of incidence, diffraction peaks are measured that correlate with the inter atomic spacing of the crystal lattice planes.\textsuperscript{[173,174]} Bragg’s law is used to determine the spacing between crystal planes (Equation 2.14),

\[ n\lambda = 2dsin\theta, \]  

(2.14)

where, \( n \) is the lattice number, \( \lambda \) is the wavelength of the X-ray beam, \( d \) is the interatomic spacing, and \( \theta \) is the angle of incidence.

Due to the small cross sectional area of a thin film, a grazing-angle XRD geometry is used to study FETF crystal structure.\textsuperscript{[175]} Grazing-angle XRD uses an extremely small angle of incidence (less than 1°) to enhance measurements of the thin film crystalline lattice over the bulk supporting material. Figure 2.14 shows the grazing angle XRD geometry. Based on the angular position of the Bragg peaks, it is possible to determine the crystalline structure of the ferroelectric thin film.\textsuperscript{[144,176-178]}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{grazing_angle_XRD.png}
\caption{Schematic of grazing angle X-ray diffraction.}
\end{figure}
3. Fabrication of Ferroelectric Ultra-Smooth Lead Zirconium Titanate Thin-Films for Use in Aqueous Environments

3.1 Introduction

Fabrication of ultra-smooth FETFs is essential for the measurement and control of EDL formation in aqueous environments. Here, we present a novel process for the fabrication of ultra-smooth 52/48 PZT thin films from a sol-gel precursor. The presented procedure results in US-PZT thin films that have mean surface roughness that is below the EDL inverse Debye length for dilute electrolyte solutions.

The integration of ferroelectric materials into micro-electromechanical devices,\textsuperscript{[13,179]} field effect transistors,\textsuperscript{[180,181]} and high permittivity capacitors\textsuperscript{[182]} has enabled a multitude of solid state device capabilities.\textsuperscript{[22,183-185]} With the continued decrease in device size and ferroelectric film thickness, device function is increasingly sensitive to interfacial roughness.\textsuperscript{[40,184,186-188]} The ability of ferroelectric thin films (FETFs) to retain electric polarization without the continued supply of external power also makes them attractive for integration into self-contained, liquid-phase sensing devices.\textsuperscript{[189-192]} FETF integration into interfacial sensing devices could circumvent the common problems associated with electrode-based analogs, such as Faradaic currents and electrolysis.\textsuperscript{[193,194]} Using the non-Faradaic surface charge densities expressed by polarized FETFs could lead to the development of new, passive diagnostic testing devices.\textsuperscript{[192]} For example, the
The bi-stable polarization state of FETFs may provide another route for the guided deposition of target molecules, e.g., proteins, from solution.\cite{195-197} Integration of FETFs into such applications, requires their ferroelectric, chemical, and mechanical stability in water.\cite{192} Another important aspect for fluid-based sensing applications is low surface roughness, which is required for detection of nanometer-scale analytes from solution.\cite{121,122,124,198} We thus anticipate that the fabrication of crack-free, low roughness FETFs is an important objective to enable FETF based sensing devices in aqueous environments and will provide new functionality for interfacial sensing and lab-on-a-chip devices.\cite{61,181,199}

Synthesis of FETFs for functional devices has steadily improved \cite{190,200-203} due to a better empirical understanding of how fabrication conditions affect thin-film properties.\cite{45,202,204} The alteration of annealing conditions, for example, affects the orientation of ferroelectric crystals,\cite{205} dielectric properties,\cite{206} and ferroelectric phase formation within the FETF.\cite{207} Furthermore, differences in thermal expansion coefficients between the bottom platinum electrode and the FETF increase residual stress in the FETF, with deleterious effects on its properties.\cite{204,208-211} The large residual stress in the film is responsible for both film cracking and the decrease in ferroelectric remnant polarization.\cite{29,174,212} Research is still needed, however, to determine how these changes affect surface roughness and structural integrity in water.
Various methods are available for the fabrication of FETFs and include laser ablation,\cite{213,214} sputtering,\cite{215} milling,\cite{216,217} and sol-gel processing.\cite{22,184,218} Compared with sol-gel processing, the other methods have a number of drawbacks that include high cost, the need for specialized equipment, the lack of compositional control, and a high risk of contamination.\cite{213,219-221} Sol-gel fabrication of FETFs, on the other hand, is a multi-step, path-dependent process (Figure 3.1) that can be integrated easily with established device fabrication schemes.\cite{222,223}

![Fabrication steps involved in producing US-PZT thin-films from a sol-gel precursor.](Figure 3.1: Fabrication steps involved in producing US-PZT thin-films from a sol-gel precursor.)
Lead zirconium titanate (PZT) is one of the first and most commonly studied types of ferroelectric materials.\cite{224-227} Typically reported PZT surface roughness values range between 10 and 20 nm over a 25 µm² area.\cite{226,228} Only one example of a sol-gel PZT thin-films with nanometer scale root mean square (RMS) surface roughness has been reported; however, neither a detailed description nor a rationale was provided as to why the chosen processing conditions resulted in lower film surface roughness.\cite{187,229} As such, there remains a need to systematically study how PZT film topography changes with processing conditions.

Here, we demonstrate a reliable, sol-gel based synthesis approach for ultra-smooth lead zirconium titanate thin-films with surface roughness values between 2 and 4 nm over a 25 µm² area. We define our films as “ultra-smooth” to indicate the order-of-magnitude reduction in surface roughness compared with PZT thin-films previously reported as “smooth”. We find that careful consideration of heating and cooling rates throughout the sol-gel fabrication process minimizes the FETFs’ residual stress and results in crack-free US-PZT with nanometer-scale surface roughness. By using an optimized fabrication process, our film roughness values were uniform across a 3 inch wafer and the films were largely defect free. We also demonstrate that the lack of cracks,
pinholes, and other defects is essential for maintaining film integrity and functionality after prolonged exposure to aqueous environments.

3.2 Experimental Section

Sample Preparation: Silicon wafers (<100>, Virginia Semiconductor) were first cleaned by sonication for 10 min in 0.5 % SDS solution, rinsing 10 times with Milli-Q grade water (18.2 MΩ·cm), immersion for 20 min in 3:1 H₂O₂:H₂SO₄ (Piranha solution), rinsing 10 times with Milli-Q grade water, and drying in a stream of N₂. Next, 200 nm of titanium and 100 nm of platinum were deposited using a Kurt Lesker PVD 75 e-beam source evaporator at ~4x10⁻⁵ Torr (Figure 3.1, Step 1).

Sol-Gel Synthesis: US-PZT thin-films were fabricated from a sol-gel precursor (52/48/125, Mitsubishi Materials Corp.). The sol-gel solution was stored under dry conditions at 5°C and protected from light. Prior to deposition, the sol-gel was warmed to room temperature and sonicated for 15 min. The precursor was passed through a 0.1 μm filter and deposited onto the platinum-coated silicon substrate, making sure to completely cover the substrate surface. The sol-gel precursor was then spin-coated using a two stage ramp profile (5 sec spin at 500 RPM followed by 35 – 45 sec at 1250 - 3000 RPM). Next, the solvent was evaporated on a hot plate (Figure 3.1, Step 2). We tested hot plate temperatures of 60°C, 90°C, and 200°C and evaporation times between 60 sec
and 300 sec. The films were next pyrolized in a Thermolyne Benchtop annealing furnace, in which we tested pyrolization temperatures of 350 and 450°C (Figure 3.1, Step 3). The films were allowed to cool at a rate of either 0.5°C sec\(^{-1}\) or 10°C sec\(^{-1}\) post pyrolization. Next, the films were annealed using either a rapid thermal annealer (Jipelec JetFirst 100) or an annealing furnace (Figure 3.1, Step 4). Rapid thermal annealing (RTA) temperatures tested included 600°C and 700°C for 15 or 60 sec. Alternatively, final annealing was performed in a conventional annealing furnace at 700°C for 20 min. All PZT samples were stored in a desiccator between measurements.

Among the wide range of tested processing conditions, we found that US-PZT films were produced by a combination of the following conditions: 1) hot plate evaporation at 90°C for 120 sec, 2) pyrolization at 450°C for 35 min followed by slow cooling at a rate of 0.5°C sec\(^{-1}\), and 3) film annealing by RTA at 700°C for 20 sec followed by rapid cooling (~5°C/sec). Table 3.1 outlines some of the critical processing conditions used in the fabrication of rough and US-PZT thin films discussed in this paper.

**Crystal Characterization:** Grazing angle X-ray diffraction spectra (Panalytical X'Pert PRO MRD HR, \(\lambda_{CuK\alpha} = 1.5419 \ \text{Å}\)) were obtained with an incidence angle of 0.6°. High resolution scans were taken for a range of 2θ values around 31° (corresponding to the <110> peak), with an angular step size of 0.02° and acquisition times ranging from 1 sec to 8 sec per step. High resolution scans were repeated for a range of Psi angles (\(\psi =\)
5°, 10°, 20°, 30°, and 40°). Interplanar spacing was determined using Bragg’s law.\textsuperscript{[173]} To determine the residual stress of the film, the 2θ peak position for each Ψ angle was determined using Equation 3.1.\textsuperscript{[230]}

\[
\frac{d_{\alpha\Psi} - d_0}{d_0} = \frac{1+v}{E} \sigma \cos^2 \alpha \sin^2 \Psi + \frac{1+v}{E} \sigma \sin^2 \alpha - \frac{2v}{E} \sigma, \tag{3.1}
\]

where \(v\) is Poisson’s ratio, \(E\) is Young’s modulus, \(d_0\) is the interplanar spacing at \(\psi = 0\), \(d_{\alpha\Psi}\) is the interplanar spacing at \(\psi \neq 0\), and \(\alpha\) is the peak position minus 0.6° (the grazing angle of incidence) at \(\psi = 0\). The residual stress of the PZT film was calculated using literature values for Poisson’s ratio and elastic modulus of PZT thin-films.\textsuperscript{[227,231]}

X-ray photoelectron spectroscopy (XPS) spectra were acquired on a Kratos Analytical Axis Ultra Photoelectron Spectrometer equipped with a monochromatic Al K\(\alpha\) source. Charge neutralization was active during spectrum acquisition, and the binding energy spectra were referenced to the C 1s peak set at 285.0 eV.

**Ferroelectric Characterization:** Prior to ferroelectric characterization, gold contacts with a diameter of 50 \(\mu\)m were evaporated (Kurt Lesker PVD 75) onto the surface of PZT thin-films by a shadow masking process. Ferroelectric hysteresis measurements were made with a ferroelectric tester (Radiant RT66B) by ranging the applied bias voltage from -6 to 6 V over a 500 ms test period. Prior to testing, the US-PZT thin-film was switched 10 times with a ±6 V square pulse. The relative FETF
dielectric constant ($\varepsilon$) was determined to be 133 at 1 kHz using an Agilent 4284A LCR meter.

**Surface Topology Characterization:** Contact mode scanning probe microscopy images were obtained with a Bruker NP silicon-nitride tip using an Asylum MFP-3D AFM. Surface morphology and film thickness were obtained by scanning electron microscopy (FEI XL30 SEM-FEG). Cross-sectional imaging was performed on freshly cleaved samples. For water exposure, both the rough and ultra-smooth PZT samples were submerged in clean glass vials filled with Milli-Q grade water (resistivity 18 MΩ cm$^{-1}$) at room temperature (~22 °C). Sample vials were capped during prolonged submersion and samples were blown dry with N$_2$ before measurements.

### 3.3 Results and Discussion

Fabrication of US-PZT using a sol-gel precursor requires special consideration of each processing step. Although thick FETFs have been generated by the sequential addition of layers through spin coating,$^{[232]}$ we found dramatic increases in film surface roughness with the deposition of additional layers. Our observations agree with previously published results that show an increase in porosity and surface discontinuities with increasing number of layers.$^{[233]}$ In the following discussion, we therefore limit our analysis to single layer PZT films. The thickness of our US-PZT thin
films depended on the spin coating conditions and ranged between 90 nm and 215 nm (Table 3.2).

**Table 3.1:** US-PZT film thicknesses and surface roughness values as a function of spin duration and spin speed.

<table>
<thead>
<tr>
<th>Spin Duration (sec)</th>
<th>Spin Speed (RPM)</th>
<th>Film Thickness (nm)</th>
<th>25 µm² Surface Roughness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>3000</td>
<td>123</td>
<td>4.9</td>
</tr>
<tr>
<td>40</td>
<td>3000</td>
<td>110</td>
<td>2.4</td>
</tr>
<tr>
<td>40</td>
<td>2500</td>
<td>135</td>
<td>3.8</td>
</tr>
<tr>
<td>40</td>
<td>2000</td>
<td>174</td>
<td>4.8</td>
</tr>
<tr>
<td>40</td>
<td>1500</td>
<td>195</td>
<td>3.8</td>
</tr>
<tr>
<td>40</td>
<td>1000</td>
<td>212</td>
<td>5.8</td>
</tr>
<tr>
<td>45</td>
<td>3000</td>
<td>90</td>
<td>5.1</td>
</tr>
</tbody>
</table>

After extensive testing, we found that PZT thin-film surface roughness is substantially affected by the thermal processing conditions, specifically, i) the hot plate temperature during solvent evaporation, ii) the pyrolysis cooling rate, and iii) the cooling rate after rapid thermal annealing. The results from five sets of experiments, for which we systematically varied processing conditions, are shown in Table 3.1. We note that only processing condition (labeled V) results in US-PZT.
**Table 3.2:** Residual Stress and surface roughness of single layer PZT thin films fabricated from a sol-gel precursor as a function of thermal processing conditions.

<table>
<thead>
<tr>
<th>Processing Conditions</th>
<th>(I)</th>
<th>(II)</th>
<th>(III)</th>
<th>(IV)</th>
<th>(V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvent Evaporation Temp ($^\circ$C)</td>
<td>200</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>Pyrolysis Cooling Rate ($^\circ$C sec$^{-1}$)</td>
<td>0.5</td>
<td>10</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Final Annealing</td>
<td>RTA</td>
<td>RTA</td>
<td>RTA*</td>
<td>OVEN</td>
<td>RTA</td>
</tr>
<tr>
<td>Final Film Roughness over 25 $\mu$m$^2$ (nm)</td>
<td>19.7</td>
<td>24.5</td>
<td>19.2</td>
<td>49.9</td>
<td>2.4</td>
</tr>
<tr>
<td>Final Film Residual Stress (MPa)</td>
<td>1188±12</td>
<td>1216±54</td>
<td>1155±8</td>
<td>930±11</td>
<td>862±6</td>
</tr>
</tbody>
</table>

* Indicates using RTA with a slow cooling rate post-anneal

**Effect of hot plate evaporation temperature** The film surface roughness is dramatically affected by the hot plate solvent evaporation temperature (Figure 3.1, Step 2). The surface roughness values were lowest when the hot plate temperature was maintained at about 90°C, i.e., below the boiling point of the 1-Butanol solvent (117°C) used in the Mitsubishi sol-gel. Temperatures below 90°C, led to incomplete solvent removal and caused a large increase in surface roughness, which ultimately resulted in inferior ferroelectric properties (data not shown). Solvent evaporation at 200 °C, i.e., a
temperature which is well above the boiling point of the solvent, also increased the surface roughness of the PZT thin-film significantly. The latter observation agrees with previous results that show that high solvent evaporation temperatures induce cracks and bubbles in PZT thin-films.\textsuperscript{[234,235]} Thus, we deduce that a solvent evaporation temperature slightly below the boiling point is important for synthesizing low roughness PZT thin-films from a sol-gel precursor.

**Effect of pyrolysis conditions** The pyrolysis conditions can also affect the surface roughness of PZT films significantly (Figure 3.1, Step 3). After testing a range of pyrolysis temperatures, we found that heating at 450°C for 35 min in a bench-top oven is ideal. This agrees with previous reports showing the removal of carbon content from the film.\textsuperscript{[233]} Use of pyrolysis temperatures below 450°C resulted in incomplete removal of carbon and production of rough films with inferior ferroelectric properties. Importantly, the cooling rate after pyrolysis impacted PZT surface roughness significantly (Figure 3.1, Step 2). Cooling rates greater than \(\sim10^\circ\text{C/min}\) increased surface roughness and induced crack formation after the final annealing step. Conversely, cooling rates below \(\sim0.5^\circ\text{C/min}\), when combined with the optimized processing conditions in the other fabrication steps, resulted in ultra-smooth, crack free PZT films (see Table 3.1).
Effect of final annealing conditions Final annealing was performed with either an oven or with rapid thermal annealing equipment (Figure 3.1, Step 4). While both approaches led to similar, polycrystalline films, oven annealing increased surface roughness and caused bubble formation. Previous studies on FETF annealing with RTA reported a dramatic decrease in surface defects and improvement in ferroelectric properties.\cite{187,236} These benefits have been attributed to high nucleation rates and a reduced thermal load.\cite{237} While the film surface roughness was unchanged with heating times between 15 sec and 60 sec (data not shown), we found that the RTA cooling rate significantly affected the final film roughness. Surprisingly, we found that decreasing the cool-down rate after RTA significantly increased film roughness and the propensity for crack formation (Table 3.2). We attribute increased roughness and crack formation to higher residual stresses within the film due to an increased thermal load in the final RTA step.\cite{200,238,239}

PZT crystallinity and residual stress We found that processing conditions did not change the film crystallinity. The crystalline orientation for both rough and ultrasmooth PZT thin films was predominantly in the \textless 100\textgreater and \textless 110\textgreater directions, in agreement with the orientations found in PZT thin-films with morphotropic composition (Figure 3.2).\cite{218}
During the fabrication process, lattice mismatch, defect formation, and grain boundaries all contribute to the build-up of internal film stress which can cause an increase in surface roughness.\textsuperscript{174,211,213,240-242} To assess the effect of processing conditions on film stress, we determined the residual stress of the PZT thin-films using the $\sin^{2}\Psi$ method. After recording high-resolution grazing angle XRD scans of the $<110>$ peak at different substrate tilt angles ($\Psi$), we calculated the interplanar spacing as a function of $\sin^{2}\Psi$. Figure 3.2 B shows that a residual compressive stress is present in all our films and that our US-PZT has the lowest reported residual stress (Table 3.2). We thus conclude that the identified processing conditions which minimize internal film stress are also conducive to producing films with low surface roughness.\textsuperscript{174}
Figure 3.2: (A) Grazing angle X-ray diffraction spectra, and (B) $\sin^2 \Psi$ plots for PZT thin-films fabricated with five different thermal processing conditions (Labels I-V refer to the processing conditions in Tab. 1). The slopes of the regression lines in Figure 3.1B reflect the residual stress in the PZT thin films.
**US-PZT surface topography** Figures 3.3 A and 3.3 B compare SPM scans between rough and ultra smooth PZT films over a 400 µm² area. Rough PZT surfaces, fabricated using processing condition I, exhibit a 21.1 nm RMS surface roughness over a 25 µm² area, regardless of the location chosen within the SPM image. The US-PZT surface, however, exhibits a 2.4 nm RMS surface roughness over the same area. RMS roughness evaluation of US-PZT thin films is supported by the Gaussian height frequency distribution obtained from the analysis of the 20 x 20 µm topography image shown in Figure 3.3 B. Figure 3.4 B shows that the RMS surface roughness depends on sampling length, where roughness increases up to a sampling length of about 100 nm, and then remains stable at an RMS roughness of about 2.4 nm up to a sampling length of 10 µm. The average grain size for US-PZT and rough PZT was determined to be 63.6 ± 25.4 nm and 109.1 ± 5.1 nm, respectively. The smaller average grain size of the US-PZT has previously been shown to reduce the RMS surface roughness of FETFs.\cite{187,243} We note that US-PZT surface topography and roughness were nearly identical across the whole wafer surface.
Figure 3.3: Representative SPM topography scans (z scale ±10 nm) of (A) rough PZT thin-film (Table 3.2, processing condition I) with a RMS roughness value of 21.1 nm, and (B) US-PZT thin-film (Table 3.2, processing condition V) with a RMS roughness value of 2.4 nm, both measured over a 25 μm² area.

Figure 3.4: (A) Gaussian height frequency distribution obtained from the analysis of the 20 x 20 μm topography image (Figure 3.3 B). (B) RMS surface roughness as a function of sampling length.
**US-PZT ferroelectric properties** Figure 3.5 shows representative hysteresis curves for rough and ultra-smooth PZT thin films, respectively. The remnant polarization values of US-PZT thin films were +5.38 µC cm\(^{-2}\) and -9.25 µC cm\(^{-2}\), with a coercive field strength of +66 kV cm\(^{-1}\) and -35 kV cm\(^{-1}\) for upwards and downwards polarization states, respectively. However, the remnant polarization values of rough PZT thin films, as fabricated by processing condition I, were only 5.20 µC cm\(^{-2}\) and -2.5 µC cm\(^{-2}\), with a coercive field strength of +77 kV cm\(^{-1}\) and -26 kV cm\(^{-1}\). The observed asymmetry in the electrical hysteresis of PZT thin-films has been reported previously and was attributed to the presence of domain pinning within the interfacial screening layer.\[^{244,245}\] We attribute the lower remnant polarization for the rough PZT film to the higher residual stress within the film.\[^{209}\] We note, however, that low remnant polarization can also be attributed to other factors including differences in composition,\[^{238}\] and crystallinity.\[^{246}\]
Figure 3.5: Representative ferroelectric hysteresis loops for rough (Table 3.2, processing condition I) and US-PZT (Table 3.2, processing condition V) samples measured over a ±6 V range, and a 500 ms cycle time.

**US-PZT surface chemical composition** PbO evaporation or changes in the relative concentrations of titanium and zirconium can induce lattice mismatch and cracking.\[200,258,239\] We used XPS to determine the presence of such compositional changes on the PZT surface, and found, with the exception of the sample fabricated using processing condition II, no significant differences in the surface composition between rough and US-PZT surfaces (Table 3.3). The relative intensity of the spectral peaks of lead (centered at 138 eV), zirconium (at 332 eV), and titanium (at 458 eV) are consistent
with the expected atomic composition of 52/48 PZT thin-films (Table 3.3). We note, however, that a significant amount of carbon (~6-20%) was present on the surface of both rough and US-PZT thin-films. Argon ion milling of the PZT thin-films showed that this carbon layer is isolated to the top few nanometers of the film and thus likely stems from film processing (data not shown).[169,170] Two peaks are seen in the oxygen high resolution scans in Figure 3.6, where the smaller peak at higher binding energy is attributed to adsorbed oxygen, and the larger peak at lower binding energy is attributed to PbO.[247] Spectral deconvolution of the O 1s envelope reveals no difference in the amount of adsorbed oxygen for the different thermal processing conditions, and suggests that the number of oxygen defect sites does not substantially change. Furthermore, the spectral signatures of the Pb 4f and the Ti 2p envelopes were found to be independent of the thermal treatment conditions. The XPS measurements thus support the conclusion that changes in surface roughness between the PZT films are not due to compositional differences.
Figure 3.6: High-resolution XPS spectra of the (A) oxygen 1s envelope (B) lead 4f envelope, and (C) Ti 2p envelope for a range of thermal processing conditions as noted in Table 3.2.

<table>
<thead>
<tr>
<th>Processing Condition</th>
<th>Oxygen (atomic %)</th>
<th>Lead (atomic %)</th>
<th>Zirconium (atomic %)</th>
<th>Titanium (atomic %)</th>
<th>Zr/Ti Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>62.4±0.1%</td>
<td>23.9±0.1%</td>
<td>7.6±0.1%</td>
<td>6.1±0.2%</td>
<td>55/45</td>
</tr>
<tr>
<td>II</td>
<td>61.2±0.2%</td>
<td>26.0±0.1%</td>
<td>6.0±0.1%</td>
<td>6.8±0.4%</td>
<td>47/53</td>
</tr>
<tr>
<td>III</td>
<td>59.4±0.2%</td>
<td>25.6±0.1%</td>
<td>7.6±0.1%</td>
<td>7.2±0.4%</td>
<td>51/49</td>
</tr>
<tr>
<td>IV</td>
<td>59.7±1.2%</td>
<td>26.2±0.5%</td>
<td>7.8±0.1%</td>
<td>6.2±0.3%</td>
<td>55/45</td>
</tr>
<tr>
<td>V (US-PZT)</td>
<td>61.3±0.1%</td>
<td>24.1±0.1%</td>
<td>7.8±0.2%</td>
<td>6.6±0.1%</td>
<td>54/46</td>
</tr>
</tbody>
</table>

3.4 Conclusions

By optimizing the thermal processing conditions in sol-gel derived FETFs it is possible to synthesize ultra-smooth films. Specifically we found that reduced residual
stresses are necessary for both low surface roughness and enhanced integrity of US-PZT in aqueous environments. We were able to fabricate US-PZT films (1) by maintaining the temperature in the solvent evaporation step below the boiling point of the solvent, (2) by ensuring a slow cooling rate in the pyrolization step (less than one degree per second), and (3) by rapid thermal annealing followed by fast cooling to reduce the thermal load on the film. The ability to synthesize crack-free, ultra-smooth FETFs from a sol-gel precursor thus enables their integration into interfacial sensing micro-devices.

This chapter is a manuscript draft prepared for submission to Langmuir. Co-authors: Drs. Yellen and Zauscher. We thank Dr. Massoud for his helpful discussions and input.

4.1 Introduction

Integration of ferroelectric thin films (FETFs) into solid-state micro-devices has already enabled a number of advanced device capabilities, ranging from ferroelectric memory devices to high-frequency actuators.\cite{22,183-185,248} Ferroelectrics maintain a localized, bi-stable, and switchable polarization state without the need for an external power supply.\cite{60,202,249} Recently, FETFs have been considered also for interfacial sensing (Figure 4.1);\cite{250} e.g. previous work showed that the polarization state of a FETF can alter gas phase adsorption.\cite{59,251} To date it is not known, however, if FETFs can withstand exposure to aqueous environments and, if so, for how long. Furthermore, by understanding how FETFs interact with aqueous environments we can better assess their potential integration into liquid-phase interfacial sensing devices.
Figure 4.1: Schematic showing a charged (bio)macromolecule depositing onto a polarized ferroelectric thin film for interfacial sensing applications.

Lead zirconium titanate (PZT) is a well studied,[168,185,234,252] perovskite ferroelectric that has a large bi-stable, switchable, remnant polarization state.[14,15] While a few studies showed that exposure of PZT to ionic solutions results in minimal change in the remnant polarization,[80,92,197] other studies demonstrated that the prolonged exposure of PZT to humid environments results in degradation of the interface.[168] Although it was proposed to use locally-polarized PZT to control the adsorption of charged peptides from solution,[197] the prevalence of non-specific deposition prevented a clear demarcation of peptide deposition on the patterned surface charge. These examples call
for the systematic study of how the PZT surface changes with the prolonged exposure to aqueous environments.

Here, we present the first comprehensive study of how ultra-smooth PZT thin film (US-PZT) surface topography, composition, and electronic properties change with extended exposure to aqueous environments. We use the term ultra-smooth to indicate a root mean squared (RMS) surface roughness of only 2.4 nm over a 25 µm² area, which reflects an order of magnitude reduction in RMS surface roughness from previously reported smooth PZT thin films. Our results show that the exposure of US-PZT to liquid environments induces a progressive surface degradation of the perovskite structure producing oxygen defects sites and entail the eventual loss of ferroelectric properties. Our work thus illuminates the limitations for integrating US-PZT into interfacial sensing devices.

4.2 Materials and Methods

US-PZT Fabrication Silicon Wafers (Viriginia Semiconductor) were used to grow 300 nm of thermal oxide. The Si/SiOx wafers were then cleaned by sonication for 10 min in 0.5% SDS solution, rinsing 10 times with Milli-Q grade grade water, immersion for 20 min in 3:1 H₂O₂:H₂SO₄ (Piranha solution), rinsing 10 times with Milli-Q grade water, and
drying in a stream of N₂. Next, 200 nm of titanium and 100 nm of platinum were deposited using a Kurt Lesker PVD 75 e-beam source evaporator at ~4x10⁻⁵ Torr.

US-PZT thin films were fabricated from a sol-gel precursor (52/48/125, Mitsubishi Materials Corp.). The sol-gel solution was stored under dry conditions at 5°C and protected from light. Prior to deposition, the sol-gel was warmed to room temperature and sonicated for 15 min. The precursor was passed through a 0.1 µm filter and deposited onto a platinum-coated silicon substrate, making sure to completely cover the substrate surface. The sol-gel precursor was then spin-coated using a two stage ramp profile (5 s spin at 500 RPM followed by 35 – 45 s at 1250 - 3000 RPM). Next, the solvent was evaporated on a hot plate (90°C, 120 s). The films were then pyrolized in a Thermolyne Benchtop annealing furnaces at 450 °C for 35 min and allowed to slowly cool. Final annealing was performed in a Jipelec JetFirst 100 Rapid Thermal Annealer at 700 °C for 20 s.

For water exposure, the ultra-smooth PZT samples were submerged in clean glass vial filled with Milli-Q grade water (resistivity 18 MΩ cm⁻1) at room temperature (~22°C). Samples were covered with a cap during prolonged submersion and blown dry with N₂ before measurements were taken. All samples were stored in a desiccator between measurements.
**Scanning Probe Microscopy Imaging** Surface topography was imaged using an Asylum MFP-3D Atomic Force Microscopy. A 100 μm² area images were taken using intermittent contact mode with a Bruker NP silicon nitride tip. Surface roughness \( \sigma \) (equation 4.1) and structure function \( S(\tau) \) (Equation 4.2).\cite{253,254}

\[
\sigma = \sqrt{\frac{1}{L} \int_0^L (z(x) - \mu)^2 dx}, \quad (4.1)
\]

\[
S(\tau) = \lim_{L \to \infty} \frac{1}{L} \int_0^L [z(x) - z(x + \tau)]^2 dx, \quad (4.2)
\]

where \( z \) is the sample height, \( L \) is the sampling length, and \( \tau \) is the spatial distance. For calculations, the height at any point was considered a random variable. This assumption was justified because the height frequency distribution was Gaussian. Individual height profiles were considered for surface characterization. Calculated values were averaged across individual profiles.

**Scanning Electron Microscopy** Images of the surface were taken under high vacuum using a FEI XL30 SEM-FEG with source voltage of 1.7 kV and spot size of 3. Samples were grounded during imaging to reduce charging of the surface.

**X-ray Diffraction** Grazing angle X-ray diffraction spectra (Panalytical X’Pert PRO MRD HR, \( \lambda(\text{CuK}\alpha) = 1.5419 \text{ Å} \)) were obtained with an incidence angle of 0.6 degrees, over a 2θ scan range from 0 to 75 degrees taken at 0.1 degree increments.
**Raman Spectroscopy** Raman Spectroscopy was performed (Horiba Jobin Yvon LabRam ARAMIS) in reflection mode with a 442 nm HeCd laser and a grading of 2400. Raman shift spectra were taken between 100 and 1600 cm\(^{-1}\) and 3500 and 3800 cm\(^{-1}\).

**X-ray Photoelectron spectroscopy** survey spectra (Kratos Analytical Axis Ultra Photoelectron Spectrometer equipped with a monochromatic Al K\(\alpha\) source) were taken with a pass-energy of 160mV. High-resolution scans were taken with a pass-energy of 40mV. Angle resolved XPS was performed at a 60° angle of incidence. Charge neutralization was active during spectrum acquisition. Spectra and envelope binding energies were shifted to set the C 1s peak to 285.0 eV. Spectral analysis and de-convolution was carried out with Casa XPS software. All curve fittings was performed using a symmetric 30/70 Gaussian-Lorentzian peak structure and least squares method.

**Electrical characterization** After exposure to Milli-Q grade water and an N\(_2\) dry, gold electrodes with a known diameter of 50 microns were evaporated (Kurt Lesker PVD 75) onto the US-PZT thin films by a shadow masking process. Ferroelectric hysteresis measurements were taken with a ferroelectric tester (Radiant RT66B) over a 50 ms test period, using a maximum of \(\pm 6\) V applied bias. Prior to testing, the US-PZT thin film was switched 10 times with a \(\pm 6\) V square pulse. The FETF dielectric constant and loss values (Agilent 4284A LCR meter) was determined between 10 Hz and 1 MHz. Current-voltage measurements (Keithley 4200-SCS Parametric Analyzer) were taken
using a 0.05 V bias step with a 1 sec delay before measurement and 1 sec hold before step.

4.3 Results and Discussion

4.3.1 US-PZT thin film structural stability in water

We investigated the integrity of our US-PZT thin-films as a function of water exposure duration. Figure 4.2 shows SEM images of rough and US-PZT thin-films for different water exposure times ranging from 4 hours to 100 days. Rough PZT thin-films degraded progressively with increasing exposure duration (Figure 4.2 A), while US-PZT thin films maintained their integrity even after 100 days of water exposure (Figure 4.2 B). We found that film degradation nucleates around surface defect sites such as cracks and bubbles. We believe that the presence of cracks allows for water to infiltrate the platinum-PZT interface, which induces progressive film delamination with increasing exposure time. These experiments underscore the need to produce crack-free PZT thin-films for integration with sensing devices that will be exposed to aqueous environments.
4.3.2 US-PZT thin film topography

We studied the root mean square (RMS) surface roughness and the fractal dimension of US-PZT thin films as a function of exposure duration to monitor potential surface morphological changes of the thin film. The RMS surface roughness and 2D fractal dimension of the US-PZT surface were calculated from high resolution scanning probe microscopy (SPM) images obtained in contact mode before and after exposure to Milli-Q grade water. The surface of PZT thin films has previously been characterized using a 2D structure function, and revealed that the crystalline domain structure is self-similar.\textsuperscript{255,256} Figures 2 A and B show the height frequency distribution and RMS surface roughness of US-PZT before and for two different exposure times to Milli-Q grade water. For all three cases, the height frequency distribution is Gaussian. Furthermore,
the RMS surface roughness increased by 1.1 nm after 100 days of water exposure. Table 1 lists the 2D fractal dimension of the US-PZT surface before and after exposure to Milli-Q grade water. The data show that the fractal dimension of the US-PZT surface does not change with increasing exposure length to Milli-Q grade water, indicating that surface topographical characteristics of the film do not change substantially. These findings suggest that the surface topography of US-PZT thin films is, if at all, only slightly affected by prolonged exposure to Milli-Q grade water.

**Table 4.1:** Fractal dimension and RMS surface roughness for US-PZT as a function of water exposure duration.

<table>
<thead>
<tr>
<th>Exposure Duration (hrs)</th>
<th>Fractal Dimension ($D$)</th>
<th>Average Surface Roughness over 5 μm sample distance (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.57</td>
<td>2.9</td>
</tr>
<tr>
<td>24</td>
<td>2.63</td>
<td>2.9</td>
</tr>
<tr>
<td>2400</td>
<td>2.61</td>
<td>3.8</td>
</tr>
</tbody>
</table>
Figure 4.3: US-PZT (A) height frequency distribution and (B) RMS surface roughness as a function of sample distance before and after exposure to Milli-Q grade water.

4.3.3 US-PZT crystal structure

Next, we investigated film crystallinity before and after exposure to Milli-Q grade water using grazing angle X-ray diffraction (XRD) and Raman spectroscopy.\cite{257,258}

Figure 4.4 A shows grazing angle XRD measurements before and after exposure to Milli-Q grade water. The US-PZT thin films maintain a predominantly \(<100>\) and \(<110>\) orientation both before and after exposure. No change in the crystalline structure was observed, even after 100 day of exposure to Milli-Q grade water. Additionally, no peak broadening is visible, which suggests that the average domain size within the film remained constant.\cite{243} Raman spectroscopy has been used to determine both the crystalline structure and changes in ferroelectric properties due to hydrogen infiltration.\cite{259} Figure 4.4 B shows Raman spectroscopy scans of the US-PZT before and after exposure to Milli-Q water. In agreement with the XRD scans, the presence of
A1(1TO), E(2TO), B1 + E, A1(2TO), E(2LO) + A(2LO), E(3TO), A1(3TO) and E(3LO) + A1(3LO) phonon modes in the Raman spectra, support the presence of a ferroelectric, tetragonal phase within the US-PZT surface before and after exposure to Milli-Q grade water.\[^{[258]}\] No change in the Raman shift spectra was observed, even after 100 days of exposure. Additionally, high frequency Raman scans were taken to determine the possibility of hydrogen incorporation into the film.\[^{[260]}\] No peak is apparent between 3500 and 3800 cm\(^{-1}\), which suggests that hydrogen has not been incorporated into the film even after 100 day so exposure to Milli-Q water.

**Figure 4.4:** (A) Grazing angle XRD and (B) Raman Spectroscopy of US-PZT before and after exposure to Milli-Q grade.

### 4.3.4 US-PZT ferroelectric hysteresis and dielectric measurements

Capacitance and hysteresis measurements of US-PZT before and after exposure to Milli-Q grade water were made to quantify the ferroelectric and dielectric properties
as a function of water exposure duration. An increase in mobile charge carrier density at the surface of the US-PZT will decrease the measured dielectric constant.\cite{206, 241} Figure 4.5 A shows US-PZT capacitance measurements after prolonged exposure to Milli-Q grade water. There is a dramatic decrease in the thin film’s dielectric constant with increasing exposure duration; i.e., after 100 days of water exposure, the US-PZT thin film was conductive. This increase in the number of mobile charge carriers after prolonged exposure to Milli-Q grade water is also reflected in the changes of the hysteresis loop.\cite{202} Figure 4.5 B shows the ferroelectric hysteresis loops of US-PZT thin films before and after exposure to Milli-Q grade grade water. Before exposure, US-PZT thin films have a remnant polarization ranging from -7 µC cm\textsuperscript{-2} to +5 µC cm\textsuperscript{-2}, which indicates a slightly preferential “down” polarization state before exposure. We find that prolonged exposure to Milli-Q grade water results in a gradual decrease in polarization saturation and dramatic changes in the coercive field (Table 4.2). These trends also indicate that there is an increase in the number of mobile charge carriers within the film with increasing exposure duration.\cite{261} Others have reported increased mobile charge carrier densities after exposure to a hydrogen-rich atmospheres,\cite{260} or oxygen defect formation.\cite{262} Because no hydrogen was detected in the film with high frequency Raman scans, the increase in mobile ion charge density is attributed to oxygen defect sites at the US-PZT surface.
Table 4.2: Remnant polarization, coercive field and polarization saturation values for US-PZT as a function of water exposure duration.

<table>
<thead>
<tr>
<th>Exposure Duration (hrs)</th>
<th>Remnant Polarization (μC cm$^2$)</th>
<th>Coercive Field (kV/cm)</th>
<th>Polarization Saturation (μC cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5.6 / -7.8</td>
<td>-3.4 / 60.3</td>
<td>±48.6</td>
</tr>
<tr>
<td>24</td>
<td>10.2 / -4.7</td>
<td>-94.8 / 38.8</td>
<td>±41.8</td>
</tr>
<tr>
<td>2400</td>
<td>1.1 / -10.1</td>
<td>-10.3 / 137.3</td>
<td>±30.1</td>
</tr>
</tbody>
</table>
Figure 4.5: (A) Dielectric constant and (B) polarization-voltage hysteresis for US-PZT before and after exposure to Milli-Q grade water.

4.3.5 Surface composition and structure

We next employed XPS and angle-resolved XPS to determine the US-PZT surface composition and bonding moieties as a function of water exposure duration. XPS is a
useful tool in determining the surface composition, structure, and degradation of PZT thin films.\[169-171] Specifically, we performed both survey and high-resolution XPS scans to detect changes in surface chemical composition and the bonding environment as a function of water exposure duration.

XPS reveals that our US-PZT contains a large percentage of carbon (between 6 and 12 at %) on the surface. Ion milling of the top few nanometers of the FETF, however, reveals that less than 1% carbon content resides beneath the US-PZT film surface (data not shown). We attribute the presence of carbon on the surface largely to the fabrication conditions of the sol-gel derived ferroelectric thin-films. Analysis of XPS survey scans show that the 52/48 Zt/Ti ratio does gradually decreases and the oxygen concentration increases with increasing water exposure duration (Table 4.3), indicating the desorption of zirconium oxide over time.

**Table 4.3:** US-PZT film composition as determined by XPS before and after exposure to Milli-Q grade water.

<table>
<thead>
<tr>
<th>Exposure Duration (hrs)</th>
<th>Oxygen (atomic %)</th>
<th>Lead (atomic %)</th>
<th>Zirconium (atomic %)</th>
<th>Titanium (atomic %)</th>
<th>Zr/Ti Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>66.5±0.1%</td>
<td>19.5±0.1%</td>
<td>6.8±0.1%</td>
<td>7.2±0.2%</td>
<td>51/49</td>
</tr>
<tr>
<td>24</td>
<td>66.8±0.2%</td>
<td>19.2±0.1%</td>
<td>6.6±0.1%</td>
<td>7.4±0.4%</td>
<td>47/53</td>
</tr>
<tr>
<td>2400</td>
<td>67.9±0.2%</td>
<td>17.4±0.1%</td>
<td>6.1±0.1%</td>
<td>8.5±0.4%</td>
<td>42/58</td>
</tr>
</tbody>
</table>
Next, we employed high-resolution XPS scans to investigate the chemical structure of the US-PZT interface before and after prolonged exposure to Milli-Q grade water. The degradation of the US-PZT interface can result in the shielding of the internal electric field, and reduction in the ferroelectric properties.\textsuperscript{263} High-resolution XPS spectra of the O 1s and Pb 4f envelopes show an increase in oxygen defect sites with increasing exposure duration (Figures 4.6 A and 4.6 B). Deconvolution of the O 1s envelope reveals three bonding moieties at 529.4 eV, 530.0 eV, and 531.5 eV, that we attribute to Pb-O, oxygen absorbed Pb-O, and C-O absorbed Pb-O, respectively.\textsuperscript{171} The data suggest that there is degradation of the PZT surface into simple oxides.\textsuperscript{169} Figures 4.6 A and 4.6 B show the angle resolved, high-resolution O 1s and Pb 4f spectra of the US-PZT surface before and after exposure to Milli-Q grade water. These particularly surface-sensitive analyses conclusively show that the US-PZT surface degrades with increasing exposure duration.
Figure 4.6: High-resolution XPS spectra of the (A) O 1s and (B) Pb 4f envelope of the US-PZT interface before and after exposure to Milli-Q grade water.
Figure 4.7: Grazing angle high-resolution XPS spectra of the (A) O 1s and (B) Pb 4f envelope of the US-PZT interface before and after exposure to Milli-Q grade water.

Figure 4.8 plots the relative contribution of the three binding moieties found within the O 1s envelope as a function of exposure time. We find that the relative contribution of the oxygen absorbed Pb-O (at 530 eV) and Pb-CO$_2$ increases exponentially with increasing exposure duration. Likewise, the relative concentration of lead oxide (Pb-O) decreases exponential with increasing exposure duration. These results further support our conclusion that the surface of our US-PZT thin-films undergo gradual degradation while exposed to aqueous environments.
4.4 Conclusions

This chapter presents the first comprehensive study of US-PZT thin-film stability in aqueous environments. While the film topography and crystallinity were largely maintained after 100 days of water exposure, the ferroelectric and dielectric properties gradually degraded with increasing exposure duration. The measured decrease in dielectric constant and hysteresis properties were further supported by XPS and angle resolved XPS measurements, which showed increased surface oxidation with increasing exposure duration. However, surface compositional analysis by XPS showed no change after extended exposure to Milli-Q grade water. These results help us understand
current limitation for integration of US-PZT with interfacial sensing devices and provide a foundation for further work to investigate the stability of alternative FETFs in aqueous environments.
5. Electric Double Layer Formation above Polarized Ferroelectric Surfaces

The work presented below resulted from collaboration with Dr. Mark Wiesner, Shihong Lin, and Mathieu Therezien of the Civil Engineering Department at Duke University. A manuscript based on this work has been provisionally accepted to ACS Applied Materials and Interfaces.

5.1 Introduction

Ferroelectric thin films (FETFs) belong to a class of materials that can maintain an electric polarization state in the absence of an externally applied electric field.\textsuperscript{15,264,265} The film’s polarization state and the resulting surface charge density originate from a bistable, switchable dipole moment, maintained across the ferroelectric domains of the material.\textsuperscript{14,15} The charge density on the exposed surface of a polarized FETFs is equal to the normal component of the remnant polarization vector ($\sigma_{\text{FETF}} = \vec{P} \cdot \hat{n}$). The net surface charge density can be induced to be either positive or negative depending on the direction of the applied polarizing electric field.\textsuperscript{41,60,266}

The ability to control the remnant polarization state has led to the widespread use of ferroelectrics in a range of semiconductor-based devices.\textsuperscript{180,183,185} Recently, new sensing applications for ferroelectrics have been proposed where the polarization state of the FETF can influence interfacial forces in liquid environments.\textsuperscript{192} FETFs ability to
control electric double layer EDL formation has a wide range of potential applications, including, interfacial sensing,[267] microfabrication,[195] and micromixing.[5] Figure 5.1 A is a schematic of the electric double layer (EDL) structure between a native, non-polarized FETF, with a positive surface charge, and a negatively charge colloidal probe in an aqueous environment. The interactions between the oppositely charged surfaces give rise to interfacial attraction. Figures 5.1 B and 5.1 C show a polarized FETF expressing a net negative surface charge or net positive surface charge, respectively. Here, the uncompensated charge at the top surface of the FETF induces EDL formation. Because of the high ferroelectric surface charge densities a Stern layer forms at the FETF-liquid interface. The outer-Helmholtz plane (OHP) is indicated by the dotted line. At the bottom surface, the polarization charge is compensated by free charges held in the bottom, metal electrode.

Although switching of the polarization direction induces a change in the EDL counter-ion distribution, there are still significant challenges for operating FETFs in aqueous environments. We have found that careful selection of the substrate and processing conditions can increase FETF stability in aqueous environments by reducing in-plane stress, surface roughness, and crack formation. Our results demonstrate how the FETF polarization state influences interfacial forces in aqueous environments and highlights the potential of FETFs to mediate surface forces.
Figure 5.1: Schematic showing the electric double layer structure and interaction force between a negatively charged colloidal probe and (A) a native, non-poled FETF with a positive native surface charge, (B) a polarized FETF with a negative surface charge and, (C) a polarized FETF with a positive surface charge.

Surface charges for common oxides typically arise from proton exchange or ion binding reactions between the ions in solution and surface sites.\[268-270\] For polarized, perovskite-based FETFs in aqueous environments, the effective surface charge density is due to the combination of the polarization induced surface charge ($\sigma_F$) and the surface charge density of the native oxide layer ($\sigma_S$) (Eqn. 5.1),

$$\sigma_T = \sigma_F + \sigma_S.$$ (5.1)
The relative magnitudes of these two surface charge contributions, however, can differ greatly. The surface charge density for a typical oxide surface is limited by the number of reactive surface site density, which are typically on the order of 0.1 μC cm\(^{-2}\).\[^{168,185,234,252}\] Alternatively, FETFs such as lead zirconium titanate (PZT) can maintain surface charge densities that are several orders of magnitude higher (values can exceed 30 μC cm\(^{-2}\)),\[^{168,185,234,252}\] which implies that the charge density of a polarized FETF film should dominate over the native surface charge density.

Our use of ultra-smooth, 52/48 lead zirconium titanate (US-PZT) thin films for control over electric double layer formation requires fabrication of FETFs that have nanometer scale mean surface roughness, high remnant polarization, and are stable in aqueous environments. Figure 5.2 A shows a typical hysteresis curve for our US-PZT thin films. Because the high surface charge of the polarized US-PZT thin films will result in high surface potentials, it is reasonable to assume that the EDL structure is partitioned into a Stern layer and a diffuse double layer of counter-ions. The inclusion of a Stern layer is consistent with EDL modeling of surfaces that have a high charge density in solution,\[^{133,149,271}\] and has been reported for polarized PZT surface in solution (Figure 5.2 B).\[^{87}\] Within the Stern layer, the condensed sheet of counter ions is energetically trapped proximal to the solid-liquid interface, and the layer can be modeled as a parallel plate capacitor.\[^{129}\] In the adjacent diffuse double layer, however, the ions are modeled as a
distributed cloud where both the ion concentration and the electric potential decay exponentially with increasing distance away from the surface.\cite{129} Since ferroelectric hysteresis properties can be accurately measured before the FETF is placed in solution, the effective surface charge density at the inner-Helmholtz plane (IHP of Figure 5.2 B) of the Stern layer is known. The remaining surface charge (or potential) measured at the outer-Helmholtz plane of the Stern layer (OHP of Figure 5.2 B), represents the boundary condition for the adjacent diffuse double layer region.

![Figure 5.2:](image)

**Figure 5.2:** (A) Hysteresis loop of our 52/48 US-PZT thin film. Remnant polarization values are -16.3 μC cm\(^{-2}\) and 15.3 μC cm\(^{-2}\), the coercive field values are -16.3 μC cm\(^{-2}\) and 15.3 μC cm\(^{-2}\), coercive field values of -146.5 kV/cm and 155.2 kV/cm. (B) Schematic of the electric double layer structure above a polarized FETF with a negative surface charge in dilute electrolyte solution and a corresponding sketch of the potential profile.
The study of electric double layer (EDL) formation has been driven by applications ranging from colloidal stability (e.g. aggregation\[272\] and filtration\[273\]) to interfacial sensing (e.g. biosensors\[274\] and lab-on-a-chip development\[275\]).\[276\] Although a deeper understanding of interfacial forces has led to improvements in interfacial engineering, it is still difficult to determine the effective charge density of a surface in solution because it usually depends on an equilibrium reaction between the surface sites and the surrounding environment, which in turn depend on solution conditions such as pH,\[277-279\] ionic strength,\[118,133,280\] or ion type.\[271,281\] Additionally, any attempt to change the surface charge density, either through functionalization or chemical treatment, invariably results in an unquantifiable change in the surface charge density at the inner Helmholtz plane (IHP). By contrast, ferroelectrics have the unique property of maintaining either a positive or negative surface charge density independent from the solution conditions or by chemical modification. Additionally, the surface charge density of a FETF can be experimentally determined prior to exposure, which allows for better estimation of the potential at the IHP. These advantages suggest that ferroelectric surfaces can significantly advance the study of EDLs.

We present, for the first time, the experimental measurement of an electric double layer induced by the remnant polarization state of a FETF in water. Using colloidal probe force microscopy (CPFM), we measured the EDL interaction force as a
function of separation distance between a negatively charged colloidal probe (borosilicate sphere) and ultra-smooth PZT (US-PZT) surfaces over a range of ionic strengths. We demonstrate that the polarization state of the FETF dominates the net surface charge and thus the interaction force. Furthermore, the comparison of experimental and theoretical modeling of the EDL interactions reveals that the theoretically predicted IHP surface charge density matches the measured ferroelectric remnant polarization of the US-PZT film. Our observations motivate the continued development of FETF for interfacial-sensing applications.

5.2 Materials and Methods

Substrate Preparation: Silicon wafers (<100>, Virginia Semiconductor) were first cleaned by sonication for 10 min in 0.5% SDS solution, followed by rinsing 10 times with Milli-Q grade water (18.2 MΩ·cm). The wafers were then immersed for 20 min in 3:1 H₂O₂:H₂SO₄ (Piranha solution), followed by rinsing 10 times with Milli-Q grade water, and finally dried in a stream of N₂. Next, 200 nm of titanium and 100 nm of platinum were deposited onto the wafer surface using a Kurt Lesker PVD 75 e-beam source evaporator at ~4x10⁻⁵ Torr.

Sol-Gel Synthesis: US-PZT thin-films with a Zr/Ti atomic ratio of 52/48 were fabricated from a sol-gel precursor (17 wt% Type E1 with relative atomic ratio: 125/52/48
Pb/Zr/Ti, Mitsubishi Materials Corp). The excess lead was added to the sol-gel precursor to compensate for the loss of lead oxide during final film annealing.\textsuperscript{[225]} The sol-gel solution was stored under dry conditions at 5°C and protected from light. Prior to deposition, the sol-gel was warmed to room temperature and sonicated for 15 min. The precursor was passed through a 0.1 µm filter and deposited onto a platinum-coated silicon substrate, making sure to completely cover the substrate surface. The sol-gel precursor was then spin-coated using a two-stage ramp profile (5 sec spin at 500 RPM followed by 40 sec at 3000 RPM). Next, the solvent was evaporated on at a hot plate of 90°C for 120 sec. The films were then pyrolyzed in a Thermolyne Benchtop annealing furnace at 450°C for 35 min followed by cooling at a rate of 0.5°C sec\textsuperscript{-1}. Finally, the films were annealed using a rapid thermal annealer (Jipelec JetFirst 100) at 700°C for 15 sec. This fabrication process resulted in ultra-smooth PZT thin films with mean thickness of \~116 nm and RMS roughness of \~2.4 nm. All US-PZT samples were annealed immediately prior to measurement.

**Ferroelectric Property Testing:** The dielectric constant and remnant polarization of our US-PZT thin films were measured with a Radiant RT66b ferroelectric tester using circular platinum capacitors (50 µm diameter) evaporated onto the US-PZT surface. The platinum capacitors were annealed at 350°C for 15 min to ensure good electrical contact. The dielectric constant of the US-PZT was \~1200.
**Colloidal Probe Preparation:** Colloidal probes were fabricated by attaching a 10 µm diameter borosilicate sphere with a mean surface roughness of 5.5 nm (Duke Scientific Cat: 9010) onto a Bruker NP “D” cantilever using Norland Products NOA 81 UV curing epoxy. The cantilever stiffness was determined from the thermal noise spectrum in air.\(^{[282]}\) Prior to measurements each colloidal probe was cleaned with a 1 min oxygen plasma ash followed by a 10 min immersion in Milli-Q water. This was followed by a 7 min exposure to UV/ozone before rinsing with ethanol and Milli-Q grade water.

**Solution Preparation:** All dilute electrolyte solutions were prepared and stored in clean glass vials. Dilute monovalent salt solutions were prepared using; Lithium Chloride (CAS#10515-30), Potassium Chloride (CAS#87626-18), Potassium Nitrate (CAS#11008-14), and Sodium Chloride (CAS#7647-12-5). NaCl solutions were acidified with dilute HCl. Solution concentration and pH were measured using an Oakton Acron CON 5 Conductivity meter and an Oakton Ion 510 Series pH meter, respectively.

**Force-Separation Measurements:** Colloidal probe force microscopy measurements were performed using an Asylum Research MFP-3D scanning probe microscope. To avoid hydrodynamic forces, all force curves were collected with a tip speed of 400 nm sec\(^{-1}\) over separation distances ranging from 500 to 1000 nm.\(^{[118]}\) Once the colloidal probe and the sample were mounted in the AFM, a 150 µL droplet of electrolyte solution was placed on the US-PZT sample, and held in place during
measurements by capillary forces acting between the cantilever holder and the US-PZT surface. For each condition tested, force curves were taken using force-volume mapping over a 100 \( \mu \text{m}^2 \) area. The presented data uses a random selection of the measured force-separation curves. For each experimental condition, 12 curves were randomly selected for analysis. Obviously deviating curves were eliminated. Prior to polarization, CPFM force-separation curves were taken on the freshly-annealed (native) US-PZT surface. The sample was then removed from solution, dried, and poled to express a negative surface charge. After poling, the sample was re-immersed in ionic solution for subsequent CPFM measurements while isolated from ground. Next, the polarized US-PZT sample was removed from solution, dried, and poled to express a positive surface charge. In all cases, the bottom electrode was isolated from ground. A new US-PZT sample was used for each ionic solution.

**Polarization of US-PZT:** Polarization of the US-PZT was performed *ex situ* by placing a clean, platinum-coated silicon wafer on top of the FETF surface. Figure 5.3 depicts the polarization process. The platinum-coated silicon wafer was placed, platinum side down, on top of the US-PZT thin film (Figure 5.3 A). The US-PZT sample was uniformly polarized over an area of 1 cm\(^2\) by applying a \( \pm 40 \) V bias with a Keithley 6487 Piccoammeter/Voltage source (Figure 5.3 B). Ferroelectric polarization produces an alignment of the FETF internal polarization with the externally applied electric field. To
ensure polarization saturation, the films were switched 10 times before the final polarization direction was induced. After the final polarization state was achieved, the bias was removed, the circuit was broken, and the top electrode removed (Figure 5.3 C). This polarization process leads to free charges to persist in the bottom metal electrodes, which compensate the charges expressed by the bottom surface of the FETF. The charge density of the top surface on the ferroelectric film, on the other hand, remains uncompensated after removal of the top electrode, leading to an effective charge density equal to the remnant polarization of the FETF ($\sigma_F$) (Figure 5.3 D) that is opposite in sign from the charge held within the top electrode during polarization.

![Figure 5.3: Scheme for polarization of ferroelectric US-PZT thin film.](image)

**Electric Double Layer Model and Fitting:** The Derjaguin approximation was used to relate the normal force measured for a sphere-plate geometry ($F_{sp}$) to the total interaction energy per unit area between two parallel plates ($W_T$) (Equation 5.2).$^{[129]}$

$$F_{sp} = 2\pi R W_T,$$  \hspace{1cm} (5.2)
where \( R \) is the colloidal probe radius (5 \( \mu \text{m} \)). The Derjaguin approximation is valid for our colloidal probe interacting with a flat plate because the inverse Debye length (\( \kappa \)) multiplied by the colloidal probe radius (\( R \)), is larger than 10 for all ionic strengths.\(^{[129,283]}\)

The total interaction energy per unit area between two parallel plates (\( W_T \)) is obtained by the summation of van der Waals (\( W_V \)) and electrostatic interactions (\( W_E \)) energies (Equation 5.3),

\[
W_T = W_E + W_V,
\]

(5.3)

The non-retarded van der Waals contribution to the interaction energy per unit area between two parallel plates was calculated by Equation 5.4,

\[
W_V = \left( \frac{A_{132}^{132}}{12\pi d^2} \right),
\]

(5.4)

where \( d \) is the separation distance, and \( A_{132}^{132} \) is the Hamaker constant for US-PZT (medium 1) and \( \text{SiO}_2 \) (medium 2) interacting through a uniform electrolyte solution (medium 3).

We used Lifshitz Theory\(^{[135,142]}\) (Equations 5.4 – 5.6) and commonly reported values for the refractive index of PZT (Table 1)\(^{[284,285]}\) to determine a Hamaker constant of 0.66x10\(^{-20} \) J. This value agrees with previously reported values for oxide surfaces interacting through water.\(^{[139,145]}\)

\[
A_{132}^{132} = A_{V=0}^{132} + A_{V>0}^{132},
\]

(5.4)

\[
A_{V=0}^{132} = \frac{3k_B T}{4} \left( \frac{\varepsilon_1-\varepsilon_3}{\varepsilon_1+\varepsilon_3} \right) \left( \frac{\varepsilon_2-\varepsilon_3}{\varepsilon_2+\varepsilon_3} \right),
\]

(5.5)
where $\varepsilon_i$ is the dielectric constant and $n_i$ is the index of refraction of each material, listed in Table 5.1.

**Table 5.1**: Dielectric constant ($\varepsilon$) and index of refraction ($n$) to determine the Hamaker constant.

<table>
<thead>
<tr>
<th>Medium 1:</th>
<th>$\varepsilon$</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PZT</td>
<td>1200$^*$</td>
<td>2.58$^{[285]}$</td>
</tr>
<tr>
<td>Medium 2:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Silica bead</td>
<td>5.8$^{**}$</td>
<td>1.56$^{**}$</td>
</tr>
<tr>
<td>Medium 3:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>80$^{[286]}$</td>
<td>1.335$^{[287]}$</td>
</tr>
</tbody>
</table>

$^*$ Determined experimentally  
$^{**}$Reported manufacturing specifications from Duke Scientific Cat: 9010

**Electrostatic Interaction Energy Using a Constant Potential Boundary Condition**: To determine the surface potential of the polarized US-PZT surface we considered either a constant charge$^{[140]}$ or a constant potential$^{[288]}$ EDL model derived from the linearized Poisson-Boltzmann equation (Equation 5.7). We found that the constant charge EDL model consistently over-predicted the interaction force as a function of separation distance for known values of the inverse Debye length. The constant potential EDL model (Equation 5.8), however, provided good fits to the
measured force-separation data, indicating that a significant amount of charge regulation occurs at the US-PZT surface. Fitting the measured force-separation approach curves to a charge-regulation EDL model also indicates significant charge regulation.

\[ \nabla^2 \psi = \kappa^2 \psi, \]

\[ W_{\text{EP}} = \frac{\varepsilon_0 \varepsilon_r \kappa}{\theta} \{(\psi_1^2 + \psi_2^2) [1 - \coth(x)] + 2\psi_1 \psi_2 \text{cosech}(x)\}, \]

where \( W_{\text{EP}} \) describes the electrostatic interaction energy using a constant potential boundary condition, \( \psi_1 \) is the non-dimensionalized potential \( (\psi e / k_B T) \) of the borosilicate probe, \( \psi_2 \) is the non-dimensionalized potential of the US-PZT surface, \( x \) is \( 2kd \), \( \varepsilon_0 \varepsilon_r \) is the dielectric constant, \( \kappa = \left[ \frac{2\varepsilon_0^2 \theta n}{\varepsilon_0 \varepsilon_r k_B T} \right]^{1/2} \) is the inverse Debye length, \( k_B \) is the Boltzmann’s constant, \( T \) is absolute temperature, and \( n \) is atomic concentration.

The total interaction force equation was determined by substituting equations 3, 4, and 6 into equation 2. The total interaction force equation was fitted to the measured force-separation approach curves for native and polarized US-PZT thin films using a least-squares method and Tablecurve (Systat) software. During fitting, the Debye length \( (\kappa^{-1}) \) and the US-PZT surface potential \( (\psi_1) \) were treated as fitting parameters while the surface potential of the borosilicate probe \( (\psi_2) \) was set to -39 mV. This surface potential was determined experimentally from colloidal force probe measurements on a silica surface, and found not to change within the range of the ionic strengths used in the measurements. During sensitivity analysis, we found that changing the Hamaker
constant by up to one order of magnitude did not significantly impact the fitting values (surface potential and Debye length). The measured force-separation data on approach were also compared with predictions from a non-linear Poisson-Boltzmann model with a constant potential boundary condition.\textsuperscript{[289,290]} However, we did not find significant difference in the prediction of the US-PZT surface potentials. The surface charge at the OHP was calculated from the fitted surface potential values using the Grahame equation.\textsuperscript{[269,270]}

**Electrostatic Interaction Energy Using a Charge-Regulation Boundary Condition:** The electrostatic contribution to the interaction energy as a function of separation distance between a polarized US-PZT and borosilicate probe was also modeled using a linear charge regulation boundary condition (Equation 5.9).

\[
W_E^{CR} = \frac{e \kappa}{4 \pi} \left( 2 \psi_1 \psi_2 e^{-\kappa d} - (\Delta_2 \psi_1^2 + \Delta_1 \psi_2^2) e^{-2\kappa d} \right) \left( 1 - \Delta_2 e^{-2\kappa d} \right)
\]  

(5.9)

where \( W_E^{CR} \) describes the electrostatic interaction energy using a charge regulation boundary condition, \( \Delta_i = \frac{K - e\kappa/4\pi}{K + e\kappa/4\pi} \) is the relative ratio of the diffuse layer capacitance \((e\kappa/4\pi)\) to the regulation capacitance \((K)\). The interaction energy as a function of separation distance was fitted (Tablecurve, Systat Software) to each of the experimentally measured CPFM approach curves. The surface charge density of a Stern layer can be represented by equation E6.\textsuperscript{[130,132]}

\[
\sigma_S = eN_S \frac{\delta \sinh (\theta_S)}{1 + \delta \cosh (\theta_S)}
\]  

(5.10)
where \( e \) is the unit charge density, \( N_S \) is the density of reactive surface groups, and 
\( \theta_S = 2.303(pH_0 - pH) - \gamma_S \), where \( pH_0 = 0.5(pK_+ - pK_-) \). \( \gamma_S \) is the reduced potential 
\( (\gamma_S = \frac{e\psi}{k_B T}) \) and 
\( \delta = 2 \left( \frac{K_-}{K_+} \right)^{1/2} \), where \( K_- \) and \( K_+ \) are the dissociation constant for reactive surface groups. Combining Equations 5.10 with Equation 5.7 and simplifying, we determine the boundary condition of a polarized FETF in solution (Equation 5.11),

\[
-\varepsilon \varepsilon_0 \frac{\partial \gamma_S}{\partial z} = \frac{4\pi e^2 N_S}{k_B T} \left[ \frac{\delta \sinh (\theta_S)}{1 + \delta \cosh (\theta_S)} + \frac{\sigma_F}{e N_S} \right].
\]

(5.11)

Rewriting Equation 5.11 into the linear charge-regulation form of 
\( -\varepsilon \varepsilon_0 \frac{\partial \gamma_S}{\partial z} = S - K\gamma_S \),

We find that for small \( \theta_S \) 
\( S = \frac{e^2 N_S \delta \psi_N}{k_B T (1 + \delta)} + \sigma_F \) and \( K = \frac{e^2 N_S \delta}{k_B T (1 + \delta)} \). Using the surface potential and \( \Delta \) as fitting parameters, we can now estimate the number of surface sites and the ferroelectric surface charge density (\( \sigma_F \)) of a polarized FETF in solution.

**Determination of the Borosilicate Probe Surface Potential:** CPFM was used to measure the interaction force between a clean silica surface and the borosilicate probe while submerged in a known ionic strength solution. The surface potential of the borosilicate probe and the silica surface were determined by fitting a symmetric constant-charge boundary condition DLVO model to the experimentally measured force-separation CPFM approach curves. The Derjaguin approximation was used to relate the normal force measured for the sphere-place geometry to the total interaction energy. The electrostatic contribution to the interaction energy was determined from a
linearized Poisson-Boltzmann equation with a constant-charge boundary condition (Equation 5.9). Using Lifshitz theory, the Hamaker constant for the silica-water-silica interaction was determined to be $4.3 \times 10^{-21}$ J. Curve fitting was performed using Tablecurve (Systat) software.

$$W_{EC} = \frac{\varepsilon_0 \varepsilon_r \kappa}{2} \left\{ 2\psi_{sil}^2 \text{cosech}(x) - \left( 2\psi_{sil}^2 \right)[1 - \coth(x)] \right\}, \quad (5.9)$$

where $(W_{EC})$ is the electrostatic EDL interaction energy using a constant charge boundary condition.

We found that the surface potential of the silica probe was -39 mV and did not significantly change with the ionic strength of solution. Figure 5.4 presents the measured force-separation approach curves with the fitted EDL model.
Figure 5.4. Force-separation approach curves with fitted constant-charge EDL model between a borosilicate probe and a silica surface in a 1 mM NaCl solution (top curve) and a 0.1 mM NaCl solution (bottom curve).

The total interaction force equation was determined by substituting equations 3, 4, and 6 into equation 2. The total interaction force equation was fitted to the measured force-separation approach curves for native and polarized US-PZT thin films using a least-squares method and Tablecurve (Systat) software. During fitting, the Debye length ($\kappa$), and the US-PZT surface potential ($\Psi_2$) were treated as fitting parameters while the surface potential of the borosilicate probe ($\Psi_1$) was set to -39 mV. This surface potential was determined experimentally from colloidal force probe measurements on a silica surface, and found not to change with the ionic strength of the solution. During
sensitivity analysis, we found that changing the Hamaker constant by up to one order of magnitude did not significantly impact the fitting values (surface potential and Debye length). The measured force-separation data on approach were also compared with predictions from a non-linear Poisson-Boltzmann model with a constant potential boundary condition.\textsuperscript{[269,290]} However, we did not find significant difference in the prediction of the US-PZT surface potentials. The surface charge at the OHP was calculated from the fitted surface potential values using the Grahame equation.\textsuperscript{[269,270]}

### 5.3 Results and Discussion

#### 5.3.1 The US-PZT thin film surface

The interaction distance and strength of interfacial forces in aqueous liquids depend not only on surface charge characteristics, the ionic strength, and the material composition, but also on surface roughness. Increases in surface roughness result in a decrease in the interaction force and an increase in the effective separation distance.\textsuperscript{[121,122]} Preparation of ultra-smooth ferroelectric surfaces is thus necessary for the accurate measurement of electric double layer forces. Figures 5.5 A and 5.5 B presents the surface topography of US-PZT before and after submersion in Milli-Q grade water for 100 days. The mean surface roughness before and after water exposure is unchanged and has a value of 2.4 nm over a 25 mm\(^2\) area. This demonstrates that even after extended
exposure, the US-PZT films are structurally stable in Milli-Q Grade water. Reverse imaging of the borosilicate colloidal probe with SPM revealed a mean surface roughness of about 5 nm over a 25 mm² area.

Figure 5.5: AFM contact mode images of our US-PZT surface (A) before and (B) after 100 days of exposure to Milli-Q grade water. The mean surface roughness and topography are unchanged. The lines indicate the location of the height profiles shown below the images.

5.3.2 Measurement of electric double layer forces of native ferroelectric thin films

Prior to polarization, CPFM measurements between a freshly annealed (native) US-PZT surface and a borosilicate colloidal probe were performed in Milli-Q grade water and in a variety of dilute electrolyte solutions. Previous studies have
demonstrated that sodium and chlorine are not indifferent ions.\textsuperscript{[291]} Changes in interaction force as a function of separation distance would reflect how ion type could change the surface potential of native US-PZT. As shown in Figure 5.6, the type of 1:1 electrolyte solution at constant ionic strength, did not affect the attractive interaction force or distance between the borosilicate probe and the native US-PZT surface. This suggests that ion-complexation does not affect the US-PZT surface potential and that native, non-poled US-PZT surface maintains a positive surface charge in aqueous environments. The positive surface charge agrees with previous acid/base titration experiments of lead oxide thin films and other ferroelectric perovskites.\textsuperscript{[292-294]} This supports the conclusion that the native surface charge of the US-PZT arises from protonation of reactive surface sites. Using a constant potential boundary EDL model we were able to determine the surface potential of the native US-PZT surface in aqueous solutions with different ionic strengths (Table 5.2).
Figure 5.6: Force-separation approach curves for native US-PZT in Milli-Q water and in different types of 0.1 mM electrolyte solution. Force separation curves are normalized for colloidal probe radius.

5.3.3 Measurement of electric double layer forces above polarized ferroelectric thin films

Figure 5.7 shows force-separation approach curves for polarized US-PZT with a negative (Figure 5.7 A) and positive surface charge (Figure 5.7 B) for a range of NaCl concentrations. The long-range interaction between the negatively charged colloidal probe and the polarized FETF with a negative surface charge was increasingly repulsive upon approach, until final snap-in occurred at close range. This long-range repulsive interaction is characteristic for overlapping EDLs between two like-charged surfaces.
Although the native US-PZT surface has a positive charge, these results suggest that the polarization induced surface charges dominate the interaction energy. Upon polarization reversal the US-PZT has a positive surface charge and as a result its long-range interaction with the colloidal probe becomes increasingly attractive. Upon approach, this attractive interaction is characteristic for overlapping EDLs between oppositely charged surfaces. For both polarization states, the extent of the EDL interaction decreased with increasing ionic strength, as expected with the decreasing Debye length. At ionic strengths above 10 mM we were unable to resolve any further changes in the EDL interactions, because at these electrolyte concentrations, the Debye length (< 2 nm) is smaller than the root-mean-square (RMS) surface roughness of the US-PZT (~ 2.4 nm) and the colloidal probe (~5 nm). Short-range hydration forces were also not observed.
Figure 5.7: Force-separation approach curves for (A) a polarized US-PZT with a negative surface charge and (B) a polarized US-PZT with a positive surface charge, measured for a range of ionic strengths. The solid lines represent the best fit to the data calculated using a constant potential EDL model. Fitting values are shown in Table 5.3.

In control experiments we switched the polarization state of a US-PZT substrate repeatedly from a surface positive to a surface negative charge state and observed that the EDL interactions also switched accordingly. These experiments unequivocally demonstrate that the interaction behavior in aqueous environments is governed by the polarization state of the US-PZT films and not the charge state of the reactive surface sites.

The polarity observed on the US-PZT surface was opposite that one would have expected if mere charge injection had occurred. We thus conclude that the US-PZT surface charge is due to ferroelectric polarization.
We acquired XPS spectra before and after polarization to detect any polarization-induced surface chemical changes (e.g. oxidation or reduction) of the US-PZT thin film. Specifically, the binding energies of the oxygen 1s and the lead 4f peaks are sensitive to changes in the chemical bonding structure at the PZT surface.\cite{168} Figure 6 presents high-resolution XPS spectra of the oxygen 1s and lead 4f regions before and after polarization. Deconvolution of the oxygen 1s envelope reveals three binding moieties, which have been attributed to (I) adsorbed carbon containing species (e.g. −CO or −CO$_2$), (II) adsorbed oxygen, and (III) PbO.\cite{247} Figure 5.8 A shows that there is no significant change in the composition of oxygen binding moieties between the three samples. Furthermore, no significant difference in the doublet binding energy of the lead 2p envelope is apparent (Figure 5.8 B). Taken together, these observations shows that the chemical structure in the three samples do not change, which suggests that the polarization process does not induce appreciable changes in the chemical composition of the US-PZT surfaces and is not responsible for the observed changes in EDL interaction force.
Figure 5.8: High-resolution XPS spectra for (A) oxygen 1s and (B) lead 4f regions.

5.3.4 Effects of Grounding on Electric Double Layer Induced by Polarized US-PZT

To further demonstrate that the measured interaction forces primarily depend on the polarization state of the US-PZT, we used CPMF experiments to test the effect of grounding the bottom platinum electrode of the US-PZT sample, which is expected to remove the free charge carriers on the bottom surface (Figure 5.9). While isolated from ground, the force-separation approach curves for native and polarized US-PZT with a
negative surface charge reflect that the ferroelectric polarization state controls the EDL interaction force. Upon grounding, however, we observe that the effects of the polarization are removed and that the interaction again resembles that of native US-PZT. This effect is expected because of the small aspect ratio of the polarized region within the US-PZT thin film. By grounding the bottom electrode, the free charges present in the metal, that were compensating the polarization charges at the bottom surface of the FETF, were drained and the remnant-field propagating from the polarized FETF became effectively negligible. Both the results of the XPS measurements and the disappearance of the EDL repulsion upon grounding demonstrate that the electric field propagating from the polarized FETF into the fluid results from the uncompensated charges present at the top surface of the ferroelectric.

Figure 5.9: Force-separation approach curves in 1 mM NaCl solution for (A) native (non-poled) US-PZT thin film isolated from ground, and a polarized US-PZT thin film expressing a negative surface charge (B) while isolated from ground and, (C) after being connected to ground.
5.3.5 Determination of US-PZT surface potential using constant-potential EDL model

To determine the surface potential of the US-PZT interface as a function of polarization direction, the measured force-separation approach curves between the polarized US-PZT surface and the colloidal probe were fit to EDL theory using a constant potential boundary condition with a linearized Poisson-Boltzmann equation (Table 5.2). The theoretically predicted OHP potentials agree with values reported for metal oxide surfaces in aqueous environments.\[111] Deviations of the theoretical fits from experimental results occur at small separation distances, which is common for EDL interaction force equations derived from a linearized Poisson-Boltzmann equation.\[129] The fitted Debye lengths agree reasonably well those derived from the experimentally measured solution ionic strengths. Differences at low ionic strength may be attributed to water evaporation during measurement and experimental error. Previous work indicates that a Stern layer is present above polarized FETFs in both air and liquid.\[41,68,87,105,298] The Stern layer can be composed of mobile surface charges, in the form or adsorbents (e.g., water or contaminants) or free charge carriers (e.g., oxygen vacancies or unit cell defect sites) on the surface.\[299] By assuming the presence of a Stern layer, we calculated the IHP surface charge density of the US-PZT films. Using a linear capacitance across a condensed counter ion layer,\[129] we calculate IHP surface charge
densities of -16.4 $\mu$C cm$^2$ and 15.8 $\mu$C cm$^2$. These values agree well with the independently measured remnant polarization values of our US-PZT of -16.3 $\mu$C cm$^2$ and 15.3 $\mu$C cm$^2$ for both polarization states, respectively. The near symmetry in the magnitude of the surface charge density and the change in sign reflect the ability to switch the surface charge state of the FETF through polarization, thereby altering the probe-surface interactions.
Table 5.2: Average fitted values for a constant potential boundary condition EDL model to CPM force-separation approach curves for polarized US-PZT in a range of NaCl electrolyte solutions.

### Polarized US-PZT to express a negative surface charge

<table>
<thead>
<tr>
<th>Concentration (mM)</th>
<th>Measured Kappa 1 (nm)</th>
<th>Kappa 1 (nm)</th>
<th>OHP Potential (mV)</th>
<th>OHP Charge (µC/cm²)</th>
<th>IHP Potential (mV)</th>
<th>IHP Charge (µC/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01 ± 0.001</td>
<td>137.7 ± 0.5</td>
<td>129.8 ± 4.3</td>
<td>-63.8 ± 2.0</td>
<td>-0.035 ± 0.0006</td>
<td>-362 ± 2.0</td>
<td>-16.4 ± 0.001</td>
</tr>
<tr>
<td>0.1 ± 0.001</td>
<td>43.4 ± 0.02</td>
<td>34.8 ± 9.2</td>
<td>-37.0 ± 3.2</td>
<td>-0.081 ± 0.03</td>
<td>-334 ± 3.2</td>
<td>-16.5 ± 0.03</td>
</tr>
<tr>
<td>1.0 ± 0.1</td>
<td>14.6 ± 0.01</td>
<td>15.3 ± 8.5</td>
<td>-13.2 ± 3.6</td>
<td>-0.073 ± 0.03</td>
<td>-311 ± 3.6</td>
<td>-16.4 ± 0.03</td>
</tr>
</tbody>
</table>

### Polarized US-PZT to express a positive surface charge

<table>
<thead>
<tr>
<th>Concentration (mM)</th>
<th>Measured Kappa 1 (nm)</th>
<th>Kappa 1 (nm)</th>
<th>OHP Potential (mV)</th>
<th>OHP Charge (µC/cm²)</th>
<th>IHP Potential (mV)</th>
<th>IHP Charge (µC/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01 ± 0.001</td>
<td>137.7 ± 0.5</td>
<td>83.1 ± 19.4</td>
<td>42.5 ± 0.6</td>
<td>0.005 ± 0.01</td>
<td>331 ± 0.6</td>
<td>15.9 ± 0.01</td>
</tr>
<tr>
<td>0.1 ± 0.001</td>
<td>43.4 ± 0.02</td>
<td>35.9 ± 5.9</td>
<td>32.0 ± 0.02</td>
<td>0.065 ± 0.01</td>
<td>320 ± 0.02</td>
<td>15.9 ± 0.01</td>
</tr>
<tr>
<td>1.0 ± 0.1</td>
<td>14.6 ± 0.01</td>
<td>13.2 ± 1.6</td>
<td>4.0 ± 0.8</td>
<td>0.02 ± 0.002</td>
<td>293 ± 0.8</td>
<td>15.9 ± 0.002</td>
</tr>
</tbody>
</table>

### Native US-PZT

<table>
<thead>
<tr>
<th>Concentration (mM)</th>
<th>Measured Kappa 1 (nm)</th>
<th>Kappa 1 (nm)</th>
<th>OHP Potential (mV)</th>
<th>OHP Charge (µC/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01 ± 0.001</td>
<td>137.7 ± 0.5</td>
<td>194.9 ± 18.9</td>
<td>39.6 ± 2.9</td>
<td>0.014 ± 0.002</td>
</tr>
<tr>
<td>0.1 ± 0.001</td>
<td>43.4 ± 0.02</td>
<td>29.8 ± 13.3</td>
<td>31.8 ± 1.4</td>
<td>0.092 ± 0.06</td>
</tr>
<tr>
<td>1.0 ± 0.1</td>
<td>14.6 ± 0.01</td>
<td>10.4 ± 0.7</td>
<td>22.9 ± 3.6</td>
<td>0.156 ± 0.03</td>
</tr>
</tbody>
</table>
Although the force-separation approach curves were well fit by a constant potential boundary condition EDL model, charge-regulation processes may occur at the surface. Specifically, our use of a Stern layer to model the interaction force between a polarized FETF and a charged colloidal probe in solution may require the consideration of free charge carriers. Previous reports have supported that mobile charge carriers within the FETF may be capable of responding to externally applied electric fields.\textsuperscript{[41,68,266]} Alternatively, the presence of a Stern layer has been shown capable of charge regulation.\textsuperscript{[130,132,139,297]} To better model the effects of a charge regulation process, we have also fitted the measured force-separation approach curves using a linear-charge regulation model.\textsuperscript{[132]}

### 5.3.6 Determination of US-PZT surface potential using charge-regulation EDL model

To better model the effects of a charge regulation on the measured interaction energy between a polarized US-PZT thin film and a charged borosilicate probe, we have fitted the measured force-separation approach curves using our linear-charge regulation model (Figure 5.10).\textsuperscript{[132]} Using the FETF surface potential and the $\Delta$ as fitting parameters, we estimate the number of surface sites and the ferroelectric surface charge density. The linear-charge regulation model is a reasonably good fit to the measured force-separation
curves, confirming that the US-PZT surface is charge regulating and that the IHP charge density matches the independently measured ferroelectric charge density. To calculate the IHP values shown in Table 5.3, we assumed the dissociation constant ratio was equal to one. We find that the IHP surface charge, determined using the fitted values, is in good agreement with the measured ferroelectric surface charge density of our US-PZT. Additionally, we find that $\Delta$ for polarized FETF are between 0 and 1, indicating the FETF surface acts more like a constant potential boundary condition.$^{[150]}$ Varying the dissociation constants ratio by over 50% did not significantly change the predicted surface charge density. As with the constant potential boundary condition EDL model, the linear charge regulation model was also insensitive to changes in the Hamaker constant by up to one order of magnitude. The average fitting values and standard deviations are presented in Table 5.3. To calculate the values shown in Table 5.3, we assumed the dissociation constant ratio was equal to one. Varying the dissociation constants ratio by over 50% did not significantly change the predicted surface charge density. As with the constant potential boundary condition EDL model, the linear charge regulation model was also insensitive to changes in the Hamaker constant by up to one order of magnitude.
Figure 5.10. Force-separation approach curves with for (A) a polarized FETF expressing a negative surface charge and (B) a FETF expressing a positive surface charge measured in a range of NaCl concentrations. The solid line represents the best fit to the data calculated using the charge regulation EDL model. Fitting values are presented in Table 5.3.

<table>
<thead>
<tr>
<th>Measured Kappa (nm)</th>
<th>Fitted Kappa (nm)</th>
<th>Fitted Surface Potential (mV)</th>
<th>Fitted Δ</th>
<th>IHP Surface Charge (mC/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.3</td>
<td>10.0 ± 0.2</td>
<td>-360 ± 1</td>
<td>0.81 ± 0.03</td>
<td>-16.2 ± 0.2</td>
</tr>
<tr>
<td>30.7</td>
<td>20.4 ± 0.6</td>
<td>-397 ± 5</td>
<td>0.50 ± 0.2</td>
<td>-15.8 ± 0.13</td>
</tr>
<tr>
<td>97.4</td>
<td>40.6 ± 0.2</td>
<td>-431 ± 9</td>
<td>-0.02 ± 0.01</td>
<td>-15.7 ± 0.2</td>
</tr>
</tbody>
</table>

US-PZT Polarized to Express Negative Surface Charge

<table>
<thead>
<tr>
<th>Measured Kappa (nm)</th>
<th>Fitted Kappa (nm)</th>
<th>Fitted Surface Potential (mV)</th>
<th>Fitted Δ</th>
<th>IHP Surface Charge (mC/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.3</td>
<td>10.3 ± 0.6</td>
<td>360 ± 0.4</td>
<td>0.80 ± 0.05</td>
<td>15.2 ± 0.1</td>
</tr>
<tr>
<td>30.7</td>
<td>13.1 ± 0.2</td>
<td>371 ± 0.4</td>
<td>0.45 ± 0.06</td>
<td>15.2 ± 0.1</td>
</tr>
<tr>
<td>97.4</td>
<td>55.7 ± 0.3</td>
<td>42 ± 0.5</td>
<td>0.80±0.004</td>
<td>14.2 ± 0.1</td>
</tr>
</tbody>
</table>

US-PZT Polarized to Express Positive Surface Charge
5.3.7 Determination of US-PZT surface potential using the non-linear Poisson-Boltzmann equation

We also fitted the measured force-separation approach curves to an EDL model that uses the full, non-linear Poisson-Boltzmann (NLPB) equation. The NLPB force-separation EDL model was developed by Fröberg et al, and used previously in a number of publications.\cite{289,290} We found good agreement between the NLPB EDL model predictions and our measured force separation curves, particularly at close separation (Figure 5.11). The NLPB EDL model, however, was not able to predict the interaction force as a function of separation distance in the case of a positively charged US-PZT surface and a negatively charged colloidal probe in 1 mM NaCl solution. In all other cases we found that the predicted OHP potentials for our polarized US-PZT surfaces were nearly identical to those predicted by the linearized PB model (Table 5.4).
**Figure 5.11:** Force-separation approach curves with for (A) a polarized FETF expressing a negative surface charge and (B) a FETF expressing a positive surface charge measured in a range of NaCl concentrations. The solid line represents the best fit to the data calculated using NLPB EDL model. Fitting values are presented in Table 5.4.

**Table 5.4:** Fitted values for the NLPB EDL model fit to the CPFM force-separation approach curves presented in Figure 5.11.

<table>
<thead>
<tr>
<th>Measured Kappa (nm)</th>
<th>Fitted Kappa (nm)</th>
<th>Fitted Surface Potential (mV)</th>
<th>IHP Surface Charge (mC/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.3</td>
<td>13.7</td>
<td>-364</td>
<td>-16.4</td>
</tr>
<tr>
<td>30.7</td>
<td>14.5</td>
<td>-376</td>
<td>-16.4</td>
</tr>
<tr>
<td>97.4</td>
<td>108.2</td>
<td>-328</td>
<td>-16.4</td>
</tr>
</tbody>
</table>

**US-PZT Polarized to Express Positive Surface Charge**

<table>
<thead>
<tr>
<th>Measured Kappa (nm)</th>
<th>Fitted Kappa (nm)</th>
<th>Fitted Surface Potential (mV)</th>
<th>IHP Surface Charge (mC/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.3</td>
<td>13.7</td>
<td>309</td>
<td>15.9</td>
</tr>
<tr>
<td>30.7</td>
<td>14.5</td>
<td>324</td>
<td>15.9</td>
</tr>
<tr>
<td>97.4</td>
<td>51.8</td>
<td>389</td>
<td>15.9</td>
</tr>
</tbody>
</table>
5.3.8 Effects of surface roughness

Interfacial roughness on the US-PZT and colloidal probe can also decrease the measured interaction force in dilute electrolyte solutions and lead to under-prediction of the true surface charge density.\textsuperscript{122,126,198} Even though our US-PZT thin films have a mean surface roughness of only 2.4 nm, the probe surface roughness was about 5 nm. The domain structure of a FETF results in nano-scale surface asperities (i.e. roughness) that increases the effective separation distance between surfaces and thus reduces the measured interfacial forces.\textsuperscript{123,121} As such, domain size and crystallographic orientation are important consideration in integrating polarized FETFs for interfacial sensing applications in aqueous environments.

5.3.9 US-PZT thin films stability at low pH

We found that prolonged exposure of the native US-PZT surface to acidic solutions (pH < 4.2) induced a change from long-range attraction to long-range repulsion (Figure 5.12). Some interfacial softening was also observed (data not shown). Interfacial softening has been associated with the formation of a hydration layer on oxide surfaces.\textsuperscript{116,300-302} The inversion of the interaction force observed here indicates a change in the chemical structure of the US-PZT surface.\textsuperscript{292} It is well known that simple-oxide materials have a lower point-of-zero charge, which may be responsible for the observed
negative potential when placed in dilute electrolyte solutions. Our claim that the US-PZT interface degrades into simple oxide components is also supported by high resolution XPS spectra of the O 1s and Pb 4f regions (Fig. 10). XPS results show the severe degradation of the US-PZT interface after exposure to low pH solutions. Deconvolution of the O 1s envelope shows the increases in oxygen adsorbed Pb-O (peak II at 530.5 eV) and Pb-CO$_2$ (peak I at 532 eV) binding moieties and degradation of the Pb-O binding moiety (Figure 5.12 A). Furthermore, the splitting of the Pb 4f doublet envelope into higher binding energy components supports our claim of US-PZT surface oxidation (Figure 5.12 B). Furthermore, no surface degradation is observed after exposure to a solution of pH 9. Both the CPMF interfacial approach curves and the XPS results are consistent with reports of interfacial degradation of PZT after exposure to water-vapor. Therefore, possible degradation of perovskite-structured ferroelectrics in low pH solutions needs to be considered in potential applications in aqueous environments.
Figure 5.12: Native US-PZT in $10^{-4}$ M NaCl solution at pH 5.5 and $10^{-4}$ M NaCl solution at pH 4.2. The decrease in pH induces a long range repulsion between the US-PZT and the negatively charged colloidal probe.
5.4 Conclusions

We present the first study of an EDL induced by polarized ferroelectric US-PZT in dilute ionic solutions. We show that the surface charge density expressed by the ferroelectric polarization US-PZT thin films dominates over the native oxide surface. The ability to switch the polarization state of ferroelectric materials, i.e., switching their surface charge without altering other surface properties, makes this system attractive for
isolating the effect of EDLs in the study of interfacial forces. The measured force-separation curves were fit to three different EDL models, i) an EDL model using the linearized Poisson-Boltzmann equation and a constant potential boundary condition and a Stern layer, ii) an EDL model using a linear charge-regulation boundary condition, and iii) a NLPB EDL model using a constant potential boundary condition and a Stern layer. In all cases the EDL model fit well to the measured force-separation approach curves. Using these models, we were able to conclusively determine the US-PZT surface potential and charge density at the IHP for either polarization state. Our results are the first to quantify the interactions between polarized FETFs and colloidal materials, and highlight the potential of FETFs for applications in guided deposition and interfacial sensing devices.
6. Guided Deposition of Charged Nanoparticles using Polarized Ultra-Smooth Lead Zirconium Titanate

This work was performed in collaboration with Dr. Benjamin Yellen and Dr. Mark Wiesner.

6.1 Introduction

The guided deposition of charged, colloidal particles onto patterned, charge-heterogeneous surfaces has applications for sensing and lab-on-a-chip diagnostic devices.\cite{156,305} The electrostatic contribution to the electric double layer (EDL) interaction force has the longest range and thus dominates the deposition characteristics for colloidal particles from solution. The magnitude and interaction distance of the electrostatic force component is largely limited by the surface charge density and the electrolyte concentration in solution. Surface charge patterns are typically fabricated using a charge injection or chemical modification process.\cite{5,9} These patterning methods typically entail low charge densities, dependence on solution conditions, and fail to reliably provide high deposition selectivity. We have previously shown that ferroelectric thin films (FETFs) can maintain a high, persistent surface charge density in liquid environments, without the application of an externally applied electric field. Here, we use the high surface charge density available through the remnant polarization of our US-PZT to induce the guided deposition of charged particles from solution.
FETFs can locally express a positive or negative charge without altering other surface properties.\textsuperscript{[41,60,266]} Our work demonstrates that the ferroelectric polarization charge density can be an order of magnitude higher than that of common oxide surfaces in aqueous environments (see Chapter 5).\textsuperscript{[168,185,234,252]} Furthermore, we have shown that the interaction force depends on the ferroelectric polarization direction. Ion patterns, i.e., charge patterns, can be created with serial or parallel patterning processes.\textsuperscript{[192]} We surmise that polarization patterned FETFs enable the guided deposition of charged species from solution (Figure 6.1).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{charging.png}
\caption{Schematic of charged colloidal particles depositing onto locally polarized FETFs.}
\end{figure}

While FETFs can maintain a stable charge density in aqueous environments, the total interaction force between the FETF and the particle still depends on the solution
conditions, including ionic strength, pH, particle size, and interfacial roughness. Solutions of high ionic strength compress the diffuse double layer and decrease the electrostatic interaction distance. Changes in the solution pH can alter the colloidal particles’ surface charge density, and increasing the surface roughness of the FETF or the colloidal particle decreases the electrostatic contribution to the EDL force, which in turn increases the incidence of non-specific binding. Increasing the particle size reduces the effects from Brownian motion while at the same time increasing the effective area for interaction.\cite{121,126,158} The use of FETFs for guided deposition of charged colloidal particles thus still requires careful consideration of the deposition conditions.

Here we use polarization patterned ultra-smooth lead zirconium titanate (US-PZT) to create a charge-heterogeneous surface and induce the guided deposition of charged colloidal particles from solution. Using a clean copper TEM grid, we pattern the surface of the US-PZT, setting the ferroelectric polarization state. Depending on the polarization direction, the US-PZT surface was then incubated with positively or negatively charged colloidal particles (Invitrogen), suspended in a range of diluted electrolyte solutions. We demonstrate that US-PZT induces the guided deposition of charged particles from solution, similar to that observed for other charged surfaces. These results are encouraging, as they for the first time demonstrate how the
polarization state of FETFs can be used for particle deposition from aqueous media, with implications for the use of FETFs in interfacial sensing devices.

6.2 Materials and Methods

**Substrate Preparation:** Silicon wafers (<100>, Virginia Semiconductor) were first cleaned by sonication for 10 min in 0.5% SDS solution, rinsing 10 times with Milli-Q grade water (18.2 MΩ·cm), immersion for 20 min in 3:1 H₂O₂:H₂SO₄ (Piranha solution), rinsing 10 times with Milli-Q grade water, and drying in a stream of N₂. Next, 200 nm of titanium and 100 nm of platinum were deposited using a Kurt Lesker PVD 75 e-beam source evaporator at ~4x10⁻⁵ Torr.

**Sol-Gel Synthesis:** US-PZT thin-films were fabricated from a sol-gel precursor (52/48/125, Mitsubishi Materials Corp) using previously published methods.[ref US-PZT Fab paper] Briefly, the sol-gel solution was stored under dry conditions at 5°C and protected from light. Prior to deposition, the sol-gel was warmed to room temperature and sonicated for 15 min. The precursor was passed through a 0.1 μm filter and deposited onto a platinum-coated silicon substrate, making sure to completely cover the substrate surface. The sol-gel precursor was then spin-coated using a two-stage ramp profile (5 sec spin at 500 RPM followed by 40 sec at 3000 RPM). Next, the solvent was evaporated on a 90°C hot plate for 120 sec. The films were next pyrolyzed in a benchtop
annealing furnace (Thermolyne) at 450°C for 35 min. The films were allowed to cool at a rate of 0.5°C sec\(^{-1}\) before being annealed using a rapid thermal annealer (Jipelec JetFirst 100) at 700°C for 15 sec. This fabrication process results in ultra-smooth PZT thin films with mean thickness of ~116 nm and RMS roughness of ~2.4 nm. All US-PZT samples were annealed just prior to measurement. The dielectric constant and remnant polarization of our US-PZT were measured separately by evaporating circular gold capacitors (50 µm diameter) onto the US-PZT surface with a Radiant RT66b ferroelectric tester.

**Polarization patterning:** Charge patterning of the US-PZT thin films was performed using a clean TEM grid (Ted Pella 3HGC500) that was brought into contact with the US-PZT surface using a PDMS plug. A +40V bias voltage was applied between the TEM grid and the bottom platinum electrode using a Keithley 6487 Piccoammeter/Voltage source. After the final polarization state was achieved, the potential difference between the top and bottom electrodes was brought to 0 Volts. The circuit was then broken and the TEM grid was removed. This polarization process results in an US-PZT surface expressing an effective surface charge density set by the ferroelectric US-PZT.

**Colloidal Suspension Preparation:** Colloidal suspensions were purchased from Invitrogen/Life Technologies. Aliphatic amine latex particles (100 nm diameter, 2% w/v,
Product Number: A37358), have a positive surface charge in Milli-Q grade water with an aliphatic amine charge of 71.8 mEq/g (manufacturer specifications). Though the charge density depends on the solution pH, if fully reacted this is equivalent to a charge density of 24 μC cm⁻². Carboxyl latex particles (100 nm diameter, 2% w/v, Product Number: C37485), have a negative surface charge density of -3.4 μC cm⁻² in Milli-Q grade water (manufacturer specifications). All colloidal suspensions were stored at 4°C and protected from light. Prior to deposition, the colloidal suspension was warmed to room temperature and sonicated for 10 min at level 4.

**Exposure to Colloidal Suspension:** The polarization patterned US-PZT was exposed to a colloidal suspension using a double drop technique. First, a 150 μL drop of Milli-Q water or ionic solution was deposited onto the surface. Then, a 150 μL drop of colloidal suspension was pipetted onto the liquid droplet. Gentle mixing was performed using the micropipette to ensure solution homogeneity. By pre-wetting the US-PZT surface, we reduce non-specific binding of colloidal particles onto the polarized US-PZT surface. After the desired exposure time is reached, the US-PZT surface was gently rinsed three times with Milli-Q grade water and dried with a stream of N2.

**Sample Imaging:** Clean dry samples were sputter-coated (Denton Desk IV) with 20 nm of gold prior to SEM imaging (FEI XL30 SEM-FEG) at 10 kV. The deposition
process was observed with a Leica DM LFS microscope through an air immersion lens. The microscope phase contrast was adjusted to optimize imaging of the US-PZT surface.

6.3 Results and Discussion

6.3.1 Effect of colloidal particle charge on deposition

We charge patterned the US-PZT thin film with a positively biased (+40 V), copper TEM grid, resulting in negative surface charge patterns. The non-polarized regions of the US-PZT maintained a positive surface charge, due to the native oxide surface. Figure 6.2 A shows an SEM image of the boundary between a non-polarized region (right) and a negatively charged region (left), after a 3 hour exposure to negatively charged colloidal particles. As expected, we find that negatively charged colloidal particles preferentially deposit onto positively charged regions. Figures 6.2 B and C show SEM images of a locally polarized US-PZT surface after a 3 hour exposure to positively charged colloidal particles. Here, the positively charged particles selectively deposited onto the negatively charged regions of the US-PZT. The images reveal some degree of non-specific particle deposition onto the like-charged regions. We presume that the adhesion between particle and surface is essentially due to van der Waals forces, once the samples are dried. Particle deposition patterns were not observed when a grounded TEM grid was placed into contact with the US-PZT surface, further
demonstrating that the polarization state of the US-PZT is responsible for the surface charge pattern.

**Figure 6.2:** SEM images of charge-heterogeneous US-PZT after 3 hours of exposure to (A and B) 400 nm diameter, negatively charged, carboxyl terminated latex particles and (C and D) 100 nm diameter, positively charged, amine terminated latex particles in Milli-Q grade water. In each image, we have included a deposition schematic and noted the local polarization direction.

High particle densities are observed at the charge boundary after deposition of positively charged colloidal particles. At the charge boundary, the charged colloidal particle interacts with both the positively and negatively charged regions. The
combination of interaction energies between the two charged regions induces a lateral force on the colloidal particle.\textsuperscript{[154]} Theoretical and experimental results have demonstrated similar deposition characteristics of charged nanoparticles on charge heterogeneous surface.\textsuperscript{[8,161]} Furthermore, previous work with PZT thin films in liquid environments has demonstrated Stern layer disruption between neighboring grain boundaries that are oppositely polarized.\textsuperscript{[87]} A Stern layer disruption decreases the charge shielding effect and further enhance the electric fields at these interfaces.

### 6.3.2 Effect of solution ionic strength on deposition

For the interaction between like-charge surfaces, an increase in the solution ionic strength compresses the double layer thickness and reduces the repulsive interaction force. In many instances, the decrease in electrostatic repulsion results in an increase in non-specific deposition.\textsuperscript{[8,161]} Figure 6.3 shows SEM images of US-PZT thin films after a 3 hour exposure to a suspension of positively charged colloidal particles (100 nm diameter) for a range of ionic strengths. With increasing ionic strength we observe an increase in the non-specific deposition of the positively charged nanoparticles (Table 6.1), resulting in a loss of pattern fidelity (figures not shown). These results demonstrate that while US-PZT can guide the deposition of charged colloidal particles, deposition is susceptible to changes in the solution conditions.
**Figure 6.3:** SEM images of US-PZT after deposition of positively charge amine terminated latex nanoparticles (100 nm diameter) in (A) 0.01 mM NaCl, (B) 0.1 mM NaCl, and (C) 1 mM NaCl solution. The inserted images are at a higher-magnification.

**Table 6.1:** Particle surface density as a function of ionic strength.

<table>
<thead>
<tr>
<th>Solution</th>
<th>0.01 mM NaCl</th>
<th>0.1 mM NaCl</th>
<th>1 mM NaCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particles per $\mu m^2$</td>
<td>2.07 ± 0.5</td>
<td>4.18 ± 0.7</td>
<td>20.9 ± 6.2</td>
</tr>
</tbody>
</table>

### 6.3.3 Effect of particle size on deposition

As long as the buoyancy and gravitational forces are negligible an increase in the size of the charged, colloidal particle increases the effective interaction area, decreases thermal noise effects, and thus should improve deposition selectivity on charge heterogeneous surfaces\(^8\),\(^{161}\). We have found in practice, however, that larger particles are also more susceptible to fluid forces such as convection. Figure 6.4 shows SEM
images of US-PZT thin films after exposure to positively charged colloidal particles with diameters between 100 and 400 nm. We find that after 3 hours of exposure 100 nm and 200 nm diameter particles have low non-specific deposition with particle densities of $0.07 \pm 0.04 \ \mu\text{m}^2$ and $0.03 \pm 0.02 \ \mu\text{m}^2$, respectively. With 400 nm diameter particles, however, we find a dramatic increase in non-specific deposition with a particle density of $1.97 \pm 0.75 \ \mu\text{m}^2$. While deposition patterns could be observed with 100 and 200 nm diameter particles, no deposition patterns could be seen with 400 nm diameter particles (data not shown). Possible explanations for these observations include, a decrease in surface charge density for the 400 nm particles, particle settling, or colloidal deposition during mixing. Because the particles were stable in solution prior to exposure, it is unlikely that there was a significant decrease in the particle surface charge density; and given the size and density of the particles, gravitational forces should be insignificant. Instead, the increase in non-specific binding of the 400 nm diameter particles likely occurred during the mixing and rinsing steps. Chapter 7 discusses alternative deposition methods that may improve the deposition selectivity of larger colloidal probes.
Figure 6.4: SEM images of US-PZT after deposition of (A) 100 nm diameter, (B) 200 nm diameter, and (C) 400 nm diameter positively charge amine terminated latex nanoparticles in Milli-Q grade water.

Table 6.2: Particle surface density as a function of particle size.

<table>
<thead>
<tr>
<th></th>
<th>100 nm Amine Particle</th>
<th>200 nm Amine Particle</th>
<th>400 nm Amine Particle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particles per µm²</td>
<td>0.07 ± 0.04</td>
<td>0.03 ± 0.02</td>
<td>1.97 ± 0.75</td>
</tr>
</tbody>
</table>

6.3.4 Effect of surface roughness on deposition

An increase in surface roughness dramatically decreases the EDL contribution to the interaction force felt between the FETF surface and a particle.\textsuperscript{[121-123,198]} To test the effects of surface roughness on particle deposition, we compared the incidence of non-specific binding between ultra-smooth (2.4 nm RMS surface roughness over a 25 µm² area) and rough (24 nm RMS roughness over a 25 µm² area) PZT thin films and positively charged colloidal particles. Rough PZT thin films have a measured RMS surface roughness of 24 nm over a 25 µm² area. Figures 6.5 A and 6.5 B present SEM
images of native ultra-smooth and rough PZT surfaces after 3 hours of exposure to positively charged latex particles immersed in Milli-Q grade water. With the tenfold increase in mean surface roughness of the PZT film, we also find a dramatic increase in non-specific adsorption. The US-PZT film has a deposited particle density of 0.1 ± 0.04 particles µm$^2$, the rough PZT film has a particle density of 24 ± 4.2 particles µm$^2$. This observation suggests a dramatic increase in non-specific binding, and is in line with the notion of a reduced, repulsive EDL interaction. Figure 6.5 C shows a SEM image of non-polarized, rough PZT after 3 hour exposure to positively charged latex particles in 1 mM NaCl. The density of the deposited particle was 23 ± 3.3 particles µm$^2$, which is, within experimental error, identical to the particle density obtained with Milli-Q grade water. This further supports the notion that the EDL interaction force does not contribute substantially to the deposition of charged colloidal particles onto rough PZT surfaces. We did not observe guided deposition onto charge patterned rough PZT thin films. Comparison between polarized regions of US-PZT and rough PZT, however, is complicated by the dramatic reduction in the remnant polarization maintained by rough PZT thin films (see Chapter 3). These results emphasize the need to fabricate ultra-smooth PZT thin films to maximize the effect of polarization charge driven interactions.
Figure 6.5: SEM images of (A) US-PZT after a 3 hour exposure to 100 nm positively charged amine functionalized colloidal particles in Milli-Q grade water, (B) rough PZT after a 3 hour exposure to positively charged 100 nm amine functionalized colloidal particles in Milli-Q grade water, and (C) rough PZT after 3 hours of exposure to positively charged 100 nm amine functionalized colloidal particles in 1 mM NaCl solution.

Table 6.3: Particle surface density for images presented in Figure 6.5.

<table>
<thead>
<tr>
<th></th>
<th>0.01 mM NaCl Solution</th>
<th>0.1 mM NaCl Solution</th>
<th>1 mM NaCl Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particles per µm²</td>
<td>2.07 ± 0.5</td>
<td>4.18 ± 0.7</td>
<td>20.9 ± 6.2</td>
</tr>
</tbody>
</table>

6.3.5 Effect of solution pH on deposition

While polarized US-PZT can maintain essentially the same surface charge density regardless of the solution conditions, it is possible to alter the particle surface charge density by changing the solution pH. While positively charged amine-functionalized colloidal particles had good deposition selectivity in Milli-Q grade water (see Figure 6.1), 100 nm diameter carboxyl terminated nanospheres had a great deal of non-specific binding in the polarized regions (Figure 6.6 A). An increase in the solution
pH should increase the carboxyl terminated particle surface charge density. We have previously shown that US-PZT is stable in aqueous solutions at high pH (see Chapter 5). Figure 6.6 B shows an SEM image of a locally patterned, US-PZT surface after exposure to 100 nm diameter, negatively charged colloidal particles. With an increase in the solution pH, we find improved selectivity along the boundary of polarized and non-polarized regions.

![Figure 6.6: SEM images of charge patterned US-PZT after exposure to (A) 100 nm carboxyl functionalized colloidal particles in Milli-Q grade water, and (B) 100 nm carboxyl functionalized colloidal particles in NaOH solution (pH ~10). In each image, we have included a deposition schematic and noted the local polarization direction.](image)

### 6.4 Conclusions

We have demonstrated the first guided deposition of positively and negatively charged colloidal nanoparticles (Latex micro-spheres) onto locally polarized, US-PZT
thin films from aqueous environments. Furthermore, we showed how nanoparticle deposition is affected by ionic strength, solution pH, particle size and surface roughness. We confirmed that nanoparticle deposition onto charge patterns on US-PZT is similar to previous demonstrations of guided nanoparticle deposition onto charge heterogeneous surfaces. The results from this work motivate further study and development of US-PZT thin films as polarizable elements for particle deposition in interfacial sensing applications.
7. Conclusions and Future Direction

7.1 Conclusions

In this dissertation, I have demonstrated that the polarization state of a FETF controls the EDL interaction force with a charged-surface in aqueous environments. Using experimental results and theoretical calculations I show how the high surface charge density of FETFs affects the EDL structure and interaction force as a function of solution condition. The four major outcomes discussed in this thesis include i) fabrication of ultra-smooth lead zirconium titanate thin films, ii) demonstration of US-PZT thin film stability in aqueous environments, iii) measurement and modeling of the EDL interaction force between a polarized US-PZT surface and a charged colloidal probe, and iv) prototypical demonstration of guided deposition of positively and negatively charged colloidal particles onto charge heterogeneous US-PZT thin films from an aqueous environment. My work extends the potential use of FETFs from traditional semiconductor applications towards applications in interfacial sensing and colloidal deposition in liquid environments.

Fabrication of ultra-smooth, ferroelectric PZT thin films from a sol-gel precursor was accomplished through careful control of critical heating and cooling steps during fabrication. The final US-PZT has a RMS surface roughness of only 2.4 nm, an order of magnitude lower than values reported by others for FETFs. We found that the reduction
in surface roughness was found to correlate with the minimization of the thin film residual stress, as measured by grazing angle XRD. Furthermore we found, that the topography and crystal structure of the US-PZT thin film did not change with extended exposure to aqueous environments. The top few nanometers of the US-PZT thin films, however, underwent gradual oxidation with extended exposure to aqueous environments. This oxidation resulted in the gradual decrease in film resistivity and measured remnant polarization. These results indicate that the US-PZT thin film is susceptible to chemical degradation after prolonged exposures to aqueous environments.

Interfacial force measurement of polarized US-PZT thin films in aqueous environments was performed with colloidal probe force microscopy (CPFM). CPFM force-separation approach curves were used to quantify the ferroelectric surface charge density at the inner Helmholtz plane (IHP) using a constant potential electric double layer (EDL) model with a Stern layer. We found that the IHP surface charge density matched well with the independently measured ferroelectric remnant polarization. Furthermore, we developed a charge regulation boundary condition EDL model to quantitatively predict the surface potential and Stern layer charge density of polarized FETFs in aqueous environments. Using these models, we demonstrated that the outer Helmholtz plane (OHP) potential and interaction force with the polarized FETF is
roughly equivalent to that of traditional oxide thin films in a range of aqueous environments with a range of ionic strengths.

Finally, we showed the guided deposition of positively and negatively charged colloidal particles from aqueous environments onto polarization patterned US-PZT. Using a TEM grid, we patterned a charge heterogeneous surface making use of the ferroelectric polarizability of the US-PZT thin films. We then used the resulting surface charge patterns to guide the deposition of positively and negatively charged colloidal particles for a range of solution conditions, including solution ionic strength and pH, particle size, and surface roughness.

The above results are a promising first demonstration of how FETFs can be used for guided deposition. The development of a ferroelectrically-based interfacial sensing device, however, requires additional investigation. We found that while the surface charge density of the polarized FETF dominates the interaction force between charged surfaces in water, the EDL interaction force is still susceptible to charge shielding by a Stern layer and EDL compression at high ionic strength. The observed results demonstrate that at this point FETFs only offer an incremental improvement over alternative charged surfaces. As such, additional work is needed to investigate the benefits of using alternative FETFs and deposition conditions. Below is a list of potential avenues to continue the integration of FETFs with interfacial sensing devices.
7.2 Future Directions

In this section, I provide possible avenues for the continued investigation of FETFs for interfacial sensing devices. The first subsection addresses alternative FETFs and compares these to US-PZT. The second section provides preliminary results on the potential of US-PZT for guided deposition in non-aqueous media.

7.2.1 Alternative ferroelectric thin films

One potential avenue for the further development of a FETF based interfacial sensing device is to use other FETFs. Alternative FETF candidates should maintain or improve on the nanometer-scale surface roughness and stability in aqueous environments, compared with US-PZT. Through collaboration with the Center for Nanophase Materials Science (CNMS) at Oak Ridge National Labs, we have fabricated a number of FETFs using pulsed laser deposition (PLD). PLD offers a reliable method for deposition of ultra-smooth, epitaxial FETFs of various compositions. Unfortunately, experimental PLD has limited sample size, typically on the order of 1 cm². PLD FETF samples that were tested included barium titante (BTO), lead titanate (PTO), bismuth ferrite (BFO), and lithium niobate (LN). For each sample the mean surface roughness, composition, and structure was measured before and after exposure to Milli-Q grade water for 3 hours. Our preliminary findings suggest that bismuth ferrite is the only FETF
that is sufficiently stable in aqueous environments and thus warrants additional investigation.

**Barium Titanate Stability in Aqueous Environments**

Similar to PZT, barium titanate is a common perovskite ceramic ferroelectric material. Epitaxial BTO samples were fabricated at the CNMS at ORNL using PLD. We examined BTO topography, surface composition, and surface chemical structure before and after exposure to Milli-Q grade water. Figure 7.1 shows SPM topography images of the BTO surface before and after exposure, respectively. Prior to exposure, the surface roughness of the BTO was 3.3 nm over a 25 µm² area. After exposure, the surface roughness of the BTO decreased to 2.0 nm over a 25 µm² area. Using XPS, we determined the surface composition of the BTO thin film before and after exposure (Table 7.1). After a 24 hour exposure to Milli-Q grade water, we find a decrease in the atomic % of surface barium and oxygen. This indicates the selective desorption of barium oxide from the surface during exposure to Milli-Q grade water. This agrees with previous work on the titration of Barium titanate colloidal particles.\(^{292}\) Finally, high resolution XPS scans of the oxygen 1s and barium 3d envelopes were used to assess changes in the surface chemical binding environment (Figure 7.2). In both the O 1s and Ba 3d envelopes, we find a dramatic decrease in high-energy oxidative species on the BTO surface. These results indicate that
the BTO surface is unstable in aqueous environments and not suitable for integration with interfacial sensing devices.

Figure 7.1: SPM topography scans of barium titanate thin film (A) before and (B) after exposure to Milli-Q grade water for 24 hours. The line indicates location of the topography plot.

Table 7.1: Atomic surface composition of barium titanate thin films before and after exposure to Milli-Q grade water.

<table>
<thead>
<tr>
<th></th>
<th>Barium (at%)</th>
<th>Titanium (at%)</th>
<th>Oxygen (at%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-Exposure</td>
<td>10.9±0.2%</td>
<td>10.2±0.7%</td>
<td>78.9±0.1%</td>
</tr>
<tr>
<td>Post Exposure</td>
<td>8.3±0.1%</td>
<td>19.2±0.1%</td>
<td>72.5±0.2%</td>
</tr>
</tbody>
</table>
**Figure 7.2:** High-resolution XPS scans of the (A) Oxygen 1s and (B) Barium 3d envelopes before and after a 12 hour exposure to Milli-Q grade water.

### Lead Titanate Stability in Aqueous Environments

Lead titane is the ferroelectric component in PZT thin films. While also being a perovskite ceramic material it typically has a higher coercive field than PZT but nearly equal remnant polarization. Epitaxial PTO samples were fabricated at the CNMS at ORNL using PLD. We examined the PTO topography, surface composition, and surface chemical binding environment before and after exposure to Milli-Q grade water. Figure 7.3 shows SPM topography images of the PTO surface before and after exposure, respectively. Prior to exposure, the surface roughness of the PTO was 924.8 pm over a 25 \( \mu \text{m}^2 \) area. After exposure, the surface roughness of the PTO decreased to 717.7 pm over a
Using XPS, we determined the surface composition of the PTO thin film before and after exposure (Table 7.2). After a 24 hour exposure to Milli-Q grade water, we find a decrease in the atomic % of surface lead and oxygen. This indicates the selective desorption of lead oxide from the surface during exposure to Milli-Q grade water. Finally, high resolution XPS scans of the oxygen 1s and lead 4f envelopes were used to assess changes in the surface chemical binding environment (Figure 7.4). Similar to PZT, the PTO O 1s envelope shows an increase in Pb-O oxidation, (530 eV) after exposure. This indicates that the PTO surface oxidizes with exposure to Milli-Q grade water. These results indicate that the PTO surface is unstable in aqueous environments and also not suitable for integration with interfacial sensing devices.
Figure 7.3: SPM topography scans of lead titanate thin film (A) before and (B) after exposure to Milli-Q grade water for 24 hours. The line indicates location of the topography plot.

Table 7.2: Atomic surface composition of lead titanate thin films before and after exposure to Milli-Q grade water.

<table>
<thead>
<tr>
<th></th>
<th>Lead (at%)</th>
<th>Titanium (at%)</th>
<th>Oxygen (at%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-Exposure</td>
<td>24.7±0.3%</td>
<td>12.1±0.2%</td>
<td>63.2±0.4%</td>
</tr>
<tr>
<td>Post Exposure</td>
<td>22.9±0.2%</td>
<td>15.1±0.7%</td>
<td>62.0±0.4%</td>
</tr>
</tbody>
</table>
Figure 7.4: High-resolution XPS scans of the (A) Oxygen 1s and (B) Lead 4f envelopes before and after a 12 hour exposure to Milli-Q grade water.

Bismuth Ferrite Stability in Aqueous Environments

Bismuth ferrite is a relatively new ferroelectric compound with reported remnant polarization values as high as 60 µC cm\(^{-2}\).\[306\] Epitaxial BFO samples were fabricated at the CNMS at ORNL using PLD. We examined the BFO topography, surface composition, and surface chemical binding environment before and after exposure to Milli-Q grade water. Figure 7.5 shows SPM topography images of the BFO surface before and after exposure, respectively. Prior to exposure, the surface roughness of the BFO was 3.6 nm over a 25 µm\(^2\) area. After exposure, the surface roughness of the PTO increased slightly to 4.0 nm over a 25 µm\(^2\) area. Using XPS, we determined the surface
composition of the BFO thin film before and after exposure (Table 7.3). After a 24 hour exposure to Milli-Q grade water, we find no change in the surface composition. Finally, high resolution XPS scans of the oxygen 1s and bismuth 4f envelopes were used to assess changes in the surface chemical binding environment (Figure 7.5). We find no change in the O 1s envelope or binding moieties nor in the Bi 4f envelope. This indicates that the BFO is stable in aqueous environments and a potential candidate for integration with interfacial sensing devices.

**Figure 7.5:** SPM topography scans of bismuth ferrite thin film (A) before and (B) after exposure to Milli-Q grade water for 24 hours. The line indicates location of the topography plot.
**Table 7.3:** Atomic surface composition of bismuth ferrite thin films before and after exposure to Milli-Q grade water.

<table>
<thead>
<tr>
<th></th>
<th>Bismuth (at%)</th>
<th>Iron (at%)</th>
<th>Oxygen (at%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-Exposure</td>
<td>22.6±0.03%</td>
<td>8.4±0.01%</td>
<td>69.0±0.01%</td>
</tr>
<tr>
<td>Post Exposure</td>
<td>22.6±0.01%</td>
<td>8.5±0.04%</td>
<td>68.9±0.02%</td>
</tr>
</tbody>
</table>

**Figure 7.6:** High-resolution XPS scans of the (A) Oxygen 1s and (B) Bismuth 4f envelopes before and after a 12 hour exposure to Milli-Q grade water.

**Lithium Niobate Stability in Aqueous Environments**

Lithium niobate is a perovskite ceramic which exhibits ferroelectric hysteresis just below its’ Curie temperature of 1210°C. At room temperature, however, the coercive field is typically above the break down voltage. As such, polarization is typically performed at elevated temperatures and the crystal is then cooled to lock in the polarization pattern.
LN wafers were purchased from Crystal Technology (PPLN). We examined the LN topography, surface composition, and surface chemical structure before and after exposure to Milli-Q grade water. Figure 7.7 shows SPM topography images of the LN surface before and after exposure, respectively. Prior to exposure, the surface roughness of the LN was 193.9 pm over a 25 µm² area. After exposure, the surface roughness of the LN decreased slightly to 172.6 pm over a 25 µm² area. The LN surface was cut from a single crystal and polished similar to a silicon wafer. Using XPS, we determined the surface composition of the LN wafer before and after exposure (Table 7.4). After 24 hours, we find a slight decrease in relative atomic concentration of lithium. Finally, high resolution XPS scans of the oxygen 1s and niobium 3d envelopes were used to assess changes in the surface chemical structure (Figure 7.8). We find that after 24 hours of exposure, the O 1s envelope has a higher binding energy and dramatic increase in high-energy oxidative species at 530.4 eV and 531.8 eV. A slight increase in the Bi 4f envelope binding energy was also observed. These observations indicate that the LB surface oxidizes with exposure to Milli-Q grade water and that LN is not stable in aqueous environments.
Figure 7.7: SPM topography scans of lithium niobate (A) before and (B) after exposure to Milli-Q grade water for 24 hours. The line indicates location of the topography plot.

Table 7.4: Atomic surface composition of lithium niobate thin films before and after exposure to Milli-Q grade water.

<table>
<thead>
<tr>
<th></th>
<th>Lithium (at%)</th>
<th>Niobium at%</th>
<th>Oxygen at%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-Exposure</td>
<td>61.3±0.2%</td>
<td>8.2±0.2%</td>
<td>30.5±0.5%</td>
</tr>
<tr>
<td>Post Exposure</td>
<td>60.5±1.3%</td>
<td>9.3±1.5%</td>
<td>30.1±1.5%</td>
</tr>
</tbody>
</table>
Figure 7.8: High-resolution XPS scans of the (A) Oxygen 1s and (B) Niobium 3d envelopes before and after a 12 hour exposure to Milli-Q grade water.

Organic Ferroelectric Thin Films

An alternative to ceramic FETFs are polymeric FETFs such as polyvinylidene fluoride (PVDF) or polyvinylidene fluoride-tetrafluoroethylene (PVDF-TrFE) co-polymers.[199] Polymeric FETF, like PVDF, may provide a surface with switchable surface charge densities while circumventing the problems associated with oxidation by water exposure. Polymeric FETF grains are formed by alignment of the polymer’s dipole moment across the backbone. These grains are typically only a few nanometers in size and reliable fabrication over large areas can be challenging. Additional complications include that polymeric FETFs typically have lower remnant polarization values and higher coercive fields.
A recent development in organic FETFs includes the discovery of ferroelectric diisopropylammonium bromide (DIPAB). DIPAB maintains a remnant polarization of 23 μC cm\(^{-2}\) and has a Curie temperature of 426° Kelvin. This promising new organic FETF is the first to offer remnant polarization values equal to those of ceramic FETFs and over a large scale. The crystalline structure of DIPAB has two different polymorphs, only one of which is ferroelectric. Synthesis of a single crystal is performed by slow evaporation of an aqueous solution. While dissolution of the material back into water is a risk, DIPAB may provide a promising surface for advanced interfacial sensing devices.

### 7.2.2 Guided deposition in non-aqueous environments

Another approach towards reliable guided deposition of charged particles is the use of polarized FETFs for deposition from non-aqueous environments. The low dielectric constant of non-polar solvents, like toluene, will enable a longer EDL interaction distances and higher EDL interaction forces, compared to those attainable in aqueous environments, due to the lower dielectric constant and absence of ions. It was recently shown that thiol-coated gold nanoparticles suspended in toluene could be deposited onto charge patterned electret surfaces. Impressive deposition selectivity and pattern fidelity were observed using a bi-phase deposition process, where the sample was first submerged into a suspension of thiolated gold nanoparticles and then
transferred into a Milli-Q grade water phase, by pulling the substrate through the toluene-water interface. We tested this bi-phase deposition method on locally patterned US-PZT, using positively charged thiolated gold nanoparticles suspended in toluene. The US-PZT surface was first patterned using a +40V biased copper TEM grid and then submerged into the nanoparticle solution. The slide was then removed through the water-toluene interface. Figure 7.9 shows SEM images of the US-PZT surface after the deposition experiment and N\textsubscript{2} drying. We find non-specific binding of gold nanoparticles and discoloration of the surface. No TEM grid patterns were observed across the sample. We also noted that after removal of the US-PZT from solution, there was a significant increase in water contact angle, indicating surface hydrophobicity.

![Figure 7.9](image)

**Figure 7.9:** (A-C) SEM images of polarized US-PZT thin films after exposure to thiolated-gold nanoparticle solution.

To remove the non-specifically bound nanoparticles from the surface, a second US-PZT sample was polarized, exposed, and then rinsed with toluene prior to drying in N\textsubscript{2}. 161
Figure 7.10 shows SEM images of the second polarized US-PZT surface. Rinsing of the US-PZT surface removed the non-specifically adsorbed particles, however, no deposition patterns were observed.

![SEM images of polarized US-PZT thin films after exposure to thiolated-gold nanoparticle solution.](image)

**Figure 7.10:** (A-C) SEM images of polarized US-PZT thin films after exposure to thiolated-gold nanoparticle solution.

Additional are thus required to test the feasibility of using non-aqueous solutions for the guided deposition of charged colloidal particles from solution onto charge patterned FETFs. We find that rinsing with a good non-aqueous solvent removes all adsorbed particles, which does not occur with particles adsorbed from aqueous solutions. Further experiments should explore alternative non-aqueous solvents, such as hexane or chloroform, which may change the particle interaction force with the US-PZT. Also, use of larger colloidal particles that maintain a stable surface charge in organic solution may enhance the electrostatic contribution to the EDL interaction force. Attempts to fabricate thiolated gold nanoparticles with a 10 nm diameter have been
unsuccessful because the larger particles are not able to transfer from the aqueous to toluene phases during synthesis. Finally, continued reduction in the mean surface roughness will also improve the guided deposition selectivity. Previous demonstrations with electret surfaces have all been on surfaces with picometer surface roughness.
Appendix

A.1 Nanosurface Patterning of Non-Fouling Polymer Brush Thin Films

As the result of collaboration with Dr. Ashtosh Chilkoti, Angus Hucknall, and Dr. Tao Chen, the following work was published in the journal Small. Also, we thank Prof. Stephen Craig (Department of Chemistry, Duke University) for helpful discussions.

A.1.1 Introduction

We demonstrate, for the first time, a facile method for the direct electrochemical patterning of hydrophilic polymer brushes in ambient conditions. Using a method we term field-induced nanolithography (FINL), we have patterned four different types of hydrophilic polymer brushes; poly(acrylic acid) (PAA), poly(N-isopropylacrylamide) (PNIPAAm), poly(sulfo betaine methacrylate) (PSBMA), and poly(oligo(ethylene glycol) methyl methacrylate) (POEGMA). Brushes were synthesized by surface initiated polymerization on conductive silicon or gold substrates. FINL patterning of polymer brushes requires the correct bias voltage polarity and results from the localized electrochemical reaction that occurs between the top metal electrode and the polymer brush surface. For POEGMA brushes specifically we report pattern width and depth as a function of applied voltage, relative humidity, and exposure time. Using X-ray photoelectron spectroscopy and aldehyde reactive reagents, we demonstrate that FINL
locally oxidizes the surface of the non-fouling POEGMA brushes to form reactive aldehyde groups. This local chemical activation of non-fouling POEGMA brushes provides a promising platform for bio-sensor device development.

Micro- and nanopatterning of polymer brush surfaces is used to engineer surface properties or to impart novel molecular functionality with high lateral resolution. Patterning of polymer brushes, particularly those with non-biofouling characteristics, has thus recently received significant attention because it promises the miniaturization of sensing or diagnostic devices. A range of methods has been used to directly pattern polymer brush films (in contrast to patterning the initiator), including scanning near-field optical lithography (SNOM), ink jet printing, micropipetting, photolithography, plasma etch shadowing, nanoshaving, and scanning electrochemical microscopy (SECM).

Here we demonstrate a facile patterning method for the direct modification of polymer brush surfaces using an electrochemically-based patterning technique that we term field-induced nanolithography (FINL). Figures A.1.1 A and A.1.1 B schematically show how both serial and parallel FINL produce localized patterns on the surface of polymer brushes. For surface patterning, FINL merely requires a conductive scanning probe microscopy (SPM) tip or a conductive stamp, and a polymer (brush) thin film anchored to a conductive substrate. To generate patterns, the conductive probe tip or
stamp is placed in intimate contact with the brush surface and a bias voltage is applied between the tip and the conductive substrate. FINL patterning depends on both the direction of the applied bias voltage and the chemical characteristics of the polymer brush. During FINL patterning the tip and substrate act as the electrodes and are separated by the polymer brush thin film. This makes FINL a new method for nanoscale pattern generation and distinctly different from other demonstrations of electrochemical polymer brush patterning.\textsuperscript{316} Because a wide variety of polymer brushes can be grown on conductive substrates, we argue that FINL could become a broadly applicable, facile surface patterning method.
Figure A.1.1: (A) Serial electric-field induced nanolithography (FINL). (B) Parallel FINL, demonstrating the localized attachment of probe molecules on the polymer brush surface. (C) Relative effects of increasing electric field ($E$), relative humidity (RH), and exposure time ($\tau$) as dictated by tip speed. (D) Serial FINL performed on POEGMA brushes, topographical scale ±10nm, FINL patterning conditions +10 V tip bias, 500 nm sec$^{-1}$, and ~43% RH.
A.1.2 Results and discussion

Similar electric field-based patterning methods have been employed for the localized electrochemical modification of inorganic surfaces\textsuperscript{[317-319]} and self-assembled monolayers (SAMs).\textsuperscript{[320,321]} Both SAM oxidation and reduction have been demonstrated.\textsuperscript{[322,323]} For example, methyl-terminated alkane SAMs can be oxidized into carboxylic acid headgroups after application of a sufficiently high positive substrate bias (negative tip bias).\textsuperscript{[324]} Alternatively, the nitroso (NO) headgroup of p-aminophenyltrimethoxysilanes can be reduced to an amino group (NH\textsubscript{2}) after application of a sufficiently high negative substrate bias.\textsuperscript{[325]} In each demonstration, chemical modification was mediated by a water layer formed between the SPM tip or stamp and the substrate.\textsuperscript{[326]} This adsorbed water acts as both the electrolyte and source of electrochemical reagents.\textsuperscript{[320,326]} Never before, however, has such an electric field-based patterning method been used for the direct patterning of polymer brush surfaces in ambient conditions.

Here, we use FINL to pattern the surfaces of four hydrophilic polymer brushes, poly(acrylic acid) (PAA), poly(N-isopropylacrylamide) (PNIPAAm), poly(sulfobetaine methacrylate) (PSBMA), and non-fouling poly(oligo(ethylene glycol) methyl methacrylate) (POEGMA). While PNIPAAm, PSBMA, and POEGMA brushes were synthesized on conductive silicon substrates using a silane initiator, PAA was synthesized on a gold substrate using a thiol initiator. Brush thicknesses ranged between
7 nm and 200 nm. Brush patterning was accomplished only with a sufficiently high bias voltage, applied with the correct polarity. While patterning of PNIPAAm and POEGMA brushes required a negative substrate (positive tip) bias voltage, patterning of PAA and PSBMA required a positive substrate (negative tip) bias (see Section A.1.5). In all cases, FINL generated topographical features occurred only on the brush surfaces and did not entail the removal of the brush from the substrate or the growth of underlying silicon dioxide. As a result, FINL offers a highly controlled mechanism for the electrochemical modification of polymer brush surfaces.

Our results for the electrochemical patterning of polymer brush surfaces suggest a different interpretation of the patterning mechanism than that observed in the electrochemical patterning of SAMs. While the latter reflects the electrochemical reaction that occurs at the substrate, we suggest that the FINL patterning of polymer brushes reflects the electrochemical reactions that occur on the tip. We intimate that a polymer brush separates the tip or stamp sufficiently from the conductive substrate which helps to isolate the electrochemical reaction that occurs at the tip or stamp surface to the surface of the polymer brush. This mechanism reconciles the opposite bias voltage polarity that is necessary (when compared with that reported for SAMs) to induce brush surface reduction or oxidation. For example, an oxidation reaction is likely responsible for the formation of aldehyde functional groups on POEGMA brushes (see below). If
this oxidation occurs at the tip-brush interface, then the positive tip bias necessary for patterning can be explained. Similar arguments can be made self-consistently for the other brushes we tested (see Section A.1.5).

Using POEGMA brush surfaces, we characterized FINL generated surface features as a function of key lithographic parameters, including applied bias voltage, relative humidity, and exposure time. Figure A.1.1 C summarizes schematically how each key lithographic parameter influences the effective lithographic volume. We demonstrate both serial (SPM tip) and parallel (stamp) based patterning methods. Finally, we use the FINL imparted chemical functionality to attach surface reactive fluorescent probes onto non-fouling POEGMA brushes.

Serial FINL patterning of POEGMA brushes was performed with conductive cantilevers coated with gold, platinum, or nitrogen-doped diamond (Figure A.1.1 D). Parallel FINL was performed on POEGMA brushes with a conductively coated silicon or polydimethylsiloxane (PDMS) stamp. FINL patterning of POEGMA brushes was only accomplished with a negatively biased substrate (positively biased tip or stamp). No additional processing steps were required to achieve pattern transfer. None of the studied patterning conditions resulted in complete removal of the brush layer and the FINL induced patterns could not be removed after rinsing with DI-Water.
Alternative SPM-based patterning methods, such as mechanical surface ablation,[327] localized Joule heating,[328] or charge injection,[9] were ruled out as follows. First, mechanical surface ablation did not occur with an electrically grounded tip or stamp under otherwise identical lithographic conditions. Second, localized Joule heating could not have produced the pattern transfer because FINL pattern generation depends on the polarity of the applied field.[328,329] Third, charge injection was eliminated after imaging of surface pattern potentials with Kelvin probe force microscopy (KPFM) and electric field force microscopy (EFM). FINL patterning of POEGMA brushes was performed with a +8 V tip bias. Post-patterning KPFM images show a highly localized reduction in surface potential, which was stable over hours (Figure A.1.2 A). Re-imaging of the exposed area using EFM showed no phase shift during imaging, indicating the local surface potential reduction was not due to hole injection.[330-332] Serial FINL patterning with a negative applied tip bias did not produce any surface potential energy shift. Thus, we conclude that FINL is a novel patterning technique resulting in the localized topographical and chemical modification of the polymer brush surface.

Using POEGMA brushes, we determined serial FINL feature width and depth as a function of applied bias voltage, relative humidity (RH), and tip speed (exposure dose). Notably, POEGMA brush modification was only observed with an applied substrate bias voltage greater than -2 V (applied tip bias greater than +2 V). Patterning
did not occur with a positively biased substrate (negative tip). For the serial FINL patterning conditions studied, the feature widths ranged between 39 nm and 178 nm, and were largely determined by the size of the water meniscus formed about the tip. Serial FINL patterning on polymer brushes produces irregular surface topography with line edge roughness of around 30 nm. Comparing serial FINL to alternative serial patterning techniques, FINL can produce patterns with lateral resolution between those accessible by E-beam lithography and SNOM.\[333,334]\ Furthermore, serial FINL patterning speeds are comparable with other serial SPM lithographic techniques,\[335]\ with tip speeds ranging from 300 nm sec\(^{-1}\) to 6 \(\mu\)m sec\(^{-1}\). For parallel FINL, minimum exposure time and features size were not studied extensively, however, surface reduction was accomplished with exposure times as low as 60 seconds.
Figure A.1.2: (A) KPFM image of surface potential after serial FINL. The dashed line in the image indicates the position of the line scan profile plotted below. (B) FINL feature width as a function of applied bias voltage (patterning in air at 45% RH, 500 nm/s tip speed, and ~200nN applied tip load). (C) Comparison of high-resolution C 1s scans of a POEGMA brush surface before and after parallel FINL patterning. (D) Deconvolution of the C 1s envelope after parallel FINL patterning.

The effect of applied bias voltage on serial FINL patterning of POEGMA brushes was studied between ±10 V bias. Figure A.1.2 B shows the trend of increasing FINL feature width (from 48 to 150 nm) with increasing applied bias voltage (3 V to 10 V). The
effect of relative humidity on feature size was studied by performing FINL within a humidity controlled chamber. FINL feature width increases with ambient relative humidity (see Section A.1.5), indicating the role of water meniscus formation in the FINL patterning process.\cite{318,336} Previous work has shown how the effective exposure area is in large part determined by the size of the water meniscus formed around the tip.\cite{326} We observed patterning even below 5% RH, which is consistent with water retention of POEGMA brushes under comparable conditions.\cite{308}

We also characterized FINL feature size with respect to exposure dosage as determined by tip speed. Applied voltage, relative humidity, and applied load were held constant while varying the rate with which the SPM tip was scanned over the POEGMA brush surface. Although FINL feature width did not depend on tip speed, the average FINL feature depths decreased from 2 to 0.3 nm with increasing tip speed (decreasing exposure dosage) (see Section A.1.5). This observation is consistent with a patterning mechanism in which the meniscus size does not significantly depend on tip speed.

To further investigate the tip-polymer brush interaction during patterning, the indentation depth of a grounded SPM tip into the POEGMA polymer brushes was recorded over a range of applied loads. The data was fitted with good agreement to a conical Sneddon indentation model (see Section A.1.5).\cite{337} We found that the tip
indented the POEGMA brush by as much as 33 nm during FINL patterning, and that the indentation depth was independent of the polarity of the applied bias voltage. Up to an applied load of 200 nN, FINL feature size and depth did not depend on the applied patterning force. Experiments at applied loads greater than 200 nN were unsuccessful due to tip fouling.

To investigate the possible electrochemical modification of POEGMA brush surfaces by FINL, we patterned the brush substrate over an area of 25 mm² by parallel FINL, and used X-ray photoelectron spectroscopy (XPS) to reveal changes in the brush surface chemistry. We did not observe a silicon peak in the XPS survey spectra, consistent with the substantial POEGMA brush thickness of ~175 nm before and after exposure. While the application of a positive substrate bias had no effect on the details of the C 1s spectral envelope, the application of a negative substrate bias produced significant shifts in the relative peak positions and intensities of carbon moieties within the C 1s envelope. The high resolution C 1s spectral envelope of the POEGMA film before FINL patterning was sufficiently fit using only three unique carbon moieties: CH₃ (285.0 eV), COC (286.5 eV), and COOC (289.0 eV) [333]. Deconvolution of the FINL-modified POEGMA brush C 1s spectrum resulted in a decrease of the relative contribution of the ether component, and a noticeable shift (+0.1 eV) of the oxidized carbon moieties within the spectral envelope (Figure A.1.2 C). This is consistent with
previous studies of brush oxidation,[166,338] Furthermore, deconvolution of the spectrum necessitated the addition of a new moiety centered at 287.9 eV, which we attribute to the formation of aldehyde (C=O) on the POEGMA brush surface (Figure A.1.2 D). The atomic concentrations for each of the moieties before and after exposure are listed in Table A.1.1. The decrease in ether component, increase in relative contribution of the C-C moiety, and formation of aldehyde groups are consistent with previous findings on the effect of photo-induced oxidation of POEGMA brushes.[333] Additionally, the surface oxidation of POEGMA brushes agrees with the notion of anodic-oxidation at the tip-brush interface during patterning.

Table A.1.1: Atomic percentages calculated from deconvolution of the high-resolution C 1s spectrum scans shown in Figure 2 D.

<table>
<thead>
<tr>
<th>Component</th>
<th>CH₃</th>
<th>C-O-C</th>
<th>COOC</th>
<th>C=O</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-Exposure [at%]</td>
<td>19.3±1.5%</td>
<td>71.7±1.2%</td>
<td>9.0±0.96%</td>
<td>-</td>
<td>100%</td>
</tr>
<tr>
<td>Post-Exposure [at%]</td>
<td>26.1±3.7%</td>
<td>64.6±3.7%</td>
<td>7.3±0.6%</td>
<td>2.0±0.9%</td>
<td>100%</td>
</tr>
</tbody>
</table>

Finally, we immersed FINL patterned POEGMA brushes in either Tollens’ Reagent (aqueous diamminesilver(I) complex) or Alexa Fluor 488® aldehyde reactive probe to test FINLs’ ability to impart chemical functionality. Exposure to Tollens’ reagent is commonly used to test for the presence of chemically active aldehyde
species.\textsuperscript{339} XPS analysis revealed silver deposition on the surface of POEGMA brushes after parallel FINL patterning, thus supporting the presence of surface aldehyde moieties (Figure A.1.3 A). Control experiments on POEGMA brushes before FINL patterning did not produce any silver deposition. To further verify the chemical reactivity of the brush surface, we exposed FINL patterned POEGMA brushes to Alexa Fluor 488\textsuperscript{®} aldehyde reactive fluorescent probes. Although the surface concentration of aldehyde groups appears low in the XPS spectral analysis, high surface fluorescence intensities were observed which suggests that the chemical modification extends beyond the top few nanometers of the brush surface. Surface fluorescence was isolated to the FINL patterned regions of POEGMA brushes (Figure A.1.3 B). This demonstrates FINLs’ ability to locally attach diagnostically relevant probes to non-fouling polymer brush surfaces.
Figure A.1.3: (A) High resolution scans of C 1s and Ag 3d regions obtained on POEGMA brushes before (top) and after (bottom) FINL patterning, after exposure to Tollens’ reagent. (B) Fluorescence images of POEGMA brushes before (left) and after (right) FINL patterning, after exposure to Alexa Fluor® 488 aldehyde reactive probe.

A.1.3 Conclusion

In conclusion, we are the first to demonstrate the use of FINL for the electrochemical patterning of polymer brush surfaces. Patterning of PAA, PNIPAAm, PSBMA, and POEGMA brushes were accomplished between a conductive substrate (silicon or gold) and a conductively coated SPM cantilever. FINL patterning depends on the localized electrochemical reaction at the tip-brush interface and occurs only after application of an adequately high and directionally correct bias voltage; where the necessary applied bias polarity depends on the chemical structure of the polymer brush. For POEGMA, FINL feature width and depth were characterized as a function of
applied bias voltage, relative humidity, and exposure time. Ambient relative humidity during FINL had the largest influence on lateral feature size. Using XPS and aldehyde reactive reagents, we showed that FINL patterning results in the oxidative formation of aldehyde groups on the POEGMA brush surface. Finally, using the attachment of aldehyde reactive, fluorescent probes, we demonstrated FINL’s ability to impart local chemical reactivity to POEGMA brush surfaces. Although additional work is necessary to fully characterize the FINL patterning mechanism, the present work provides a proof-of-principle demonstration of the technique. We believe that FINL holds promise for patterning a broad range of polymer brush systems.

A.1.4 Experimental section

Silane Surface Initiator Synthesis All reagents for the synthesis of the polymer brushes were obtained from Sigma-Aldrich. Silicon wafers (University Wafer, Boston, MA) were cleaned in a solution of H₂SO₄:H₂O₂ (3:1) for 30 min. After rinsing with Milli-Q water and drying, the cleaned slides were immersed in aminopropyltriethoxysilane (10%) in ethanol for 30 min and were then rinsed with ethanol and dried at 120°C for 3 hrs. Wafers were then immersed in a solution of bromoisobutyryl bromide (1%) and triethylamine (1%) in dichloromethane for 30 min, rinsed with dichloromethane and ethanol, and blown dry with N₂.
**POEGMA Polymer Brush Synthesis** Following previously published methods,\textsuperscript{313,340-342} silane initiator coated substrates were immersed in a degassed polymerization solution of Cu(I)Br (5 mg mL\(^{-1}\)), bipyridine (12 mg mL\(^{-1}\)), and oligo(ethylene glycol) methacrylate monomer under argon. After 12 hrs at room temperature the surfaces were rinsed excessively with Milli-Q water and blown dry with N\(_2\).

**Ellipsometry** Brush film thickness was measured on an M-88 spectroscopic ellipsometer (J. A. Woollam Co., Inc) at three angles (65\(^\circ\), 70\(^\circ\), and 75\(^\circ\)) and wavelengths ranging from 400 nm to 800 nm. Ellipsometric data were fitted for thickness of the polymer films using a Cauchy layer model with fixed An (1.46) and Bn (0.01) values.

**Synthesis of PNIPAAm Brushes** Following previously published methods,\textsuperscript{343} the initiator-modified silicon substrates were placed in glass tubes under an N\(_2\) atmosphere and adding a degassed solution of NIPAM (12.6 g, 0.11 mol), CuBr (0.16 g, 1.11 mmol), and PMDETA (0.70 mL, 3.34 mmol) in 6.3 mL H\(_2\)O and 6.3 mL MeOH via syringe. The polymerization was allowed to proceed for 60 minutes at room temperature, after which the substrates were removed from the reaction flask and rinsed extensively with Milli-Q Water, MeOH, and dried under a stream of N\(_2\).

**Synthesis of PSBMA Brushes** Following previously published methods,\textsuperscript{344} polymer brush growth was achieved by placing the initiator-modified silicon substrates
in glass tubes under a nitrogen atmosphere and adding a degassed solution of SBMA (3.75 g, 26.75 mmol), bipyridine (210 mg, 1.34 mmol), CuBr (76.81 mg, 0.54 mmol), and CuBr2 (12.04 mg, 0.05 mmol) in 20 ml of methanol and 5 ml of Milli-Q water via syringe. The polymerization was allowed to proceed for 120 minutes at room temperature, after which the substrates were removed from the reaction flask and rinsed extensively with Milli-Q Water and MeOH and dried under a stream of N2.

**Thiol Initiator Synthesis** (BrC(CH3)2COO(CH2)11SH) was synthesized as previously reported. To immobilize the initiators for surface-initiated polymerization, a 450 Å thick gold substrates, with an 50 Å thick chromium adhesion layer, was prepared by thermal evaporation under a vacuum of 4×10^-7 Torr on clean silicon wafers. 

**μCP of Initiator** A PDMS stamp was inked by exposing the stamp features to an ethanol solution of the functionalized thiols initiator (~2mM) for 3 min; the stamp was then dried with nitrogen, and brought into contact with gold substrate for 30s.

**Synthesis of PAA Brushes** Poly(sodium acrylate) (PNaAc) and its protonation to poly(acrylate acid) (PAA) was done according to previous work. The organometallic catalyst, a CuBr/2,2'-dipyridine complex, was formed in a N2 atmosphere by adding CuBr (5.74 mg, 0.04 mmol) and 2,2-dipyridine (13.74mg, 0.088 mmol) to 1.0 mL of MeOH. The mixture was sonicated for 1-2 min to facilitate the formation of the CuBr/2,2'-dipyridine complex. Next, 1.88 g (20 mmol) of sodium acrylate monomer
dissolved was added to the complex solution and subsequent 8 mL of Milli-Q water was added into the solution with shaking. The polymerization solution was then transferred to a sealed flask containing the sample substrates with immobilized initiator. To terminate polymerization the substrates were removed from the N₂ atmosphere, rinsed with Milli-Q water, and dried with N₂. The PNaAc brushes were then protonated to a PAA by immersing the PNaAc brush substrate into an acid solution (pH = 2.0), followed by copious rinsing with Milli-Q water.

**Serial Field-Induced Nanolithography** Imaging and lithography were performed on either a MFP-3D Asylum Research Scanning Probe Microscope or a MultiMode™ Bruker/Digital Instruments atomic force microscope. Tip bias voltages for patterning were applied either with the SPM’s built-in voltage source or with a Keithley Instruments 6487 Picoammeter & voltage source. A variety of SPM tips were used, including; Mikro Masch NSC-14 Ti/Pt, NSC-19 Ti/Pt, or DPE-19 Ti/Pt, VEECO NP (gold coated), and NT-DPT DCP11 conductive diamond coated tips. Spring constants ranged between 1 N m⁻¹ to 9 N m⁻¹. Force calibration was performed using the Sader method.²⁹ Topographical images were obtained using intermittent contact mode imaging immediately after FINL and without additional processing steps. Tip fouling was observed with extended use, high applied surface force (>200 nN), or high humidity.
(>60%). SEM imaging revealed this to likely arise from polymer accumulation about the tip. Ambient relative humidity was measured with a Plas Labs Inc environmental chamber and controlled with an Omega PID humidity and temperature control unit.

**Parallel Field-Induced Lithography** Surface exposures were performed with an applied bias voltage of 10 V from a Keithley 6487 voltage source, over a range of exposure times (1 min to 12 hours), and a range of relative humidities (37-80%). In all cases, a platinum or gold coated electrode was placed on top of the polymer brush film with sufficient pressure applied throughout exposure to ensure contact.

**Chemical Surface Composition** X-ray photoelectron spectroscopy (XPS) was performed on a Kratos Analytical Axis Ultra Spectrometer equipped with a monochromatic Al Kα source. Charge neutralization was active during spectrum acquisition. Spectral analysis and de-convolution was carried out with Casa XPS software. Spectral shifts were referenced to the lowest energy C 1s peak at 285 eV. All curve fitting was performed using a linear peak base and symmetric 30/70 Gaussian-Lorentzian peak structure.

**Tollens’ Reagent** Silver nitrate solution (1 N Sigma Aldrich) was precipitated with Potassium Hydroxide (1 M Sigma Aldrich) and reconstituted with ammonium hydroxide (Sigma Aldrich). Sample development was performed by immersion in Tollens’ Reagent for ~15 seconds.
A.1.5 Supporting information

FINL Patterning of PNIPAAm, PSBMA, and PAA Brushes

FINL induced topographical features on PNIPAAm, PSBMA, and PAA brushes are shown in Figure A.1.4. FINL lines were patterned and reimaged using DPE 19 Ti/Pt SPM cantilevers in air. Prior to FINL patterning of each film, the patterning bias voltage polarity was determined by applying a +8 V, -8 V, and 0 V bias to the tip while scanning the brush surface in contact mode. In each case, patterning occurred only for one bias polarity and did not entail mechanical surface inscription. Like for POEMGA brushes, FINL patterning of PNIPAAm brushes required a negative surface (positive tip) bias voltage (consistent with a brush surface oxidation reaction), while FINL patterning of PSBMA and PAA brushes required a positive surface (negative tip) bias voltage (consistent with a brush surface reduction reaction).
Figure A.1.4: AFM height images in air of FINL generated patterns on A) PNIPAAm brush (z-scale ±1.5 nm, patterning conditions: +4 V tip bias, ~200 nN applied load, and 300 nm sec\(^{-1}\) tip speed), B) PSBMA brush (z-scale ±2 nm, patterning conditions: -10 V tip bias, ~50 nN applied load, and 200 nm sec\(^{-1}\) tip speed, and C) PAA brush (z-scale ±10 nm, patterning conditions: -10 V tip bias, ~200 nN applied load, and 500 nm sec\(^{-1}\)).

FINL Patterning Mechanism Discussion

Although additional work is required, our demonstration of FINL on four different types of hydrophilic polymer brushes and on two different substrates, suggests that FINL patterning of polymer brush surfaces results from the localized electrochemical reaction at the tip-brush interface (Figure A.1.5). A positive tip bias, which locally induces anodic-oxidation, is necessary to pattern POEGMA and PNIPAAm brushes. POEGMA brushes have previously been oxidized through photo-irradiation by UV light, resulting in the formation of reactive aldehyde groups. Likewise, the terminal methyl groups on the PNIPAAm side chains are available to electrochemical oxidation. Alternatively, a negative tip bias, which locally induces
cathodic-reduction, is necessary to pattern PAA and PSBMA brushes. In these cases the carboxylic acid and sulfonic acid end-groups are available for electrochemical reduction.\cite{348,349}

Figure A.1.5: Schematic for FINL induced pattern generation on polymer brushes. A positive applied tip bias (A), associated with tip induced anodic-oxidation, produces surface patterns on (B) POEGMA and (C) PNIPAAm. A negative applied tip bias (D), associated with tip induced cathodic-reduction, produces surface patterns on (E) PSBMA and (F) PAA.

FINL Feature Width as Function of Ambient Relative Humidity
FINL feature width as a function of relative humidity is shown in Figure A.1.6. FINL lines were patterned and reimaged using NSC 14 Ti/Pt SPM cantilevers within a humidity controlled chamber. Using a Veeco Digital Instruments AFM, a custom silicon cap was placed in the front of the AFM head. The sealed entrance allowed access for only a relative humidity probe and humid air source. The relative humidity was controlled by an Omega PID humidity and temperature control unit to within 1%.

**Figure A.1.6:** FINL feature size as a function of Relative Humidity (+8 V tip bias, zero applied load, and 1 µm/sec tip speed).

**FINL Feature Width as Function of Exposure Dosage**

FINL feature width as a function of exposure dosage is shown in Figure A.1.7. Exposure dosage was decreased by increasing SPM tip speed during patterning. FINL lines were patterned and reimaged using NSC 14 Ti/Pt SPM cantilevers. A topographical cross section of the FINL pattern was averaged over 50 points. Feature width was measured between feature boundaries as determined by FWHM of averaged cross
section. We observed no change in FINL feature width as a function of exposure dosage while holding tip bias, load, and relative humidity constant.

Figure A.1.7: FINL feature width as a function of exposure dosage as determined by tip speed (+8 V tip bias, 200 nN applied tip load, and at 45% RH).

FINL Feature Depth as Function of Tip Speed

FINL feature depth as a function of exposure dosage is shown in Figure A.1.8. Again, exposure dosage was decreased by increasing SPM tip speed during patterning. FINL lines were patterned and reimaged using NSC 14 Ti/Pt SPM cantilevers. A topographical cross section of the FINL pattern was averaged over 50 points. Feature width was measured between feature boundaries as determined by FWHM of averaged cross section. The increase in inscription depth with increasing exposure dosage indicates some material removal during FINL patterning.
Figure A.1.8: Feature depth as a function of exposure dosage as determined by tip speed (+10 V tip bias, 200 nN applied load, and at 45% RH).

SPM Tip Indentation Depth as Function of Applied Load

To characterize the interaction between the SPM tip and the polymer brush surface during FINL patterning, SPM tip indentation was measured as a function of applied load. Results were fit with high correlation to a conical Sneddon model. Data and model fit (blue dashed line) are presented in Figure A.1.9.

Prior to measurements, a region of the POEGMA brush was mechanically removed from the silicon substrate. The SPM tip was repeatedly scanned between the substrate and brush surface while varying the applied load. Relative penetration was calculated from the difference between brush height without and with load applied. After a loading experiment, the brush region was reimaged to verify that no surface wear occurred. Repeated experiments with a positively or negatively biased tip did not produce an appreciable change in the measured indentation depth.
Assuming a rigid SPM tip and conforming surface, relative penetration was fit to a conical Sneddon model (Equation A.1.1). Material properties and tip geometry were represented by model fitting parameter $A$. An expansion of this variable is presented in Equation A.1.2.

$$P = AD^2,$$  \hspace{1cm} (A.1.1)

where, $P$ is the applied load and $D$ is the penetration depth.

$$A = 4 \frac{\mu \cot (\alpha)}{\pi (1-\eta)},$$  \hspace{1cm} (A.1.2)

where, $\mu$ is the rigidity modulus, $\alpha$ is the cone semi-vertical angle, and $\eta$ is the Poisson ratio.

**Figure A.1.9:** SPM tip indentation as a function of applied load. Fitting was performed with Table Curve software to a conical Sneddon model.
A.2 Fabrication of Ultra-Smooth PZT

A.2.1 Characterization of PZT thin films as a function of fabrication processes

Effect of Spin Rate and Speed on Single Layer US-PZT thickness

The film thickness of single layer US-PZT was controlled by the spin speed (between 1250 and 3000 RPM) and the spin duration (between 30 and 45 sec). Table A.2.1 shows processing conditions, resulting film thickness as measured by SEM, and RMS surface roughness. All US-PZT thin films were fabricated according to the noted processing scheme and resulted in nanometer scale RMS roughness (processing conditions V).

<table>
<thead>
<tr>
<th>Spin Duration (sec)</th>
<th>Spin Speed (RPM)</th>
<th>Film Thickness (nm)</th>
<th>25 µm² Surface Roughness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>3000</td>
<td>124±0.96</td>
<td>4.9</td>
</tr>
<tr>
<td>40</td>
<td>3000</td>
<td>115±2.3</td>
<td>2.4</td>
</tr>
<tr>
<td>40</td>
<td>2500</td>
<td>138±3.3</td>
<td>3.8</td>
</tr>
<tr>
<td>40</td>
<td>2000</td>
<td>159±4.8</td>
<td>4.8</td>
</tr>
<tr>
<td>40</td>
<td>1500</td>
<td>195±5.7</td>
<td>3.8</td>
</tr>
</tbody>
</table>
Effect of Multilayer Sol-Gel Processing on Surface Roughness

Multilayer PZT thin films were processed in the same way as the single layer US-PZT thin films (processing conditions V). Multilayer PZT thin films with 2, 3, and 4 layers fabricated by repeatedly spin coating the sol-gel solution onto the PZT surface. Hot-plate evaporation was performed between each spin-coated layer. Final pyrolysis and RTA annealing were performed in the same way as a single layer PZT thin film. Table A.2.2 presents measured surface roughness values and film thicknesses for each multilayer film. AFM measurements of multilayer PZT thin films are presented in Figure A.2.1.

<table>
<thead>
<tr>
<th>Layer</th>
<th>Temperature</th>
<th>Roughness (nm)</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>1000</td>
<td>213±5.2</td>
<td>5.8</td>
</tr>
<tr>
<td>45</td>
<td>3000</td>
<td>91±3.8</td>
<td>5.1</td>
</tr>
</tbody>
</table>

Table A.2.2: Multilayer PZT thin films surface roughness and thickness values.
### Table A.2.3: Measured Surface Roughness and Film Thickness Values

<table>
<thead>
<tr>
<th>Layer Type</th>
<th>100 μm² Surface Roughness (nm)</th>
<th>25 μm² Surface Roughness (nm)</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 Layer PZT Thin Film</td>
<td>45.9</td>
<td>4.7</td>
<td>180±1.2</td>
</tr>
<tr>
<td>3 Layer PZT Thin Film</td>
<td>100.7</td>
<td>65.7</td>
<td>255±5.7</td>
</tr>
<tr>
<td>4 Layer PZT Thin Film</td>
<td>80.9</td>
<td>40.4</td>
<td>417±4.6</td>
</tr>
</tbody>
</table>

**Figure A.2.1:** AFM height images in air of multilayer PZT thin films generated by aforementioned sol-gel fabrication method on 

A) 2 layer PZT surface (z scale ±50 nm) 
B) 3 layer PZT surface (z scale ±200 nm) 
C) 4 layer PZT surface (z scale ±150 nm)

Processing conditions for all thin films included a 40 sec spin at 3000 RPM, 90°C hot plate evaporation for 120 sec (repeated in accordance with the number of layers), 450°C oven pyrolization for 35 min, and final annealing by RTA at 700°C for 20 sec.

### Effect of Hot Plate Solvent Evaporation Temperature on PZT Surface Roughness

Single layer PZT thin films were also processed using an elevated hot plate evaporation temperature of 200°C (processing condition I). Table A.2.3 presents the measured surface roughness and film thickness values. AFM measurements of multilayer PZT thin films are presented in Figure A.2.2. The increased surface roughness
is associated with an elevated solvent evaporation rate and possible bubble formation, resulting in increased surface cracking and mean surface roughness.

Table A.2.3: Surface roughness and thickness values for a single layer PZT thin film processed with elevated solvent evaporation.

<table>
<thead>
<tr>
<th></th>
<th>100 µm² Surface Roughness (nm)</th>
<th>25 µm² Surface Roughness (nm)</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200°C Hot Plat PZT Thin Film</td>
<td>19.7</td>
<td>24.7</td>
<td>116±1.2</td>
</tr>
</tbody>
</table>

Figure A.2.2: AFM topography images in air of single layer PZT thin film generated using an elevated hot plate solvent evaporation temperature of 200°C (z scale ±25 nm). Processing conditions for all thin films included a 40 sec spin at 3000RPM, 120 sec hot plate evaporation, 450°C oven pyrolysis for 35 min, and final annealing by RTA at 700°C for 20 sec.
Effect of Pyrolization Cooling Rate on PZT Surface Roughness

Single layer PZT thin films were also processed using an elevated pyrolization cooling rate temperature of ~10°C/min (processing conditions II). Table A.2.4 presents the measured surface roughness and film thickness values. An AFM topography image of the PZT thin film is presented in Figure A.2.3. The increased surface roughness can be associated with increased stressed placed on the film during cooling.

Table A.2.4: Surface roughness and thickness values for a single layer PZT thin film processed with elevated pyrolization cooling rate.

<table>
<thead>
<tr>
<th></th>
<th>100 μm² Surface Roughness (nm)</th>
<th>25 μm² Surface Roughness (nm)</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fast-Cooled PZT Thin Film</td>
<td>19.2</td>
<td>24.5</td>
<td>116±4.5</td>
</tr>
</tbody>
</table>
Figure A.2.3: AFM height images in air of single layer PZT thin film generated using an elevated pyrolysis cooling rate of 10°C/min (z scale ±25 nm). Processing conditions for all thin films included a 40 sec spin at 3000RPM, 90°C hot plate evaporation for 120 sec, 450°C oven pyrolysis for 35 min, and final annealing by RTA at 700°C for 20 sec.

Effect of Pyrolysis Cooling Rate on PZT Surface Roughness

Single layer PZT thin films were also processed using an oven for final annealing (processing conditions IV). After annealing, a cooling rate of 0.5°C/min was used. Table A.2.5 presents the measured surface roughness and film thickness values. An AFM topography image of the PZT thin film is presented in Figure A.2.4. The increased surface roughness is associated with increased stressed placed on the film during cooling.
Table A.2.5: Surface roughness and thickness values for a single layer PZT thin film processed with an oven final annealing step.

<table>
<thead>
<tr>
<th></th>
<th>100 µm² Surface Roughness (nm)</th>
<th>25 µm² Surface Roughness (nm)</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oven Annealed PZT Thin Film</td>
<td>49.9</td>
<td>4.9</td>
<td>116±5.6</td>
</tr>
</tbody>
</table>

Figure A.2.4: AFM height images in air of single layer PZT thin film fabricated with oven annealing (z scale ±25 nm). Processing conditions for all thin films included a 40 sec spin at 3000 RPM, 90°C hot plate evaporation for 120 sec, 450°C oven pyrolization for 35 min, and final annealing at 700°C for 35 min.

High-Resolution XPS Spectra for Rough and Ultra-Smooth PZT Thin Films

High-resolution XPS spectra for Pb 4f and Ti 2p were taken for rough and ultra-smooth PZT thin films (Figure A.2.5). Charge neutralization was active during spectrum acquisition, and the binding energy spectra were referenced to the C 1s peak set at 285.0
eV. The Pb 4f and Ti 2p envelopes were not affected by changes in the thermal processing conditions.

**Figure A.2.5.** High-resolution XPS spectra for (A) Pb 4f and (B) Ti 2p as a function of thermal processing conditions (Table 2.1).

**A.3 Ferroelectrically Induced Electric Double Layer Formation Above Polarized FETFs**

This work was done in collaboration with Shihong Lin, Mathieu Therezien, and Dr. Mark Wiesner.
A.3.1 Introduction

Ferroelectrics have proven to be a unique platform for liquid-phase sensing applications.\cite{59,63,251,266} The remnant polarization of a ferroelectric thin film (FETF) has been shown to influence surface piezoresponse,\cite{80} surface reactivity,\cite{87} and the electric double layer formation.\cite{350} These advances support the further study of FETF integration with interfacial sensing devices. For these applications, FETFs have a potential benefit over alternative methods of patterning surface charges because the surface charge of the FETF is constant over a range of solution conditions. Because the surface charge is equal to the normal component of the remnant polarization vector \( (\sigma_{\text{FETF}} = \vec{P} \cdot \hat{n}) \), it can be induced to be positive or negative.\cite{41,60,266} Here, we propose a theoretical model to describe how polarized FETFs drive interfacial forces over a range of solution conditions and surface properties. Using electric double layer (EDL) theory, we predict the Stern layer charge density, the counter ion concentration profile, and point of zero charge for an isolated FETF in solution. Additionally, we describe the interaction energy as a function of separation distance for a FETF approaching a dissimilar oxide surface in solution. These equations are well fit to experimentally measured force-separation approach curves and used to determine the FETF surface charge density in a range of ionic strength solutions.
Because the surface charge density of a polarized FETF can be an order of magnitude higher than the surface charge density expressed by a traditional oxide interface,\cite{[168,185,234,252]} it is reasonable to assume that the counter ion distribution is partitioned into a condensed ion (Stern) layer and a diffuse double layer. The inclusion of a Stern layer is consistent with EDL modeling of surfaces expressing a high charge density in solution,\cite{[133,149,271]} and previous reports for polarized PZT surface in solution.\cite{[87]}

Within the Stern layer, the condensed sheet of counter ions are energetically trapped proximal to the solid-liquid interface and can be modeled as a parallel plate capacitor.\cite{[129]}

In the adjacent diffuse double layer the ions are modeled as a distributed cloud where both the ion concentration and electrical potential decay exponentially with increasing distance away from the surface, as described by the Poisson-Boltzmann equation (Equation A.3.1).\cite{[129]}

\[
\nabla^2 y = \kappa^2 \sinh \left( \frac{y}{\kappa} \right), \tag{A.3.1}
\]

where \( \kappa^2 = z e^2 n / k_B T \epsilon \epsilon_0 \), whereby \( n \) is the atomic concentration, \( k_B \) is the Boltzmann constant, \( z \) is the charge number of ionic species, \( T \) is temperature, and \( \epsilon \epsilon_0 \) is the dielectric permittivity. Since the remnant polarization values of FETFs can be accurately measured before being placed in solution, the charge density at the inner-Helmholtz plane (IHP of Figure A.2.1) of the Stern layer is known. The remaining surface charge (or
potential) measured at the outer-Helmholtz plane of the Stern layer (OHP of Figure A.2.1), represents the boundary condition for the adjacent diffuse double layer region.

**Figure A.3.1:** Diagram of the counter ion distribution within the electric double layer above a polarized ferroelectric thin film induced to express a (A) positive surface charge and (B) negative surface charge. The dotted line indicates the boundary between the outer-Helmholtz plane and the diffuse double layer.

For electric double layer formation above polarized FETFs, we can explicitly state the boundary condition at the IHP as the summation of ferroelectric surface charge density \( \sigma_F \) and Stern layer charge density \( \sigma_S \) (Equation A.3.2).

\[
\sigma_T = \sigma_F + \sigma_S,
\]

(A.3.2)

where \( \sigma_F \) is considered a constant and determined only by the FETF remnant polarization value as determined by ferroelectric hysteresis measurement. Furthermore, \( \sigma_S \) is the charge held within the Stern layer, which consists of a sheet of condensed ions.
The charge density of the Stern layer is a result of ion-complexation between reactive surface groups and ionic species in solution. As such, the charge density is described by Equation A.3.3,[130,132]

\[ \sigma_S = eN_S \frac{\delta \sinh (\theta_S)}{1 + \delta \cosh (\theta_S)} \]  

(A.3.3)

where \( e \) is the unit charge, \( N_S \) is the density of reactive surface groups, and \( y_S \) is the reduced potential \( (y_S = \frac{e\psi}{k_BT}) \). The dissociation ratio, \( \delta = 2 \left( \frac{K^-}{K^+} \right)^{1/2} \) where \( K^- \) and \( K^+ \) are the dissociation constants for complexation sites within the Stern layer. Finally, \( \theta_S = 2.303(pH_0 - pH) - y_S \), where \( H_0 = 0.5(pK_+ - pK_-) \).

Here, we use the proposed boundary condition to determine the surface potential of an isolated ferroelectric surface as a function of environmental conditions. Next, we determine the interaction energy as a function of separation distance between a ferroelectric surface and a dissimilar charged flat plate. Results are presented for two mass action reaction ratios over a range of ionic strength solutions and pH values. The interaction energy as a function of separation distance between a ferroelectric interface and a traditional oxide surface is also presented for three remnant polarization values. This work extends EDL theory to ferroelectric interfaces and serves as a tool for predicting ferroelectric interfacial forces as a function of environmental conditions.
A.3.2 Surface Potential of an Isolated Ferroelectric Thin Film in Aqueous Environments

Determining the IHP surface potential of an isolated FETF as a function of solution conditions is important to understanding how the FETF interacts with the environment. The EDL model for the isolated FETF in solution applies the FETF boundary condition (Equation A.3.4) and the boundary condition for an isolated surface ($\frac{dy_s}{dz} = 0$ as $x \rightarrow \infty$) to determine Equation A.3.5.

\[-\varepsilon \varepsilon_0 \frac{dy_s}{dz} = \frac{4\pi e}{k_B T} \sigma_F, \quad (A.3.4)\]

\[\frac{\varepsilon^{\gamma S-1}}{2e^{-\gamma S/2}} = \eta [\alpha + \beta], \quad (A.3.5)\]

where $\frac{\delta e^{2\gamma S-1}}{2e^{2\gamma S+\delta(e^{2\gamma S+1})}}$ is the dimensionless surface charge due to the reactive surface sites, $\beta = \frac{\sigma_p}{eN_S}$ is the dimensionless ferroelectric surface charge, and $\eta = \frac{2\pi e^2 N_S}{\varepsilon \varepsilon_0 k_B T}$.

Figure A.3.2 plots the FETF reduced surface potential as a function of dimensionless ferroelectric charge ($\beta$) for a range of ionic strength solutions. Here, we note that Figure A.3.2 reflects a continuum of FETF remnant polarization values while in practice the remnant polarization value of a FETF is discrete, with only a single value of the positive and negative surface charge being possible. We find that the FETF surface potential decreases with increasing ionic strength. This is expected with increasing double layer capacitance. In the absence of a ferroelectric charge density the surface...
potential equals to the potential of an isolated oxide interface, in agreement with a non-ferroelectric surface in solution. For a given ionic strength solution there are two regimes for how the surface potential changes with a FETF polarization state. For small $\beta$ the surface potential is highly sensitive to the ferroelectric polarization state and varies linearly with the ferroelectric surface charge density. For large $\beta$, however, the surface potential is varied exponentially with the ferroelectric surface charge and the ferroelectric surface potential is dominated by the ferroelectric surface charge density. Within the large $\beta$ regime large surface potentials are achieved at the IHP. Figures A.3.2 A and A.3.2 B compare how the reduced surface potential varies with $\beta$ for FETFs exhibiting a low and high point of zero charge, respectively. The asymmetry of the reduced potential plot reflects the preferential surface reaction of the Stern layer in solution.

**Figure A.3.2:** Reduced surface potential over a range of ferroelectric charge ($\beta$) and (A) a low point of zero charge or (B) a high point of zero charge within a range of ionic strength solutions.
Figures A.3.3 A and B plot the dimensionless Stern layer charge as a function of $\beta$ for a low and high point of zero charge FETF, respectively. Again, we find two regimes for how the Stern layer charge responds to an imposed ferroelectric surface charge. For low $\beta$ values, we find a linear response to the ferroelectric surface charge. For large $\beta$ values, the Stern layer is saturated, with all reactive surface sites being complexed to shield the ferroelectric surface charge of the polarized FETF. The asymmetry in the Stern layer complexation reflects the preferential reactivity of the FETF. Here FETFs with a low point of zero charge resist protonation while FETFs with a high point of zero charge resist deprotonation.

![Figure A.3.3](image.png)

**Figure A.3.3:** Dimensionless Stern layer charge over a range of ferroelectric charge ($\beta$) and (A) a low point of zero charge or (B) a high point of zero charge over a range of ionic strength solutions.
Figures A.3.4 A and A.3.4 B present the FETF reduced surface potential as a function of $\beta$ for a range of pH values. With increasing solution pH we find a decrease in the reduced surface potential, we attribute this to the increase in solution ionic strength. Interestingly, we find 5 regimes for how the reduced surface potential changes with $\beta$. For low $\beta$ the reduced surface potential does not significantly change, we attribute this to the Stern layer effectively shielding the ferroelectric polarization through the surface complexation reaction. For intermediate $\beta$ the reduced surface potential has increased sensitivity and slope, we attribute this change to complete complexation of the Stern layer. Finally, for large $\beta$ we find an exponential change in the reduced surface potential. For large $\beta$ values, the reduced surface potential is again dominated by the ferroelectric surface charge.

Figure A.3.4: Reduced surface potential in 0.1 mM monovalent strength solution for a range of ferroelectric charge ($\beta$) and (A) low point of zero charge and (B) high point of zero charge over a range of pH solutions.
Figure A.3.5 plots the isoelectric point of a FETF in solution as a function of $\beta$. For low $\beta$, we find that the ferroelectric component to the surface charge density is able to shift the isoelectric point of the FETF in solution. For large values of $\beta$ we find that the polarized FETF has no point of zero charge due to the large ferroelectric surface charge. In the absence of a ferroelectric surface charge we find that the point of zero charge is equal to that of the oxide surface.

![Figure A.3.5: Isoelectric point over a range of ferroelectric charge ($\beta$) values for ferroelectric thin films with different point of zero charge values in aqueous environments.](image)

The above examples illustrate the complex interactions between the solution conditions, Stern layer, and ferroelectric surface charge. Notably, we demonstrate how
environmental conditions affect the surface potential of an isolated ferroelectric surface in solution.

### A.3.3 Interaction energy of a FETF and a charged oxide surface

The interaction energy between a FETF and an approaching surface will be a function of the charge regulation parameters. High charge regulation results in an interaction energy similar to a constant potential boundary condition while low charge regulation results in an interaction energy similar to a constant charge boundary condition. Using a linearized Poisson-Boltzmann equation the electrostatic component of the total interaction energy has been described by a linear charge regulation model (Equations A.3.6-A.3.8):[^132]

\[
\epsilon \epsilon_0 \frac{\partial \psi}{\partial z} = -4\pi \sigma_{\text{Tangent}}(\psi), \quad (A.3.6)
\]

\[
\sigma_{\text{Tangent}} = S - K\psi, \quad (A.3.7)
\]

and

\[
W_B = 2\epsilon_0\epsilon_r\kappa \frac{2\psi_1\psi_2e^{-kd} - |\Delta_1(\psi_2)^2 + \Delta_2(\psi_1)^2|e^{-2kd}}{1 - \Delta_1\Delta_2 e^{-2kd}}, \quad (A.3.8)
\]

where \(K\) is the regulation capacitance of the surface, \(S\) is the surface charge density at infinite separation \(\Delta = \frac{K=\epsilon K/4\pi}{K+\epsilon K/4\pi}\) e relative ratio of the diffuse layer capacitance to the regulation capacitance, \(\epsilon_0\epsilon_r\) is the dielectric constant of the medium, \(\kappa = \left(\frac{2\epsilon_0^2}{\epsilon_0\epsilon_r k_BT}\right)^{1/2}\) is
the inverse Debye Length, $k_B$ is the Boltzmann constant, $T$ is the absolute temperature, and $n$ is atomic concentration.

Using the above equations, we can write the linear-charge regulation parameters in terms of measurable FETF parameters (e.g. remnant polarization, surface pK values, and number of reactive surface sites). Rewriting the boundary condition for an isolated FETF in solution (Equation A.3.5) in the form of a linear-charge regulation approximation (Equation A.3.2) we find that for small $\theta_S$, $S = \frac{e^2N_\delta\psi_N}{k_BT(1+\delta)} + \sigma_F$ and $K = \frac{e^2N_\delta}{k_BT(1+\delta)}$.

These equations indicate that the charge of a FETF in solution is a function of the native surface charge density and the ferroelectric surface charge. As expected, the regulation capacitance ($K$) is only a function of the surface reaction parameters.

Using the linear charge regulation relationships for a FETF in solution, we plot the interaction energy as a function of separation distance between a FETF and a negatively charge surface in 10 mM monovalent salt solution (Figure A.3.6). As comparison, we also plot the upper (constant charge) and lower (constant potential) boundaries of the interaction energy as dashed lines. The interaction energy as a function of separation distance is intermediate to that of a constant potential and constant charge surface. Increasing the ferroelectric surface charge incrementally increases the interaction energy as a function of separation distance. Furthermore,
switching the ferroelectric surface charge from negative to positive results in switching the interaction energy from intermittent repulsion to attraction. These predictions support the polarization state of a FETF in solution can influence the interaction energy between charged surfaces in solution.

**Figure A.3.6:** Interaction energy as a function of separation distance between a FETF and a negatively charged oxide surface ($\psi$=40 mV, $\Delta$=0.9) for a range of ferroelectric surface charge densities.

### A.3.4 Conclusion

The remnant polarization of a polarized FETF in solution is capable of controlling electric double layer formation. To accurately model the electric double layer structure and interaction energy, we have used a unique boundary condition that includes a ferroelectric surface charge and a Stern layer. Using this boundary condition we have modeled the IHP potential, the Stern layer charge density, and isoelectric point...
of a polarized FETF in a variety of solution conditions. Next, we modeled the interaction energy as a function of separation distance between a polarized FETF and a negatively charge colloidal probe using the linear-charge regulation boundary condition. The interaction energy model was then fitted to measured force-separation curves between a charged borosilicate colloidal probe and a polarized US-PZT thin film. We found good agreement between the measured ferroelectric surface charge and predicted ferroelectric surface charge. This work advances our understanding of how FETF surfaces function and interact with aqueous environments and established a theoretical foundation of the implementation of ferroelectrics in interfacial sensing devices.
A.4 Matlab Code

A.4.1 Force-separation curves (asylum_forcesep_calc.m)

%% This program produces a force-distance curve from Asylum force data
%% Export Asylum Raw and versus Deflection data into a ascii / *.txt file
%% Adopted from asylum_getfd for asylum ascii export
%% Authored by Robert Ferris

function []=asylum_forcesep_calc(filename, kz) % kz [nN/nm]

a = load(filename);
for i = 1:length(filename)
    a(i) = filename(i);
end
apraw = a(:,1);
apdefl = a(:,2);
retraw = a(:,3);
retdefl = a(:,4);

% %Invols adjustment - UNCOMMENT IF NECESSARY!!!
% %If the correct defl invols value was not initially entered, enter both values here
% trueinvols = 74.27; % (nm/V)
% falseinvols = 63.92; % (nm/V)
% apdefl = apdefl * trueinvols/falseinvols;
% retdefl = retdefl * trueinvols/falseinvols;
% hold on
% plot(apraw,apdefl, 'r')

% %Force adjustment - UNCOMMENT IF NECESSARY!!!
% If the correct spring constant value was not initially entered, enter both values here
% truespring = 1.0; % (nN/nm)
% falsespring = 2.0; % (nN/nm)
% apdefl = apdefl/falsespring*truespring;
% retdefl = retdefl/falsespring*truespring;

% Find local minimum for approach curve of polarized PZT force curves
n=length(apdefl);
m=length(apdefl)-4;
intmin=1;
mindefl=0.98;
while intmin>=mindefl
    if intmin>=mindefl
        intmin=mindefl;
    end
    [mindefl, mindeflpt] = min(apdefl(m:n));
    n=n-1;
    m=m-1;
end

apmin=find(intmin==apdefl);
apmin=apmin(length(apmin));
apdeflpts=apdefl(length(apdefl)-12:length(apdefl));
aprawpts=apraw(length(apdefl)-12:length(apraw));
apdeflfit = polyfit(aprawpts,apdeflpts,1);
apdefl2 = apdefl/apdeflfit(1);
apsep = apraw-apdefl2;
apforce = apdefl2.*kz;

% Find local minimum for retration curve of polarized PZT force curves
n=4;
m=2;
intmin=3;
mindefl=0.98;
while intmin>=mindefl
    if intmin>=mindefl
        intmin=mindefl;
    end
    [mindefl, mindeflpt] = min(retdefl(m:n));
    n=n+2;
    m=m+2;
end

retmin=find(intmin==retdefl);
retmin=retmin(1);
retdeflpts=retdefl(1:retmin);
retrawpts=retraw(1:retmin);
retdeflfit = polyfit(retrawpts,retdeflpts,1);
retdefl2 = retdefl/retdeflfit(1);
retsep = retraw-retdefl2;
retforce = retdefl2.*kz;
% Adjust approach for Piezo Drift, Zero Force
[apmaxforce, apcutoff] = max(apforce);
apsepslope = apsep(1:floor(apcutoff*2/3)); % fits data to first third of retract curve (presumably flat)
apforceslope = apforce(1:floor(apcutoff*2/3));
apfit = polyfit(apsepslope, apforceslope, 1);
apforce = apforce - apfit(2) - apfit(1)*apsep;

% Adjust retract for Piezo Drift, Zero Force
[retmaxforce, retcutoff] = max(retforce);
retsepslope = retsep(floor(length(retsep)*2/3):length(retsep)); % fits data to first half of retract curve (presumably flat)
retforceslope = retforce(floor(length(retforce)*2/3):length(retforce));
retfit = polyfit(retsepslope, retforceslope, 1);
retforce = retforce - retfit(2) - retfit(1)*retsep;

% Zero Indentation
apsep = -apsep + apsep(apmin);
retsep = -retsep + retsep(retmin);

% Plot Indentation vs Force.
figure
hold off;
plot(apsep, apforce);
hold on
plot(retsep, retforce, 'r');
xlabel('Indentation (nm)');
ylabel('Force (nN)');
legend('approach', 'retract');

forcetot = [apsep, apforce; retsep, retforce];
cutoff = floor(length(apsep)/3);
forcetest = [apsep(cutoff:apmin), apforce(cutoff:apmin)];

% Plot Separation vs Force.
figure;
hold off;
plot(forcetest(:,1), forcetest(:,2));
xlabel('Separation (nm)');
ylabel('Force (nN)');

% Save Data
savename = '\force-distance_tot.txt';
save(savename, '-ascii', 'forcetot');
A.4.2 Surface potential of an isolated FETFs in solution using a charge-regulation EDL model (ISOFETF2.m)

function [totchrg] = ISOFETF2(FETFsurfchrg,Ns,pH0,pKa,conc,pH, Ki)

kB=1.3806503*10^-23; %m2 kg s^{-2} K^{-1}
T=298; %K
epi=8.85418781762*10^{-12}; %C^2/N*m^2
epiw=80;
epiFETF=1200;
epiStern=10;
z=1*10^{-9}; %m
Na=6.02214129*10^{23}; %1/mole
q=1.60217646*10^{-19}; %C
PI=3.14159265358979;

X=sym('X','real');
potISO=zeros(length(FETFsurfchrg),length(pH));
surfchrg=zeros(length(FETFsurfchrg),1);
totsurfchrg=zeros(length(FETFsurfchrg),1);
potDIFF=zeros(length(FETFsurfchrg),1);
frac=zeros(length(FETFsurfchrg),1);
totchrg=[];

for j=1:length(pH);
    H3O=10^-pH(j);
    OH=10^(-14+pH(j));
    kappa=((1000*(conc+H3O+OH)*Na*q^2)/(epi*epiw*kB*T)).^0.5; %kappa[]=m^-1
    pKb=2*pH0-pKa;
    deltak=pKa-pKb;
    delta=2*10^(-deltak/2);
    potN=2.303*(kB*T/q)*(pH0-pH(j));
    pHj=ones(length(FETFsurfchrg),1)*pH(j);
    for i=1:length(FETFsurfchrg);
        potISOi=solve(sinh(q*X/(2*kB*T))==(2*PI*Ns*q^2/(kappa*epi*epiw*kB*T))*((FETFsurfchrg(i)/(q*Ns))+delta*(FETFsurfchrg(i)/(q*Ns))*cosh(q*(potN-X)/(kB*T))+delta*sinh(q*(potN-X)/(kB*T))/(1+delta*cosh(q*(potN-X)/(kB*T))))/X);
        potISO(i,j)=potISOi;
        if potISO(i,j)>0
            potDIFF(i)=potISO(i,j)-.29;
        else potDIFF(i)=potISO(i,j)+.29
        end
    end
    frac(i)=FETFsurfchrg(i)/(q*Ns);
deltachrg(i)=delta*(sinh(q*(potN-potDIFF(i))/(kB*T))/(1+delta*cosh(q*(potN-potDIFF(i))/(kB*T))));
end

totsurfchrg=double(totsurfchrg);
totchrg=[totchrg;frac,pHj,potISO(:,j).*q/(kB*T),potDIFF,surfchrg,totsurfchrg];
end
totchrg=double(totchrg);

%save Data
savename=[
'totcharge','_','num2str(Ns,'%0.5g'),'_','num2str(pH0),'_','num2str(pKa) 
','_','num2str(conc,'%0.5g'),'.txt'];
save(savename, '-ascii', 'totchrg');

A.4.3 Interaction potential between a charge-regulating FETF and charged oxide surface in solution (LinChrgRegFETF.m)

%% This function calculates the EDL interaction potential profile between two
%% linearly charge-regulated surfaces with one being ferroelectric
%% Author: Robert Ferris
%% Revision Date: 9/15/2012

function [] = LinChrgRegFETF(FETFsurfchrg,Ns,pH0,pKa,conc,pH,Hconst,y2,d2)

%%Parameter Definition
%% FETFsurfchrg = the surface charge density of the ferroelectric thin film
%% (FETF) in C/m2 (single value)
%% NS = the number of surface sites per m2
%% pH0 = the PH at the point of zero charge
%% pKa = the pKa of the surface
%% conc = the solution concentration in moles/liter
%% pH = the solution pH

kB=1.3806503*10^-23; %m2 kg s-2 K-1
T=298; %K
epi=8.85*10^-12; %C^2/N*m^2
epiw=80;
epiFETF=1200;
epiStern=10;
z=1*10^-9; %m
Na=6.022*10^23; %1/mole
q=1.60217646*10^-19; %C
Pi=3.14159265358979;

H3O=10^-pH;
OH=10^(-14+pH);

y=sym('y','real');
\[ y_1 = \text{sym('y1','real')}; \]
\[ y_2 = \text{sym('y2','real')}; \]
\[ \text{sep} = [0.5e-9:0.5e-9:5e-9,6e-9:2e-9:100e-9]; \]
\[ \kappa = (1000*(q^2)*(\text{conc}+H3O+OH)*Na/(\text{epi}*\text{epiw}*kB*T))^{.5}; \]
\[ \%\kappa^2 = 2^*q^*\text{sum(\text{concentration})}*Na/\text{epi}*kB*T \]
\[ pK_b = 2^*pH0-pK_a; \]
\[ \text{deltapK} = pK_a-pK_b; \]
\[ \text{delta} = 2^*10^{-(\text{deltapK}/2)}; \%\text{NOTE: delta here is different than charge} \]
\[ \text{regulation delta1&delta2} \]
\[ \text{potN} = 2.303*(kB*T/q)^*(pH0-pH); \]
\[ S1 = Ns*(q^2)*\text{delta}^*\text{potN}/((1+\text{delta})*kB*T)+\text{FETFsurfchrg}; \]
\[ K1 = \text{delta}^*Ns*(q^2)/(kB*T*(1+\text{delta})); \]
\[ \text{delta1} = (K1-\text{epi}*\text{epiw}*\kappa/(4*PI))/(K1+\text{epi}*\text{epiw}*\kappa/(4*PI)); \%\text{The linear charge regulation delta} \]
\[ \%\text{potISO1} = S1/(K1+\text{epi}*\text{epiw}*\kappa/(4*PI)) \]
\[ \text{NLpotISO} = \text{ISOFETF2(\text{FETFsurfchrg,Ns,pH0,pKa,conc,pH}); \%\text{The surface} \]
\[ \text{potential of the FETF is solved using the full non-linear PB equation} \]
\[ \%\text{potISO1} = \text{NLpotISO}(1,2)*kB*T/q-(\text{NLpotISO}(1,5)*q^*Ns/Ki); \]
\[ \text{potISO1} = \text{NLpotISO}(1,4); \%\text{Calculated Diffuse Layer Potential} \]
\[ \text{dydx} = [ (y(2)) \]
\[ ((kB*T*\kappa^2)/q)^*\text{sinh(q*y(1)/(kB*T))}; \]
\[ \text{res} = \text{twobc(ya,yb)} \]
\[ \text{res} = [ (y1(1)/\kappa)-(2^*kB*T/q)^*\text{sinh(q*pot1ISO1/(2^*kB*T))-(p(y1(1)-pot1ISO1)/(1-p))^*sech(q*pot1ISO1/(2^*kB*T))} \]
\[ (y2(1)/\kappa)-(2^*kB*T/q)^*\text{sinh(q*pot1ISO2/(2^*kB*T))-(p(y2(1)-pot1ISO1)/(1-p))^*sech(q*pot1ISO2/(2^*kB*T))}; \]
\[ \text{mesh} = \text{zeros}(1,1000); \]
\[ \text{solinit} = \text{bvp4c(mesh,[.2; .04])}; \]
\[ \text{sol} = \text{bvp4c(dydx,\text{res},solinit)} \]
\[ \text{xint} = \text{linspace}(0, 4, 50); \]
\[ \text{yint} = \text{deval(sol, xint)}; \]
\[ \text{plot(xint, yint(1,:),'b');} \]
A.4.4 Point of zero charge of an isolated charge-regulating FETF in solution (ISOFETF_pzc.m)

%% This function calculates the point of zero charge of an isolated charge regulating FETFs
%% Author: Robert Ferris
%% Revision Date: 5/30/2012

function [pzctot] = ISOFETF_pzc(FETFsurfchrg,Ns,pH0,pKa,conc,pH,Ki)

%%% Parameter Definition
%%% FETFsurfchrg = the surface charge density of the ferroelectric thin film (FETF) in C/m2 (Array)
%%% NS = the number of surface sites per m2
%%% pH0 = the PH at the point of zero charge
%%% pKa = the pKa of the surface
%%% conc = the solution concentration in moles/liter
%%% pH = the solution pH
%%% Ki = Stern capacitance F/m^2

kB=1.3806503*10^-23; %m2 kg s^-2 K^-1
T=298; %K
epi=8.85418781762*10^-12; %C^2/N*m^-2
epiw=80;
epiFETF=1200;
epiStern=10;
z=1*10^-9; %m
Na=6.02214129*10^23; %1/mole
q=1.60217646*10^-19; %C
PI=3.14159265358979;

%%% Calculate the point of zero charge for an isolated plate
X=sym('X','real');
pzcISO=zeros(length(FETFsurfchrg),length(pH0));

for j=1:length(pH0);
    H3O=10^-pH;
    OH=10^-(-14+pH);

\[ \kappa = \left( \frac{1000 \cdot (\text{conc} + \text{H}_3\text{O}^+ \cdot \text{OH}^-) \cdot \text{Na}^- \cdot q^2}{(\text{epi} \cdot \text{epiw} \cdot k_B \cdot T)} \right)^{\frac{1}{2}}; \quad \% \kappa = \text{m}^{-1} \]

\[ \text{pK}_b = 2 \cdot \text{pH}(j) - \text{pK}_a(j); \]
\[ \delta \text{pK} = \text{pK}_a(j) - \text{pK}_b; \]
\[ \delta = 2 \cdot 10^{\left( -\delta \text{pK}/2 \right)}; \]

for \( i = 1 : \text{length} \left( \text{FETFsurfchrg} \right) \)

\[ \text{pzc} = \text{solve} \left( \left( \frac{-\text{FETFsurfchrg}(i) \cdot (q \cdot \text{Ns})}{\delta \cdot \sinh(2.303 \cdot (\text{pH}(j) - X)) / (1 + \delta \cdot \cosh(2.303 \cdot (\text{pH}(j) - \text{pH})))) \right), X \right); \]
\[ \text{pzcISO}(i,j) = \text{pzc}; \]

end

end

\[ \text{pzctot} = [\text{transpose} \left( \text{FETFsurfchrg} ./ (q \cdot \text{Ns}) \right), \text{pzcISO}] \]

% save Data
\[ \text{savename} = ['\text{totcharge}', '_', num2str(\text{Ns}, '%0.5g'), '_', num2str(\text{pH}(j), '%0.5g'), '_', num2str(\text{pK}_a, '%0.5g'), '.', 'totchrg'; \]
\[ \text{save} \left( \text{savename}, '-\text{ascii}', 'totchrg' \right); \]

\section*{A.4.5 Topography analysis (roughnesscalc.m)}

% This program calculates the root mean squared roughness, standard deviation, and surface structure function
% for an uploaded .ascii or *.txt The line scans are averaged to provide
% error bars.
% an uploaded TIFF image.
% Authored by Robert Ferris
% Inputs %
% * Name of text file exported from Asylum MFP3D,
% * Number of image
% * Total number of images (eg 3rd image out of a total of 7 images)
% * Frame direction, should be either 'u' or 'd' for "frame up" or "frame down"

function roughnesscalc(filename, imgnumber, imgtot, frame, imgsize)

% \text{topo} = \text{load} \left( \text{filename} \right); % IF NOT USING ASYLUM LOAD PROGRAM
topo=asylumload(filename, imgnumber, imgtot, frame);

topo=topo'; %transpose matrix so Scan direction is in one Row.
M = size(topo,1); %Number of Rows
N = size(topo,2); %Number of Columns

%topography histogram
histogramlength=[-2e-8:2e-10:2e-8];
histogram=[];
for i=1:M
    [freq,bin]=hist(topo(i,:),histogramlength);
    histogram=[histogram;freq];
end
histocalc=sum(histogram,1);
histocalc=[histocalc;bin];
%plot(bin,histogram);
%pause;

%save Hist
savehist='histogram.txt';
save(savehist, '-ascii', 'histogram');

%RMS as function of sample size
tau2=2:4:N;
roughness=[];
for i=2:4:N;
    roughness=std(topo(:,1:i),0,2); %take standard dev for all rows up to i points
    roughness=[roughness;i.*imgsize/N,mean(roughness,1),std(roughness,1)]; %
    concantate roughness with sampling distance and average roughness
end
roughness=roughness';
%loglog(taulength2,roughness);
%pause;

%RMS Slope (second moment calc)
tau3=2:4:N/2;
rmsslope=[];
for i=2:4:N/2;
    rmsslopetemp=(topo(:,i+1:N)-topo(:,1:N-i))./(i*imgsize/N);
    rmsslopetempsqr=(sum(rmsslopetemp.*rmsslopetemp,2).*(1/(N-i-1)));
    rmsslope=[rmsslope;i.*imgsize/N,mean(rmsslopetempsqr.^((1/2),1),std(rmsslope
tempsqr.^((1/2),1));
end
rmsslope=rmsslope';
%loglog(taulength3,rmsslope);
%pause;

%RMS Curvature (third moment calc)
tau4=2:4:N/2;
rmsscurv=[];
for i=2:4:N/2;
    rmsscurvtemp=(topo(:,i+2:N)+topo(:,1:N-i-1)-2*topo(:,i+1:N-1))./(i*imgsize/N);
    rmsscurvtempsqr=(sum(rmsscurvtemp.*rmsscurvtemp,2).*(1/(N-i-2)));
end
rmsscurv=[rmsscurv,i.*imgsize/N,mean(rmsscurvtempsqr.^((1/2),1)),std(rmsscurvtempsqr.^((1/2),1))];
end
rmsscurv=rmsscurv';
%loglog(taulength4,rmsscurv);
%pause;

%Structure Function
tau=2:2:N/2;
structfunct=[];
for i=2:2:N/2
    stemp=topo(:,1:N-i)-topo(:,i+1:N);
    stempsqr=(sum(stemp.*stemp,2).*(1/(N-i)));
    structfunct=[structfunct,i.*imgsize/N,mean(stempsqr,1),std(stempsqr,1)];
end
loglog(structfunct(:,1),structfunct(:,2))
structfunct=structfunct';
%pause;

%save Data
savename='\roughnesscalcs.txt';
save(savename, 'ascii', 'histocalc', 'roughness', 'rmsslope', 'rmsscurv', 'structfunct');
fclose('all');

%autocorrelation
% a=ifft2((ifft2(topo)).*conj(fft2(topo)));
% a=real(a);
% a=sqrt(a);
% a=real(a);
%
% k=M/2;
% l=N/2;
% b(1:k,1:l)=a(k+1:M,l+1:N);
% b(k+1:M,l+1:N)=a(1:k,1:l);
% b(1:k,l+1:N)=a(k+1:M,1:l);
% b(k+1:M,1:l)=a(1:k,l+1:N);
%

% surf(x,y,b);
% shading interp;
% pause;
% xcor=b(k,1:N);
% ycor=b(1:M,l)';
% x1=0:k+1;
% x2=0:k-1;
% plot(x1,xcor(1:k),x2,xcor(k+1:M));
% pause;
% y1=0:l+1;
% y2=0:l-1;
% plot(y1,ycor(1:l),y2,ycor(l+1:N));

A.4.6 Grain boundary analysis (domains.m)

% This program calculates the average and standard deviation grain size of
% an uploaded TIFF image.
% Authored by Robert Ferris
% PZT=imread('Filename'); % Insert filepath and name here
% pixdist=10000/1024; % Update denominator with number pixels in uploaded
% image
% thresh=160; % Vary threshold value based on the contrast of the uploaded image

imshow(PZT)
croppedPZT=imcrop(PZT,[80 92 500 350]);
imshow(croppedPZT)
figure
domain=im2bw(croppedPZT,thresh/255);
imshow(domain)
% domain=bwareaopen(domain,5);
% imshow(domain)

% domain=imclearborder(domain);
% imshow(domain)

[B,L]=bwboundaries(domain,'noholes');
numregions=max(L(:));
imshow(L)

stats=regionprops(L,'all')
areas=cat(1,stats.Area);
areas1 = areas(find(areas>=10));
areas1 = areas1(find(areas1<=800));

domainspix=mean(areas1).^0.5;
domainsize=domainspix*pixdist
domainsstd=std(areas1.^0.5)

bins=[2:2:max(areas1)];
dist=hist(areas1,bins);
figure
bar(bins,dist);
Bibliography


220. Tybell, T.; Ahn, C.H.; Triscone, J.-M., Control and imaging of ferroelectric domains over large areas with nanometer resolution in atomically smooth epitaxial Pb(Zr0.2Ti0.8)O3 thin films. 1998. 72 (12), p. 1454-1456.


350. Ferris, R.J.; Lin, S.; Therezien, M.; Yellen, B.B.; Zauscher, S., **Electric Double Layer Formed by Polarized Ferroelectric Thin Films.** ACS Applied Materials & Interfaces,
Biography

Robert Joseph Ferris was born in Detroit, MI on October 18th, 1982. Robert attended Lahser High School, where he played varsity soccer and track. In 2004, he received his Bachelors in Science and Masters in Engineering in Chemical Engineering from Cornell University. At Cornell, Robert was mentored by Victor Pham as part of Dr. Christopher Ober’s research group, where he learned the foundations of nanofabrication and semi-conductor processing technology. During his junior year, Robert was awarded the Intel Undergraduate Research Award and P&G Technical Excellence award (runner up). With Victor, he also published his first peer-reviewed article in Chemistry of Materials entitled, *Positive tone Photoresist Process for Supercritical Carbon Dioxide Development*. At Duke University, Robert developed his interest in commercialization of nanotechnology by pursuing concurrent degrees between The Pratt School of Engineering and The Fuqua School of Business. In each school, Robert has received a Ph.D. in Mechanical Engineering and Materials Science and a Masters in Business Administration. While at Pratt, Robert has co-authored one book chapter in Dekker Encyclopedia of Nanoscience and Nanotechnology and four peer reviewed journal articles including Small, Progress in Polymer Science, and ACS Applied Materials and Interfaces. Robert received the GP Nano Fellowship, the MRSEC Fellowship, and two Honorable Mentions for the NSF Graduate Research Fellowship. Robert was also a
member of the MEMS Leadership Committee. At Fuqua, Robert received a concentration in Entrepreneurship and Innovation.

Robert’s work as Duke demonstrates his passion for life-long learning, science, and collaboration. Looking forward, Robert is excited to continue building on his unique blend of education and experience to improve the human condition. Robert would particularly like to thank Dr. Stefan Zauscher for his mentorship. Your guidance and friendship have changed my life forever.