Ferroelectric Lithium Niobate Surfaces for Depositions of Metallic Nanostructure and ZnO Semiconducting Thin Film

by

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ABSTRACT

A distinct characteristic of ferroelectric materials is the existence of a reversible spontaneous polarization with the application of an electric field. The relevant properties ferroelectric lithium niobate surfaces include a low density of defects and external screening of the bound polarization charge. These properties result in unique surface electric field distribution with a strong electric field in the vicinity of domain boundaries, while away from the boundaries, the field decreases rapidly. In this work, ferroelectric lithium niobate (LN) is used as a template to direct the assembly of metallic nanostructures via photo-induced reduction and a substrate for deposition of ZnO semiconducting thin films via plasma enhanced atomic layer deposition (PE-ALD).

To understand the mechanism the photo-induced deposition process the following effects were considered: the illumination photon energy and intensity, the polarization screening mechanism of the lithium niobate template and the chemical concentration. Depending on the UV wavelength, variation of Ag deposition rate and boundary nanowire formation are observed and attributed to the unique surface electric field distribution of the polarity patterned template and the penetration depth of UV light. Oxygen implantation is employed to transition the surface from external screening to internal screening, which results in depressed boundary nanowire formation. The ratio of the photon flux and Ag ion flux to the surface determine the deposition pattern. Domain boundary deposition is enhanced with a high photon/Ag ion flux ratio while domain boundary
deposition is depressed with a low photon/Ag ion flux ratio. These results also support the photo-induced deposition model where the process is limited by carrier generation, and the cation reduction occurs at the surface. These findings will provide a foundational understanding to employ ferroelectric templates for assembly and patterning of inorganic, organic, biological, and integrated structures.

ZnO films deposited on positive and negative domain surfaces of LN demonstrate different I-V curve behavior at different temperatures. At room temperature, ZnO deposited on positive domains exhibits almost two orders of magnitude greater conductance than on negative domains. The conductance of ZnO on positive domains decreases with increasing temperature while the conductance of ZnO on negative domains increases with increasing temperature. The observations are interpreted in terms of the downward or upward band bending at the ZnO/LN interface which is induced by the ferroelectric polarization charge. Possible application of this effect in non-volatile memory devices is proposed for future work.
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Chapter 1

INTRODUCTION

1.1 Motivation

Ferroelectricity was first discovered by Valasek in 1921 [1]. However, until the discovery of ferroelectricity in barium titanate in the 1940s, ferroelectrics were widely used in memory devices [2], waveguides [3] and microelectromechanical systems [4].

The distinct properties of ferroelectric materials relevant to this study include a spontaneous, reversible polarization with the application of an electric field, and the surface bound charge associated with the polar surface [5]. Ferroelectric domain surfaces present different properties including work function, electron affinity, surface charge and surface potential. A range of technologies have been developed for nanoscale characterization of ferroelectric domains: piezoresponse force microscopy (PFM) [6] has been invented to study domain polarity; electrostatic force microscopy (EFM) [7] and scanning Kelvin probe microscopy (SKPM) [8] is employed for measuring surface charge and surface potential, respectively; and the polarization dependent electron affinity has been studied by UV-photoelectron emission microscopy (PEEM) [9].

The polarization orientation for thin film ferroelectrics, due to its low coercive field, is switchable by a dc biased conductive tip controlled by a scanning probe microscope (SPM) [10]. Consequently, its ferroelectric domains can be patterned to the nanoscale. In recent years, the patterned domain surfaces are intensively applied as templates for the direct assembly of nanoparticles and molecules on
their surfaces [11, 12], which is call “ferroelectric lithography”. Employ ferroelectric templates for assembly and patterning of inorganic, organic, biological and integrated structures open a new window for a vast “bottom-up” process [12]. The ferroelectric domain pattern can reach ~100nm scale thus 2-dimensional even 3-dimensional patterns of integrated inorganic and organic structures are expected through “ferroelectric lithography” process using ferroelectric templates. Direct assembly of nanoparticles on perovskite ferroelectrics, such as lead zirconate titanate (PZT) [12] and barium titanate [13] are studied and selective deposition is found. Compared to PZT and barium titanate, the spontaneous polarization of lithium niobate is the largest (71 μC/cm² for LN vs. 25 μC/cm² for BTO, 30-40 μC/cm² for PZT), while lithium niobate also exhibits little band bending due to the low defect density [9]. In this dissertation, we will study lithium niobate and photo-induced deposition processes on its polar surfaces.

By replacing the typical gate dielectric SiO₂ with a high-κ ferroelectric in Fe-FET memory device, the transconductance could be increased significantly [14]. Different ferroelectric and semiconducting materials are employed in Fe-FET devices [15, 16] with less attention on lithium niobate as ferroelectric layer between semiconductor and gate electrode. A variety of stacked structures of Fe-FET have been investigated [17], such as Fe-FETs with semiconductor/insulator/ferroelectric structure, semiconductor/ferroelectric structure. In this dissertation, the interface between ZnO semiconductor thin film
and lithium niobate single crystal with different domain orientation is characterized in order to seek possible application in memory device.

1.2 Overview

This dissertation is organized as follows: Chapter 2 gives an introduction of ferroelectric materials and is focused on the specific properties of lithium niobate. Chapter 3 describes the fundamentals of SPM with detailed description of the advanced PFM, EFM and SKPM techniques. The photo-induced Ag nanostructure formation on periodically poled lithium niobate surfaces is demonstrated in chapter 4. The nanostructure formation is described in terms of band-bending, polarization screening, and the absorption depth of the UV illumination. The formation of boundary enhanced nanowire pattern and uniform-like pattern of Ag are presented in Chapter 5. Chapter 6 explores the plasma-enhance atomic layer deposition of zinc oxide thin film on lithium niobate surface and the I-V curve characterization. The results emphasize the interface band bending and electron accumulation or depletion. Chapter 7 provides a summary of the dissertation and a prospective of future work.
REFERENCES


Chapter 2

FERROELECTRIC MATERIALS

2.1 Introduction

This chapter presents the basic properties of ferroelectrics with special emphasis on lithium niobate (LN)—the template material for research discussed later in this dissertation. The first section defines a ferroelectric and gives a brief description of crystal classes. This is followed by an introduction of ferroelectric domains and surface polarization charge. The latter section presents a detailed description of specific properties of ferroelectric materials. More specifically, this section will include an overview of LN’s properties such as crystal structure, composition, intrinsic defects, surface charge screening, and LN electrical properties. This chapter is ended with a short summary of previous work on photo-induced nanostructure formation using patterned ferroelectrics as templates.

2.2 Ferroelectrics

2.2.1 Ferroelectric definition

A ferroelectric material is both a pyroelectric and a piezoelectric. It is characterized by a spontaneous, reversible polarization in the absence of an electric field [1]. When mechanical stress is applied in the direction of the spontaneous polarization, an induced polarization and a surface charge develop through the direct piezoelectric effect [1]. Below the critical temperature, the Curie temperature ($T_c$), ferroelectric materials exhibit ferroelectric behavior, while above the Curie temperature, ferroelectric material enters the paraelectric phase in
which it no longer possesses a spontaneous polarization. In most cases, the transition between these two states is related to the crystal structure’s transition from centrosymmetric structure to non-centrosymmetric structure.

2.2.2 Crystal classes [2]

The crystal classes are depicted schematically in Figure 2.1. There are thirty-two crystal classes and twenty-one out of them lack a center of symmetry. A crystal exhibiting centrosymmetric structure does not possess polar properties, and thus cannot be piezoelectric. Of the twenty-one noncentrosymmetric classes, twenty are piezoelectric. Ten of the piezoelectric classes are also pyroelectric, which means that they have a spontaneous polarization which exists in the absence of an applied electric field or stress. This polarization is a result of a displacement between the centers of positive and negative charge in the crystal unit cell and their values change with temperature. Ferroelectric materials are a subset of pyroelectric materials with a switchable spontaneous polarization. The materials which are pyroelectrics but not ferroelectrics are because their spontaneous polarizations are not switchable by an applied electric field.

2.2.3 Ferroelectric Domains [1]

Regions in ferroelectric materials which contain a large number of dipoles aligned in the same direction with the same amplitude are called domains. Separations between domains with different dipole polarization direction are called domain walls (or boundaries). When a ferroelectric single crystal is cooled
below Curie temperature, the domains are formed in a configuration that minimizes the total surface energy. This process of domain formation is affected by domain walls, elastic stress fields and free charge carriers and influenced by vacancies, dislocations, and dopants [1].

Domain walls are usually divided into two classifications: 180° and non-180° domain walls. Figure 2.2 shows a schematic drawing of 180° and 90° domains and domain walls. Materials such as lithium niobate and lithium tantalate have only two possible polarization orientations along their c-axis. The polarization orientations in the adjacent domains are ant-parallel to each other, thus the domain walls are 180° domain walls. 180° domain walls have no polarization components normal to the domain wall, and thus there is no surface charge at the wall. Materials having tetragonal structures, such as PZT and BaTiO₃, can have both 90° domains and 180° domains. Materials having rhombohedral structures, such as BiFeO₃, can have 71° and 109° domains. The normal component is nearly continuous across the wall. While Only non-180° domains have the potential to reduce the elastic energy [2, 3].

A range of technologies has been developed characterization of ferroelectric domains, including: polarization microscopy [4]; second harmonic generation microscopy [5]; chemical etching [6]; scanning electron microscopy [7]. In this dissertation, piezoresponse force microscopy (PFM) [8] is employed for domain imaging, witch is an AFM based technique and will be discussed in more detail in chapter 3. Two other AFM based techniques-electrostatic force microscopy (EFM) [9] and scanning Kelvin probe microscopy (SKPM) [10] are developed to study
the surface bound charge and surface potential, respectively. However, for ferroelectric materials, EFM and SKPM are usually employed for measuring relative surface charge or surface potential contrast between domains.

2.2.4 Polarization Switching

Polarization is switchable under the applied electric field with the observation of the formation and movement of the domain walls. For example, in BaTiO$_3$ single crystal, the reversal process occurs with the formation of opposing 180° or orthographic 90° domains in the shape of needles and wedges [11]. These electrical switching properties depend on the grain size and shape. The switching time involves a nucleation time during which the grain forms and reaches a critical size necessary for further growth; a propagation time during which the domain wall moves from cathode to anode in a needle-like one dimensional shape, and finally, a sideways spreading-out time during which the domains fill the entire volume of the film [11]. The forward-growth time is usually just the film thickness divided by the speed of sound. Figure 2.3 show schematically the switching kinetics of a ferroelectric thin film [11]. Whether the rate-limiting parameter is the nucleation time or the sideways growth time depends on the size of the capacitor and is a function of the applied electric field. A detailed theory was developed by Ishibashi and Orihara [12]. For thin film ferroelectrics, switching of nanoscale domains may be realized using a scanning probe microscope (SPM) and a conductive tip. The switching is generated by applying an electric potential between the tip and the back of the crystal [13, 14]. Figure
2.4 is the PFM image of pattern written on a ~100nm PZT thin film deposited on Si wafer using the sol-gel method. The positive domain is written by biasing the tip at -8\(V_{pp}\) with respect to grounded Si. The negative domain is written by biasing the tip at +8\(V_{pp}\) with respect to grounded Si. The darker region in Figure 2.4 is the positive domain with spontaneous polarization pointing from bulk to surface leaving positive charge on the surface, while the brighter region is the negative domain with spontaneous polarization pointing from surface to bulk leaving negative charge on the surface.

Another approach to analyzing the polarization switching in ferroelectrics is the hysteresis loop. However, the interpretation of the loop is much more difficult as described in the following section.

2.2.5 Polarization Hysteresis

Polarization hysteresis loop is widely used in experiments to verify whether or not a crystal or thin film being ferroelectrics or not. Whenever a hysteresis loop is observed as seen in Figure 2.5 [11], the crystal or thin film is called a ferroelectric crystal or ferroelectric thin film. A ferroelectric polycrystalline thin film has zero net polarization as a result of having small crystalline grains with their domain polarization oriented in variety directions. When an external electric field is applied to the crystal, the grain domains with polarization aligned to other directions relative to the applied field switch to the direction of the applied electric field, and the net polarization beings to increase rapidly (A to B). When all of the grains are aligned parallel to the field direction, polarization reaches
saturation (point C). When the electric field is decreased from the saturation point, the net polarization decreases, however, does not return back to zero (C to D) under zero electric field. The net polarization point D is used to define the remnant polarization. An opposite electric field has to be applied (point $E_c$) to the ferroelectric film to switch the net polarization back to zero. This opposite electric field $E_c$ is called coercive field. When keep increasing amplitude of the opposite electric field, all the grain polarizations are completely switched to the opposite directions and reach the saturation (point F). When the magnitude of the opposite electric field is decrease again to zero, the net polarization of the thin film is negative at point G, which is also defined as remnant polarization. In order to switch the net negative polarization back to zero, the coercive electric field (H) has to be applied to the film. Ferroelectrics with open hysteresis loop or unsaturated loop exhibit poor ferroelectric properties.

### 2.2.6 Ferroelectric surfaces

Different orientations of polarization induce positive or negative charges at the ferroelectric material surface. The value of surface charge is given by the normal component of polarization:

$$\sigma_{pol} = \hat{P} \cdot \hat{n}, \quad (2.1)$$

where $\hat{P}$ is the polarization vector and $\hat{n}$ is the unit vector normal to the surface. The surface with unscreened bound charges is energetically unfavorable and thus has to be screened [15] to minimize surface potential. To accomplish this, the surface charges undergo external and/or internal screening. External screening is
identified by the absorption of charged molecules, or surface states due to the surface layer, while internal screening is from free carriers and defects in the bulk and distinguished by the formation of a space-charge layer near the surface. Figure 2.6 is a schematic diagram demonstrating a combination of internal and external screening of bound polarization surface charge.

Ferroelectric materials such as PZT and BaTiO$_3$ having larger defect density compared to materials such as LiNbO$_3$ and LiTaO$_3$. Hence, for PZT and BaTiO$_3$, the dominant screening is internal screening while for LiNbO$_3$ and LiTaO$_3$, the dominant screening is external screening. An example of band bending of a surface undergoing internal and external screening is depicted in Fig. 2.7. Fig. 2.7 (a) is the band structure of ferroelectric film with unscreened surface charges. The band is tilted and unstable. When the surface charges are internally screened, an internal electric field is created near the surface which leads to bending of the conduction and valence bands [16]. Upward band bending occurs at the negative domain surface, while downward band bending occurs at the positive domain surface (Fig. 2.7 (b)). When the surface charges are externally screened, a surface dipole layer is created outside the surface which leads to the change of effective electron affinity at the positive and negative domain surfaces (Fig. 2.7 (c)) [17].

For ultrathin ferroelectric films, the external screening molecules and ionic charges could even control the polarization orientations in the film. Researchers in Argonne National Laboratory demonstrate that by simply varying the chemistry environment (like the oxygen pressure) of the ultrathin PbTiO$_3$ film surface, the polarization direction is switched without applied electric field [18]. A year later
(2010), the same group proposed a new switching mechanism for ultrathin ferroelectric film [19] based on their experimental results of chemical switching. In an applied electric field, polarization switching is believed to occur through the nucleation and growth of new domains. In the chemical switching process, the nucleation is suppressed and switching occurs by uniform decrease and incursion of the polarization without domain formation.

2.3 Properties of typical ferroelectric materials

To date, there are approximately 290 individual compounds which demonstrate ferroelectric properties. A subset of this group of is the so-called oxygen-octahedral. This chapter section presents the properties of several typical ferroelectrics such as Lead Zirconate Titanate Pb(ZrxTi1-x)O3 (PZT); Barium Titanate BaTiO3 (BTO); Lithium Niobate LiNbO3 (LN) and Lithium Tantalate LiTaO3 (LT). The properties of PZT and BTO are stated briefly while the properties of LN are presented in more details, as previously mentioned, LN is the material employed in later work as a template for the photochemical deposition of metallic nanostructures and atomic layer deposition of zinc oxide thin film and thus requires a more detailed explanation.

2.3.1 Properties of PZT

Lead Zirconate Titanate Pb(ZrxTi1-x)O3 (PZT) has a cubic perovskite structure in the paraelectric phase with Pb atoms occupying the corners, O atoms at the face centers and a Zr or Ti atom at the exact center of the unit cell. Ferroelectric phases have different crystal structures which are all slight deviations from the cubic
structure. The Zr/Ti atoms displacement from the cubic center results in the net polarization. The crystal structure is tetragonal for high Ti concentrations and rhombohedral for high Zr concentrations. An example of the tetragonally distorted perovskite structure is shown in Figure 2.8 [20, 21]. Curie temperature, crystal structure, ferroelectric characteristics, and electrical properties are all dependent on the ratio of Zr and Ti components [20, 21]. For example, the Curie point varies from 230°C to 490°C with different Zr/Ti ratio. The remnant polarization and coercive electric field of Pb(Zr\(_x\)Ti\(_{1-x}\))O\(_3\) show the largest value for \(x=0.7\). While at this component ratio, the ferroelectric properties of remnant polarization and coercive field also vary according to different film annealing temperature. The remnant polarization is in the range of 30\(\mu\)C/cm\(^2\)~40\(\mu\)C/cm\(^2\) and the coercive electric field is in the range of 90~120kV/cm depending on different annealing temperature [20, 21].

2.3.2 Properties of BaTiO\(_3\)

Barium Titanate (BaTiO\(_3\), BTO) has been one of the most extensively studied materials since its discovery in 1945 by Wul and Goldman [22]. At high temperature, the structure of BTO crystal is perovskite with Ba\(^{2+}\) at the corner and O\(^{2-}\) at the center and the oxygen at the face centers. When the temperature is lowered to 130°C, 5°C or -90°C, the crystal structure becomes tetragonal, orthorhombic or rhombohedral, respectively. These three structures are distorted from cubic symmetry and result in a net displacement of the cations with respect to the oxygen octahedra thus inducing spontaneous polarization [23]. At room
temperature, the BTO crystal has the tetragonal \((a=3.99\text{Å}, c=4.04\text{Å})\) ferroelectric phase, in which 90° domain twins are formed to relieve the stresses [24]. The remnant polarization is \(~26\mu\text{C/cm}^2\) and coercive electric filed \(~50\text{kV/cm}\) ferroelectric tetragonal [23]. The dielectric constant is \(\varepsilon_a = 3700, \varepsilon_c = 135\) along \(a\) and \(c\)-axis, respectively.

2.3.3 Properties of Lithium Niobate

2.3.3.1 Introduction

Lithium niobate (LiNbO₃ or LN) has been intensively studied and applied in technology [26~29] since it was synthesized in 1965 by Fedulov in the USSR and by Ballman in the USA. On the other hand, despite this extensive research, new properties are been revealed year by year. At room temperature, LN has relatively large magnitude of remnant polarizations: \(78\pm3\mu\text{C/cm}^2\) for LN [30]. Large magnitude of polarization will generate large surface polarization charge as in equation (2.1), which is equivalent to \(~10^{14}\text{e/cm}^2\) charge density at the surface. The compensation of the surface charge is required in order to obtain a stable surface with lower surface electric potential [31].

2.3.3.2 Crystal Structure [32]

The crystal structure of LN was first studied by Zacharasen in 1928 by X-ray technique. In 1963, Shiosaki and Mitsui confirmed the R3c group of LN by neutron diffraction analysis. All the unit cell parameters were established in 1966 by Abrahams \textit{et al.}. The parameters of LN unit cells in hexagonal bases are as follows: \(c_H = 13.8631\pm0.0004\ \text{Å}, \) and \(a_H = 5.14829\pm0.00002\ \text{Å}. \) In
rhombohedral bases, the parameters are: \( a_R = 5.4944 \, \text{Å} \), and \( \alpha = 55'52' \). Figure 2.9 shows the crystallographic structure of lithium niobate. In the ideal case, the stacking sequence along the \( c \)-axis are three types of octahedral, which are \( \text{LiO}_6 \), \( \text{NbO}_6 \) (\( \text{TaO}_6 \)) and \( \Box \text{O}_6 \), where the \( \Box \) represents a vacancy. The Li and Nb ions are located along the polar \( c \)-axis and sit between the oxygen layer planes. Li and Nb ions can only displaced from the centrosymmetric position along the \( c \)-axis, hence, the resulting spontaneous polarization direction is in the direction of \( c \)-axis and only antiparallel (180°) domains can be formed in LN crystals.

The ferroelectric phase transition in LN crystal is associated with the displacement of the lithium and niobium ions. In the ferroelectric phase, the cations are displaced from the centers of the octahedral. The layered oxygen planes are at a distance of 2.310Å form each other. The niobium ion is 0.897Å from the nearest oxygen plane while the lithium ion is 0.714 Å. The oxygen octahedra are distorted and the cations are not located at the centered of oxygen octahedra. The Li ion is further from center than the Nb ion due to the difference in bond strengths i.e. the Li-O bond is weaker than the Nb-O bond [33]. When the crystal is heated above Curie temperature \( T_c \), the Li ions are believed to move towards the nearest oxygen plane, and Nb ions move closer to the center of the oxygen octahedral. The movement of cations reduces the net polarization and the LN crystal transit from ferroelectric phase to paraelectric phase. The crystallographic structure transits to cubic and exhibits centrosymmetry, which belongs to space group \( R\bar{3}c \) [34].
2.3.3.3 Composition and intrinsic defects in LN crystal

Lithium niobate exists with a wide range of possible compositions, which depend on the Li/Nb ratio. Depending on the proportions of the starting materials, LN are generally differentiated into congruent and stochiometric lithium niobate. The congruent composition contains 48.4 mol% LiO₂ and 51.6 mol% Nb₂O₅ [35], which indicate a lithium-deficient structure, while the stochiometric composition has the equal quantities of Li and Nb, Li/Nb=1. The “near stoichiometric” refers to a crystal with \( C = \text{Li}/(\text{Li}+\text{Nb}) \approx 49.8 \text{ mol\%} \). Previous work shows that many physical properties of LN crystals depend strongly on the crystal composition [1, 36], like the LN crystal density [37] and the cohesive field for domain reversal [38]. Curie temperature for LN is in the range of 1400K and also varies with the composition: \( T(K) = 9095.2 - 369.05C + 4.288C^2 \) [39].

Congruent LN with an off-stoichiometric composition has a high concentration of intrinsic defects depending on the Li/Nb ratio. Several defects structures are proposed in the history: the excess Nb ions in congruent LN occupy only the regular Li site and the local charge neutrality is guaranteed by oxygen vacancies [35] or by the Li vacancies at the Li site [40] or by Nb vacancies at Nb sites [41, 42]. However, the oxygen vacancies model is not consistent with the experiment which found the density of LN increases with decreasing Li/Nb ratio. The Nb vacancies model was calculated to be energetically unfavorable by Donnerberg et al. [43]. Later in 1997 and 1998, Yatasenko et al. [44, 45] proposed a model with a combination of Li vacancies and Nb antisites. This model best explained their nuclear magnetic resonance data. In their model, the
intrinsic defects are a random distribution of complex \( \text{Nb}_{Li}^{+}+3V_{Li} \) and \( V_{Li} \) (\( \text{Nb}_{Li} \) represents the Nb ion on Li-site, \( V_{Li} \) represents vacancy on Li-site). In 2008, Xu et al. [46] studied the intrinsic defects in LN using the density functional theory (DFT). Their conclusion was that the defects are energetically stable under Nb\(_2\)O\(_5\)-rich conditions, and defects are clusters consisting of a Nb antisite compensated by Li vacancy (\( \text{Nb}_{Li}^{+4V_{Li}} \)), which is consistent with Yatasenko’s model to a great degree.

2.3.3.4 LN surface polarization charge compensation

Congruent LN has a spontaneous polarization of \( \sim 71\mu C/cm^2 \), while stoichoiometric LN has a spontaneous polarization of \( \sim 78\mu C/cm^2 \). As stated in equation 2.1, the induced surface charge density is \(+71\mu C/cm^2 \) \((+78\mu C/cm^2)\) on the positive domain surface and and \(-71\mu C/cm^2 \) \((-78\mu C/cm^2)\) on negative domain surface for congruent (stoichoimetric) LN. The polarization surface charge has to be compensated or screened to obtain a stable surface. For LN crystal, the surface geometric structure, electronic structure and screening remain significant uncertainties. Different conclusions about surface structures and terminations have been obtained in recent years. Tabata et al. [47] observed adsorbed oxygen and hydroxyl groups on the LN surface from their XPS date. They also interpreted their experimental data in terms O-Nb termination at the surface. Kawanowa et al. studied both positively and negatively poled LN and concluded that both surfaces are terminated with oxygen layers although the Nb atoms are closer to the positive surface while the Li atoms are closer to negative surface. In 2007, Yun et al. [48]
obtained low energy electron diffraction (LEED) pattern and confirmed that the
surface displayed (1×1) bulk structure. Thus no higher order reconstruction occurs
on LN surfaces. From their experimental data, Yun et al. proposed that one
oxygen vacancy per surface unit cell on the lithium terminated surface and one
oxygen adatom per unit cell on the niobium terminated surface could compensate
the polarization charge. One year later (2008), Levchenko and Rappe employ the
first-principles density functional theory to study LN surface. From the Berry’s
phase analysis of the bulk polarization ($P_s = \pm 5e/4$ per surface unit cell = ±
4.4×10$^{18}$ e/m²), they conclude that the negative surface is compensated by an extra
Li atom while the positive surface is compensated by an O-Li pair. This
compensation will reduce the uncompensated charge to ±e/4 per unit cell, which
can be passivated by mobile carriers or by submonolayer coverage of adsorbed
ions. A rough calculation shows that e/4 per unit cell charge is equivalent to a
density of 1×10$^{18}$ e/m². Their conclusion explained the observed differences in the
evaporation rates of LiO, Li, and O$_2$ form positive and negative surfaces at
elevated temperatures [49].

2.3.4 LN electrical properties

2.3.4.1 Pyroelectric effect [35]

LN belongs to pyroelectric crystal class with spontaneous polarization varying
with temperature. The relationship between the spontaneous polarization and the
temperature change can be represented by: $\Delta P_s = p \Delta T$, where $p$ is the
pyroelectric tensor. Since the Li and Nb ions can only move along the c-axis, the pyroelectric tensor has only one non-zero component:

\[
p = \begin{bmatrix}
0 \\
0 \\
p_3
\end{bmatrix}
\]

where \( p_3 \) is the only non-zero component, and \( p_3 = -6.8 \times 10^{-3} \text{ µC/K·cm}^2 \) [50]. The negative value indicates that the magnitude of spontaneous polarization decreases with heating the crystal.

2.3.4.2 Permittivity [32]

For LN crystal, the relationship between the electric flux density and electric field is represented as \( \mathbf{D} = \varepsilon \mathbf{E} \), where \( \varepsilon \) is a second-rank permittivity tensor. In the \( \varepsilon \) tensor, the only non-zero components are the diagonal elements. In the place perpendicular to the c-axis, the permittivity components have the same value due to the symmetric about c-axis. Thus the permittivity tensor can be represented by a \( 3 \times 3 \) matrix:

\[
\varepsilon_y = \begin{bmatrix}
\varepsilon_{11} & 0 & 0 \\
0 & \varepsilon_{11} & 0 \\
0 & 0 & \varepsilon_{33}
\end{bmatrix}
\]

Measured values of \( \varepsilon_{11}/\varepsilon_0 \) are \( \sim 28.1 \) and \( \varepsilon_{33}/\varepsilon_0 \sim 84.1 \) [32]. These values are used in our later research work of ZnO thin film deposition on LN surface.

2.3.4.3 Piezoelectric effect of LN [32]

The LN crystal is also a piezoelectric solid. An induced polarization and surface charge appear under the applied mechanical stress. The relationship between induced polarization and applied stress is represented as \( \mathbf{P} = d \mathbf{\sigma} \), where
$P$ is the induce polarization, $d$ is the third-rank piezoelectric tensor and $\sigma$ is the applied stress. The tensor $d$ contains only 18 independent elements and can be written as a $3 \times 6$ matrix. In order to simplify the tensor representation, the $jk$ subscripts are reduce to a single subscript using substitutions:

\[
\begin{align*}
jk = 11 &= 1 & jk = 22 &= 2 \\
jk = 33 &= 3 & jk = 23,32 &= 4 \\
jk = 31,13 &= 5 & jk = 12,21 &= 6
\end{align*}
\]

Thus the piezoelectric tensor can be written as [32]

\[
d_{ijk} = \begin{bmatrix}
0 & 0 & 0 & 0 & d_{15} & -2d_{22} \\
-d_{22} & d_{22} & 0 & d_{15} & 0 & 0 \\
d_{31} & d_{31} & d_{33} & 0 & 0 & 0
\end{bmatrix}
\]

The piezoelectric coefficients according to Weis and Gaylord [51] are listed in Table 2.1.

2.3.4.4 Coercive field

The magnitude of the coercive field ($E_c$) for domain reversal in LN is also dependent on crystal composition. Congruent LN coercive field is $\sim 210$ kV/cm [52] while for stoichoimetric LN, the coercive field reduce to $\sim 40$ kV/cm [53]. When the external switching field is applied to LN crystal, the Li ions move through the oxygen plane to an adjacent vacant site. For the congruent composition, at the niobium antisiite defects, the Nb cation must move through the oxygen plane upon domain switching. Because it is more difficult for Nb to pass through the oxygen plane, a higher field is required [53]. In this research for a 800nm single crystal film, 9volts $dc$ bias is enough to switch the stoichoimetric
film while the congruent film with the same thickness, 20volts is the required voltage to switch the domain in our experiment experience.

2.3.4.5 Photovoltaic Effects

The dark conductivity of congruent LN crystal at room temperature is \(<10^{-18}\ \Omega^{-1}\ \text{cm}^{-1}\) [54]. However, under the illumination of light with a photon energy greater than the band gap of LN, free electron-hole pairs are generate and transferred to the surface due to the build-in electric field in the crystal. The photovoltaic current density is proportional to illumination intensity and absorption coefficient \(\alpha\). The absorption coefficient \(\alpha\) depends on the light wavelength and the vicinity of absorption edge. Redfield and Burke [54] calculate \(\alpha\) from transmission spectra of thin congruent LN crystals. Zelmon et al. measured the refractive index dispersion [55] Table 2.2 lists the absorption coefficient for five wavelength photon energies which will be employed in our later work.

Different from the dark conductivity, the resulting photoconductivity of electrons under illumination can be written in the following form:

\[
\sigma_{ph} = e\mu N_e
\]

where \(e\) is the charge of an electron, \(\mu\) is the electron mobility and \(N_e\) is the concentration of excited electrons in the conduction band, which depends on the illumination intensity and absorption coefficient. The electron mobility in congruent LN is \(0.74\times10^{-4}\ \text{m}^2/\text{V}\cdot\text{sec}\), while for stoichiomeric LN, it is one order larger \(7.4\times10^{-4}\ \text{m}^2/\text{V}\cdot\text{sec}\).

2.4 “Ferroelectric-lithography”
When above band gap light photons are illumined on ferroelectric materials, electron-hole pairs are generated. Electrons move to the positive domain driven by the downward band bending and holes move to the negative domain driven by the upward band bending. Thus for patterned ferroelectric surface, it is expected that electrons and holes are spatially separated. When the patterned ferroelectric materials are immersed in chemical solutions containing cations or ions, local reduction-oxidation reaction, REDOX reaction, are generated. Hence, ferroelectrics with domain pattern are able to be used as templates for space selective reduction and oxidation on the same surface depending on the polarization orientation.

The photo-induced Ag deposition on ferroelectric BaTiO$_3$ was first published by Giocondi and Rohrer in 2001 [56]. They related the variation of deposition location, which is positive domain dominant deposition, to the polarization orientation and band bending. Their work opened a window for selective reduction of metallic nanoparticle on ferroelectric surfaces. Kalinin et al. even proposed a novel idea of ferroelectric nanolithography-to construct 3D nanostructures on predefined locations on a ferroelectric surface through photo-induced and localized REDOX reaction [57]. Since then, space selective reduction of different metal nanostructures from different chemical solutions on different ferroelectrics, such as BaTiO$_3$, PZT and LiNbO$_3$, becomes the theme of many research papers [58~64]. The deposition of Rh, Pd, Au, Co, Ni, Fe have been achieved on PZT [61]. Ag [62] and Pt [63] nanowires were synthesized along the 180° domain boundaries. The authors for reference 61 measured the current-
voltage of the Pt nanowire and revealed that the conductivity of the self assembled nanowires exhibit an Ohmic behavior.

During the development of photo-induced reduction of vary patterned nanostructure, the basic process behind this selective deposition has also been investigated. The presence of the nanoparticles in the AFM image indicates that nucleation limits the process. The photo-excited electrons migrate to the surface and combine with cations in the solution to produce atoms. Several atoms nucleate and form small clusters. Photo-excited electrons from regions around the nucleation site are collected at the nucleation sites. The particles grow due to reduction of the Ag which deposits on the nucleated particles. Polarization and band bending induced by the internal field of the ferroelectric material are believed to be important factors determining the deposition pattern. Other than the ferroelectric properties, the effects of the chemical cation reduction potential and Stern layer on ferroelectric surface in the chemical solution were also found to have great influence on the reduction process. Stern layer screening the polarization surface charge [64]. In order for cations in the solution outside the Stern layer to reach the ferroelectric surface, there must be a disturbance in the Stern layer such that the screening molecules will be desorbed from the surface. The Stern layer will change the deposition pattern and will be discussed in more detail in chapter 5 of this dissertation. The successful reduction of metallic nanoparticles is also believed to depend on the chemical solution reduction potential relative to the band structure of the ferroelectric templates. Salts with a reduction potential greater than the chemical potential of the conduction band will
be reduced [61]. The authors of reference 61 showed that for certain cations such as Fe$^{2+}$, with a reduction potential near the edge of the conduction band of the PZT, either reduction or photodecomposition can happen. Unless the chemical reduction potential is below the ferroelectric conduction band, the metallic particle can be reduced from the solution without decomposition of ferroelectric surface [61].

Base on the understanding of the photochemical reduction process and the nucleation-limited metallic nanoparticle growth mechanism, ferroelectric lithium niobate (LN) are used as a template to direct the assembly of metallic nanostructures via photo-induced reduction reaction. The effects of UV wavelength, intensity, polarization screening and chemical concentration are studied. The subsequent results suggest that these four factors are responsible for the different deposition patterns. These findings will hopefully provide a foundation to employ ferroelectric templates for assembly and patterning of inorganic, organic, biological, and integrated structures.

2.5 Summary

Ferroelectric materials have many unique properties and thus, its study requires the knowledge of scientists from the fields of not only physics, chemistry, mathematics, biology but also mechanical and electrical engineering. Moreover, scientist’s interest is piqued due to ferroelectric materials applications in technologies such as piezoelectric sensors, actuators, surface-acoustic-wave devices or capacitors [65~70]. In this chapter, an overview of the basic physical
properties of ferroelectric materials is given to introduce the background knowledge necessary to understand the results presented in this dissertation. The discussion focused on lithium niobate which is employed as a template and substrate material for photo-induced deposition of metallic nanostructure and for atomic layer deposition of semiconducting ZnO thin film. The concepts of spontaneous polarization, domains, domain switching, surface charge and screening of lithium niobate are emphasized in this chapter, because these concepts are the principal background for understanding the later research.
REFERENCES


Table 2.1 Piezoelectric strain coefficients

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<th>$d_{15}$ ($10^{-11}$CN$^{-1}$)</th>
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Table 2.2 UV light exposure parameters.

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Figure 2.1 Diagram of the 32 crystal classes (from Christman, 1999, reference 2)
Figure 2.2 Schematic diagrams of ferroelectric domain configurations. (a) Periodic domain structure in materials with 180° domains. (b) Domain structure with 90° domain wedges in a region of a 180° domain.
Figure 2.3 Switching kinetics of a ferroelectric thin film [11]. (a) Inhomogeneous nucleation at anode or cathode. (b) Needle-like domains forward growth. (c) Needle-like domains sideways growth.
Figure 2.4 Piezoresponse force microscopy (PFM) phase image of pattern written on a ~100nm sol-gel deposited PZT thin film. The darker region is the positive domain, while the brighter region is the negative domain.
Figure 2.5 Polarization hysteresis loop for a ferroelectric sample
Figure 2.6 Schematic diagram demonstrating internal and external screenings at a ferroelectric surface.
Figure 2.7 Schematic diagrams showing the band bending of a screened ferroelectric material. (a) Unscreened surface induce electric field inside ferroelectric bulk and a tilted band structure. (b) Internal screening of polarization bound charges creates an internal electric field near the surface and causes bending of the conduction and valence bands. Upward band bending occurs at the negative face, while downward band bending occurs at the positive face. (c) External screening leaves the band structure flat. The electron affinity of positive domain surface is increased due to the surface dipoles while the electron affinity of negative domain surface is decreased.
Figure 2.8 A representation of the tetragonally distorted perovskite structure.
**Figure 2.9** Crystallographic structure and relative positions of ions in lithium niobate. The stacking sequence of the unit cell is LiO$_6$, NbO$_6$ (TaO$_6$) and □O$_6$, where the □ represents a vacancy. The Li and Nb ions are located along the polar c-axis and sit between the oxygen layer planes.
3.1 Introduction

The atomic force microscope (AFM) was firstly developed by Binning, Quate and Gerber in 1986 as a surface topography imaging tool [1]. Since then, AFMs have become the standard equipment in many research aspects due to its flexible application in material characterization and engineering. The basic components of an AFM system consist a cantilever, a photo detector which monitors the motion of the probe, and a scanner which controls the scanning the probe’s position and consequently the distance between the probe and the sample. A schematic of an AFM system is shown in Figure 3.1. A controller connecting these three components to a computer generates the electronic signals controlling the motion of the scanner as well as converts detected signals to digital data. The digital data are simulated by computer software to generate an image.

The AFM probes are usually made of heavily doped Si or Si$_3$N$_4$ which are rectangular or triangular in their shape. Sample images of the AFM probes are shown in Figure 3.2. Two types of AFM probes are used in our research: PPP-NCH (Naosensors) and Arrow-EFM (Nanoworld). Both types of probes are rectangular, but the PPP-NCH probes are not metal-coated. It is, thus, usually used for topographic imaging. The tip of Arrow-EFM, on the other hand, is conductive due to the metal Pt/Ir coating. Therefore, this probe is usually chosen to obtain both the electrical information and a topographic image of a sample simultaneously. The parameters of these two types of probes are listed in Table
3.1. The PPP-NCH probe has a higher resonant frequency and a larger force constant, which indicate that the tip is stiff and can only be used in tapping mode. The Arrow-EFM probe has a lower resonant frequency and smaller force constant. It is softer compare to the PPP-NCH probe and can be used for both tapping mode and contact mode. The 3rd probe listed in table 3.1 is the probe with the lowest resonant frequency and smallest force constant. This probe is only used for contact mode imaging. One challenge associated with AFM imaging is choosing the appropriate probe and imaging mode for different samples.

Two AFM systems are used in our research. One is an Agilent 5500 system and the other is an Asylum Research MFP-3D system. They both contain a noise isolation stage or cabinet, an optical microscope for laser beam adjustment and probe focus, a scanner, a computer with AFM operation software, a controller and electronic box which control the motion of AFM probes and collecting detection signals.

A number of different AFM operation modes have been explored to measure sample topographic and electric properties, such as electrostatic force microscopy (EFM) [2–6], piezoresponse force microscopy (PFM) [7, 8, 9] and scanning Kelvin probe microscopy (SKPM) [10, 11, 12]. In this chapter, we will give a brief introduction of the operation principles of these imaging modes.

3.2 Topographic imaging principle

When an AFM tip approaches a surface, it undergoes an attractive or repulsive force (Figure 3.3). The attractive force causes a downward bending of the
cantilever while the repulsive force causes an upward bending. The amplitude of the bending is related to the cantilever stiffness and the resonant frequency as well as the properties of the sample surface. Of course, the environment factors (temperature, humidity etc.) also affect the cantilever bending amplitude.

A laser beam shines onto the back of the cantilever and reflects off the cantilever to a photo-detector. The photo-detector is segmented into four quadrants as shown in Figure 3.1. A voltage is generated from each quadrant with the amplitude of the voltage proportional to the laser beam intensity. The sum voltage from the four quadrants records the overall intensity of the reflective laser beam. The deflection signal (Figure 3.1) is the voltage difference between the top two and bottom two quadrants. The LFM signal (Figure 3.1) is the voltage difference between the left two quadrants and right two quadrants. The deflection and LFM signals are then processed by a computer to generate images.

There are two topographic imaging modes in AFM systems, which will be discussed: contact mode and tapping mode.

3.2.1 Contact mode

In contact mode, the cantilever is in constant contact with the surface and the scanner moves the cantilever in the $X$ and $Y$ directions. The tip is within a few angstroms of the sample surface, it is acting in the repulsive force regime, as shown in Fig. 3.1. When the tip is scanning surface structures exhibiting differing heights or material components, a force gradient is applied to the tip and causes deflection of the cantilever. A voltage signal is applied on the $Z$ piezo sensor in
the scanner through a feedback loop to maintain a constant deflection of the cantilever. The surface topographic information is simulated from this voltage signal.

Because in the contact mode the tip is operating in the regime of repulsive force, the resolution is relatively higher than other imaging modes. In ambient condition, the resolution in the $X$ and $Y$ directions is 1-10nm while in vacuum it can reach 1-4nm. The disadvantage of contact mode is that due to the stronger repulsive force between the tip and the sample, it is not an ideal mode for imaging soft sample. The tip can easily scratch or damage the surface. In stead of contact mode, the tapping mode is usually employed to image soft sample and image in liquid.

3.2.2 Tapping mode

In tapping mode, the AFM probe keeps oscillating at a set frequency near its resonance (100–300Hz lower than the resonance) driven by an oscillation piezo of the scanner. When the probe is scanning a surface and oscillating at a distance of hundreds of Ångstroms from the sample, the resonance frequency of the tip is shifted from the set free oscillating frequency due to the force gradient applied on the tip. The shift of oscillation frequency leads to a change in the oscillation amplitude of the tip. The height of the cantilever is adjusted by the scanner’s $Z$ piezo through a feed-back loop to maintain constant oscillation amplitude as specified by the set point value in the controlling software. The voltage applied to the $Z$ piezo to adjust the height is simulated by the computer software to a
The set point in the tapping mode is an important parameter which determines the force applied onto the tip and the quality of the image.

The force per strike of tip operating in the tapping mode is approximately 0.5 nN. This is much smaller than the force exerted by the tip in contact mode AFM, which can be ~100 nN [13]. This smaller striking force in tapping mode makes it a better imaging technique for most soft samples.

When the topographic image is recorded, the phase image is also collected by recording the phase difference between the driven sine waves and the response of the cantilever. The phase signal is more sensitive to the variation of material components. Figure 3.4 shows the topography (a, c) and phase images (b, d) of the Ag particles deposited on lithium niobate substrate. Figure 3.4 (a) and (b) are taken with larger set point indicating smaller force between tip and sample. No structures are detected from the topography except noise, however, Ag particle are visible from the phase image. By using a smaller set point, Ag particles are clearly shown in both topography and phase images.

3.3 Piezoresponse force microscopy (PFM)

Piezoresponse force microscopy (PFM) is widely used for domain orientation imaging as well as measuring local piezoelectric properties such as piezoelectric crystal vibrations [14, 15], hysteresis loop spectroscopy [16, 17] and domain switching dynamics [18, 19] induced by applied electric field between a conductive tip and piezoelectric surface. Due to the small radius of AFM tip (~15nm), local quantitative information on ferroelectric surface such as
nanometer domain size, hysteresis loop, and inhomogeneous behavior near domain and grain boundaries can be investigated via PFM [20]. In this dissertation, PFM is applied for visualizing ferroelectric domains.

3.3.1 Operation principle of PFM

PFM is operating in contact mode of imaging while an *ac* modulation voltage is applied to a conductive AFM tip (Arrow-EFM, Nanoworld). This *ac* modulation electric field induces a deformation of the piezoelectric crystal and PFM images are generated by detecting this deformation. The topographic image and piezoresponse image can be obtained simultaneously in PFM scanning.

Figure 3.5 shows a schematic drawing of PFM setup [21]. The modulation voltage is applied between a conductive probe and the backside of a sample. A local oscillating electric field is established between the tip and sample surface:

\[
V_{tip} = V_{dc} + V_{ac} \\
V_{ac} = V_0 \cos(\omega t + \theta_0) \tag{3.1}
\]

where \(V_{dc}\) is the *dc* component of the modulation and \(V_{ac}\) is the *ac* component of the modulation. Piezoelectric material expand or contract at the *ac* modulation frequency, \(\omega\), under the established alternating electric field. The expansion or contraction of the sample at the *ac* modulation frequency results in a deflection of cantilever. The *ac* component frequency \(\omega\) (\(~10\) kHz) is chosen to be different from the resonant frequency of the cantilever (\(~75\) kHz for Arrow-EFM, Nanoworld). Two lock-in amplifiers are employed in PFM imaging. Lock-in one amplifies topography signal while lock-in two amplifies the \(~10\) kHz deflection of
the conductive tip, which reflects the piezo response oscillation. This low frequency (~10 kHz) deflection motion of the tip is given by

\[ z = z_0 + A \cos(\omega t + \theta), \]  

where \( A \) is the piezoresponse amplitude and \( \theta \) is the piezoresponse phase.

Piezoresponse amplitude \( A \) is simulated to generate a PFM amplitude image while piezoresponse phase \( \theta \) is simulated to generate a PFM phase image. For a ferroelectric crystal, such as lithium niobate, with only 180° domains, the piezoresponse amplitude \( A \) is the same for antiparallel domains and is zero at the domain boundary [22]. Figure 3.6(a) shows a PFM amplitude image, in which no contrast is observed between positive and negative domain except that the 180° domain walls appear as dark lines. Thus, from the piezoresponse amplitude image, the orientation of the 180° domain is not discernable. If a ferroelectric contains non-180° domains, the PFM amplitude can image the contrast between the 180° domain and non-180° domain. The values of domain wall width observed by PFM [23, 24] are significantly larger than the first-principle calculations, which predict a one to two unit cells 180° domain wall width [25]. This conflict might be due to the residue stress in the vicinity of domain wall resulting from the larger conductive tip radius and inhomogeneous electric field. Piezoresponse \( \theta \) is the phase difference between the modulation voltage and the piezoresponse voltage. For instance, when lithium niobate single crystal is modulated under the ac oscillation signal, negative domain will oscillate in phase with the applied electric field while the positive domain will oscillate out of phase with the field. The schematic drawing of the in- and out-of-phase oscillation is given in Figure 3.7.
Therefore, positive domains appear dark and negative domains appear bright in PFM phase images (Figure 3.6 (b)). The above PFM is called the vertical PFM, which detects the cantilever deflection. Other than the deflection vibration, the cantilever also experience torsional vibration due to piezoelectric shear deformation of the sample [26]. This torsional vibration of the cantilever can also be detected and simulated to lateral PFM image. Lateral-PFM is created to detect in-plane polarization of the non-180° domain.

When a \( dc \) voltage above the switching coercive field is applied between the conductive tip and ferroelectric sample, ferroelectric domain direction can be switched and new domain pattern can be written with software controlling the \( X \) and \( Y \) motion of the scanner.

3.3.2 Dual \( ac \) resonance tracking (DART) PFM

The above description of PFM operation depicts the conventional PFM technique. As described above, the phase image is obtained by recording the relative phase of the drive and response signal to determine the domain orientation. There may be significant cross talking between topography and piezoresponse phase measurement if the sample material component varies or there are electrostatic charges embedded in the surface. Usually, the \( ac \) modulation voltage in the commercially made AFM system is limited to \( 10V_{pp} \) amplitude. This requires the measured ferroelectric materials have a stronger electromechanical response in order to obtain direct image [27, 28]. Measurement of lower sensitivity materials requires the use of a higher voltage, which will
result in the undesired switching of domains or artifacts and cross-talking between topographic and piezoresponse signals [27, 28]. In order to overcome the above-mentioned difficulty, several modified PFM techniques have been developed. One of them is DART PFM [28]. Figure 3.8 is the schematic drawing of the operation principle of DART PFM from reference [28]. Unlike the conventional PFM, two ac oscillating voltages with frequencies near the same resonant frequency are applied to the conductive tip at the same time. One frequency $f_1$ is below the resonance while the other frequency $f_2$ is above resonance. Under the tip-sample force gradient, the resonant frequency changes, which results in the deflection changes from $A_1$ and $A_2$ (solid line in Figure 3.8) to $A_1'$ and $A_2'$ (dashed line in Figure 3.8), respectively. The original difference $A_2-A_1$ is zero before scanning. During scanning, the amplitude difference $A_2'-A_1'$ signal is input to a feedback loop, which maintains the two primed frequencies such that they are at an equal distance from the new resonance. In other words, the two new frequencies are updated to maintain a zero amplitude difference, whereby these new frequencies give the DART PFM images. The advantages of DART PFM are that it can avoid artifacts associated with changes in the contact stiffness and works for materials with small piezoelectric coefficient [29]. PFM amplitude and phase images taken with DART PFM are shown in Figure 3.6.

3.4 Electrostatic Force Microscopy

3.4.1 Introduction
Electrostatic force microscope (EFM) is a local-detecting and non-destructive technique developed to characterize material properties such as surface potential, surface charge distribution [30, 31], doping concentration [32] and dielectric constant [33]; moreover, EFM also has the ability to inject charges into the nanostructure.

EFM works in tapping mode and detects the electrostatic force between a tip and sample. The conductive probe operates in the attractive force regime under force gradients from long-range Coulomb forces. There are two methods of measuring the surface charge. The 1st method is the “interleave” or “lift” mode [34] which is use in our Asylum AFM system. Firstly, the tip traces one line in tapping mode to acquire topographic deflection information. Then the tip is raised above the surface--for example, the tip may be raised 100nm--and retraces the same line to acquire deflection vibration due to the long range electrostatic force between tip and sample. The trace and retrace scans are both operating at the same frequency, which is near the tip resonance. In the first method, the topographic and the electrostatic images are obtained sequentially and is employed in the Asylum MFP-30 system. The schematic diagram of the 1st method is shown in Figure 3.9 (a). The 2nd method acquires the topographic and electrostatic images simultaneously [35, 36] and is employed in Agilent 5500 system. A diagram of the setup for the second method is displayed in Fig. 3.9 (b). From Fig. 3.9 (b), we can see that two different frequencies are used in the second method. The near resonance frequency is employed in the first lock-in amplifier to collect topographic information while the much low frequency ~10 kHz signal
is applied to the metal-coated tip through the second lock-in amplifier to collect electrostatic information.

3.4.2 Force analysis

External $ac$ and $dc$ voltages that are applied between the tip and sample during EFM, $V_{dc}$ and $V_{ac} = V_0 \sin(\omega t)$. According to Coulomb’s law, the static force between the tip and sample is given by

$$F_{\text{coul}} = \frac{q_s q_t}{4\pi\varepsilon_0 z^2} \quad (3.3)$$

where $\varepsilon_0$ is the vacuum permittivity, $z$ is the distance between the tip and the sample surface, and $q_t$ and $q_s$ are the charge on the tip and sample, respectively.

In addition to the Coulomb force, there are also capacitive forces from external $ac$ and $dc$ voltages that are applied between the tip and the sample:

$$F_{\text{cap}} = \frac{1}{2} \frac{\partial C}{\partial z} \left( V_{dc} + V_{ac} - V_s \right)^2 \quad (3.4)$$

where $C$ is capacitance formed between tip and sample and $V_s$ is the sample surface potential.

The total force on the tip is then

$$F_z = F_{\text{coul}} + F_{\text{cap}} \quad (3.5)$$

And the total charge induced on the tip is given by

$$q_t = -q_s + q_{dc} + q_{ac} = -q_s + CV_{dc} + CV_0 \cos(\omega t) \quad (3.6)$$

After substituting equation (3.6) into equation (3.5), we find the force can be separated into three components: a static $dc$ component.
\[ F_{dc} = \frac{q_s}{4\pi\varepsilon_0 z^2}(-q_s + CV_{dc}) + \frac{1}{2} \frac{\partial C}{\partial z}(V_{dc} - V_z)^2 \]  

(3.7)

a first harmonic \( ac \) component,

\[ F_{1\omega} = V_0 \cos(\omega t) \left( \frac{Cq_s}{4\pi\varepsilon_0 z^2} + \frac{\partial C}{\partial z}(V_{dc} - V_z) \right) \]  

(3.8)

and a second harmonic \( ac \) component,

\[ F_{2\omega} = \frac{1}{2} \frac{\partial C}{\partial z} V_0^2 \cos^2(\omega t) \]  

(3.9)

EFM detects the first harmonic \( ac \) component. The deflection of cantilever induced by \( F_{1\omega} \) at frequency \( \omega \) is detected by a second lock-in amplifier.

Equation 3.8 shows that if the forms of the capacitance and sample surface potential are also known, then the surface charge can be determined. The surface potential can be determined from the Scanning Kelvin probe microscopy (SKPM) technique which will be discussed in the next section. However, due to the difficulty of determining the value of capacitance, quantitative surface charge value is difficult to obtain. Hence, EFM is usually used to measure the relative surface charge contrast between two regions for ferroelectric domains.

3.5 Scanning Kelvin Probe Microscopy

3.5.1 Introduction

Scanning Kelvin probe microscopy (SKPM) was developed to measure the contact potential difference between the tip and sample [37]. SKPM is an extension of EFM, where the conductive probe also works in the tapping mode and acquires the topographic image and surface potential image in the 1st method-
lift or in the 2nd method-two frequency mode as described in the EFM session. In SKPM, a dc-offset voltage is applied to the tip in order to minimize the Coulomb force interaction between the tip and sample. A map of the surface potential is then generated from the dc offset feedback data.

3.5.2 Working principle

The total force on the tip is the same as the total force on the tip in EFM. Within the three force terms, the most important term as far as surface potential is concerned is the second term (equ. 3.8), from which we can see that if there is a potential difference between the tip and the sample, then when an ac voltage is applied, there will be an oscillation at the frequency of the ac modulation. If the applied dc voltage equals the sample surface potential \( V_{dc} = V_s \), then the oscillations at \( \omega \) will be surface potential independent. The value of the applied dc bias used to compensate the surface potential gives a SKPM image. \( V_{dc} \) is equal to

\[
V_{dc} = V_s = \phi_t - \phi_s
\]

\[
\phi_s = \chi_s - \Delta E_{Fn} - \Delta \phi
\]

where \( \phi_t \) and \( \phi_s \) are the work functions of the tip and sample, \( \chi_s \) is the electron affinity of the surface, \( \Delta E_{Fn} \) is the difference between the Fermi level and the conduction band, and \( \Delta \phi \) is the band bending of the surface. For measuring the surface potential of the ferroelectric materials, the data is not just a contribution from work function. The surface potential contrast between positive and negative
domain of LN surfaces is observed to reverse when the crystal is heated or cooled [38, 39]. The contrast reversal is attributed to relative change between the external screening and spontaneous polarization when the temperature is varied.

3.6 Cross-talk between topography and electrostatic signal

Whenever there is potential difference between the conductive tip and the local surface, electrostatic forces are established. As well as for the PFM, EFM and SKPM measurements, the applied electric modulation induces electrostatic forces. The electrostatic forces will result in a damping of the oscillation amplitude of cantilever. Some researches found that this damping resulted in a higher topography [40] because the feedback loop retracted the tip further from the surface due to the damping. A flat surface, having patterned electric charge but no topographic features, showing variation in topography has been observed [41]. The imaging error is attributed to the cross-talk between topography and electrostatic signal. Ziegler et al. developed a ‘feed-forward’ technique to compensate the electrostatic forces in order to minimize the cross-talk. The electrostatic forces are compensated by replaying the measured surface potential as a bias voltage applied to the tip in the next topography scan line [41]. The electrostatic artifacts in topography vanish when the feed-forward loop is turned on.

3.7 Summary
In this chapter, the AFM operation modes for topographic imaging are firstly introduced. Contact mode having higher resolution, however, it is usually used to image hard surfaces, while tapping mode is used to image softer samples. AFM probes with different parameters have to be chosen by researchers for different imaging modes and samples. The later section of this chapter describes the extended application modes: PFM, EFM, and SKPM which are used to imaging ferroelectric domains, surface charges and surface potential, respectively. These methods all require a conductive AFM tip. The PFM operates in contact mode with a lower frequency $ac$ electrical modulation voltage applied between tip and sample. The EFM and SKPM, on the other hand, are operated in the tapping mode with the $ac$ modulation voltage added through a separate lock-in amplifier. In the next few chapters, lithium niobate will be used as template for wet-chemical deposition of metallic nanostructures and for atomic layer deposition (ALD) of semiconductor thin film. The AFM is an important tool used for characterizing these surfaces.
REFERENCES


Table 3.1 Specifications of cantilevers used in this research

<table>
<thead>
<tr>
<th></th>
<th>Thickness (µm)</th>
<th>Width (µm)</th>
<th>Length (µm)</th>
<th>Force Constant (N/m)</th>
<th>Resonance Frequency (kHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPP-NCH</td>
<td>4 (3.0-5.0)</td>
<td>30 (22.5-37.5)</td>
<td>125 (115-135)</td>
<td>42 (10-130)</td>
<td>330 (204-497)</td>
</tr>
<tr>
<td>Arrow-EFM</td>
<td>3 (2.5-3.5)</td>
<td>35 (30-40)</td>
<td>240 (235-245)</td>
<td>2.8 (1.4-5.8)</td>
<td>75 (58-97)</td>
</tr>
<tr>
<td>CONT</td>
<td>2 (1.5-2.5)</td>
<td>50 (45-55)</td>
<td>450 (445-455)</td>
<td>0.2 (0.07-0.4)</td>
<td>13 (9-17)</td>
</tr>
</tbody>
</table>
Figure 3.1 Schematic of the AFM setup. A piezoelectric scanner controls the movement of the tip and the distance between tip and sample. A laser beam is reflected from the backside of the cantilever to a photodetector which records the deflection of the cantilever as it moves across the sample. The data processor and feedback electronics convert the signals and generate an image of the sample surface.
Figure 3.2 Various geometries of cantilevers and probes. (a) Triangular cantilever (b) Rectangular cantilever. (The image is courtesy of (a) MikroMasch and (b) of Nanosensors.)
Figure 3.3 Lennard-Jones model of the potential energy. As the tip approaching the surface, it first experiences weak, long-range attractive van der Waals forces and then strong, short-range repulsive forces.
Figure 3.4 Tapping mode topography (a, c) vs. phase images (b, d) of Ag particles deposited on lithium niobate surface. Images (a) and (b) were taken at a larger set point than images (c) and (d).
**Figure 3.5** Block diagram of the setup used for PFM measurements (From reference 21).
Figure 3.6 DART PFM amplitude (a) and phase (b) image.
Figure 3.7 Piezoresponse of lithium niobate under a modulation voltage applied to the tip. The dashed red line in (a) indicates expansion when the tip is in contact with a negative domain. This results in an in-phase oscillation of the piezoresponse (phase) signal with the ac voltage. In (b) the red line indicates contraction of a positive domain, resulting in an out-of-phase oscillation.
Figure 3.8 Schematic diagram of Asylum Research’s new DART showing a drive phase independent feedback signal. The diagram is from reference 24.
Figure 3.9 Schematic diagrams of EFM and SKPM apparatus for Asylum MFP-30 system (a) and Agilent 5500 system (b). The diagrams are from Asylum and Agilent AFM system manual.
Chapter 4

PHOTOINDUCED Ag DEPOSITION ON PERIODICALLY POLED LITHIUM NIOBATE: WAVELENGTH AND POLARIZATION SCREENING DEPENDENCE

4.1 Introduction

Ferroelectric materials are characterized by a spontaneous, reversible polarization and polar surfaces which exhibit a surface bound charge [1]. The different domains present surfaces with different properties including work function, electron affinity, surface charge and surface potential. A range of technologies have been developed for nanoscale characterization of the electronic properties of ferroelectric domains: the domain polarity has been characterized by piezoresponse force microscopy (PFM) [2]; the surface bound charge and screening have been studied with electrostatic force microscopy (EFM) [3]; the surface potential has been studied with scanning Kelvin probe microscopy (SKPM) [4]; and the polarization dependent electron affinity has been studied by UV-photoelectron emission microscopy (PEEM) [5]. In addition, patterns of nanoscale domains may be prepared using a direct write process with a scanning probe microscope (SPM) and a conductive tip. The pattern is generated by applying an electric potential between the tip and the back of the crystal [6, 7].

The unique properties of ferroelectric surfaces have been used to achieve localized chemical reactions, nanopatterned surface functionalization [8-12], and electrowetting [13, 14]. In particular, localized charge transfer oxidation-reduction chemical reactions on polarity patterned ferroelectric templates have
been used to form patterns of metallic nanostructures [6, 15-17]. Specifically, for lead zirconate titanate (PZT) polycrystalline films and barium titanate crystals (BTO), the Ag deposition occurred predominantly on the positive domain surfaces [15-17]. In contrast, for photo-induced deposition on polarity patterned lithium niobate, the results showed enhanced Ag deposition at the domain boundaries along with deposition on the positive domains [6]. The difference in the effects was attributed to a difference in the polarization charge screening of the different materials. For materials like PZT, the concentration of defects due to oxygen vacancies and other surface states is estimated as $10^{14} \text{cm}^{-2}$ [18]. The high concentration of defect states results in internal screening of the polarization charges, and the induced built-in field modifies the energy bands near the surface and leads to large band bending (Fig. 4.1 (a) and (b)). This implies that the predominant polarization screening mechanism for PZT is internal screening. However, for materials like lithium niobate having a low density of near surface defects ($10^{12} \text{cm}^{-2}$) [5], the band bending and built-in field are weak (Fig. 4.1 (c) and (d)), and the polarization charges are mainly externally screened via the surface absorption of charged molecules [19, 20].

The different screening mechanisms also lead to different electron affinities of the positive and negative domains. For lithium niobate with screening attributed to molecular adsorption, PEEM measurements have suggested an electron affinity of 0.7 eV on the negative domains and 2.3 eV on the positive domains. A recent study has proposed that photo-induced deposition is more efficient if the photon energy results in excitation above the vacuum level [21]. In this case the process
was termed as photoelectric reduction, while for photo excitation below the vacuum level the process was termed photo-reduction.

In this study, the effects of the polarization charge screening mechanism on the photo-induced deposition process are further explored using periodically poled lithium niobate (PPLN) and oxygen implanted PPLN as templates. To establish the dependence of the illumination wavelength on the process, normalized UV illumination with photon energies above and below the ~3.9 eV band gap are employed to generate Ag deposition. The results are explained in terms of the polarization bound charge screening mechanism, the band bending, the near surface electric field distribution and the depth that the carriers are created relative to the band bending region.

To establish the effect of the polarization screening mechanism on the process, PPLN surfaces implanted with different oxygen ion doses were prepared, and the Ag deposition process was repeated. The deposition pattern was compared to that on original PPLN. The hypothesis is that oxygen implantation generates increased defect concentrations and the screening mechanism changes from external (surface) screening to internal (bulk) screening. Consequently the electric field pattern will also be changed, and the experimental results indeed present different responses of the photo-induced deposition processes on the original PPLN and oxygen implanted PPLN.

4.2 Experimental

4.2.1 Material
The 5mm×5mm×0.5mm congruent lithium niobate templates are polished, plane-parallel plates cut normal to the polar axis and periodically patterned with positive and negative domains with 180° domain boundaries (Crystal Technologies). The positive domain is defined as having polarization pointing outwards leaving the domain surface with a positive polarization charge, and the negative domain having inwards polarization and a negative polarization surface charge. A commercial scanning probe microscope (SPM), (Agilent), with a piezoresponse force microscopy (PFM) imaging module has been used in these studies. The modulation voltage was applied through a conductive probe (PPP-EFM, Nanosensors, $k = 2.8$ N/m, 1st order resonance frequency ~70kHz). The PFM measurements were done in ambient environment using an ac modulation $V_{ac} = 2$ V at 10 kHz. Figure 4.2(a) shows a topographic image of the surface of a PPLN sample, where features associated with the domain structure are not evident in the image. The PFM phase image of the same area (Fig. 4.2(b)) displays the periodic structures. The darker zones correspond to the positive domains and the brighter zones are the negative domains.

To explore the role of surface screening versus bulk screening of the polarization bound charge, identical PPLN substrates were implanted with oxygen ions at different doses. Two different PPLN surfaces were implanted with oxygen ions at an energy of ~700keV and with doses of ~2×10^{15}/cm^2 and ~6×10^{14}/cm^2. The implantation dose and location on the sample is a well controlled process. The oxygen ion beam covers ~16mm^2 of the sample surface area which is large compared to the ferroelectric domains and the AFM scan regions. PFM scans
after the implantation indicate that the ferroelectric domains are preserved (Fig. 4.2(c)) and the positive and negative domains are implanted uniformly within the PFM scanning area. Channeling measurements confirmed that the implanted regions were crystalline.

4.2.2 Photo-induced deposition and surface characterization

The PPLN sample was sonicated for 20 min first in acetone and then for 20 min in methanol. After cleaning, the sample was placed in a petri dish, and the surface was covered with a 50μl drop of a 0.001M AgNO₃ solution. The sample was then exposed to UV radiation using a 100W Hg lamp with a collimated condensing lens assembly. The spot size was adjusted to approximately 1cm².

Filters with 254nm, 291nm, 302nm, 314nm or 365nm central band pass were used to select the corresponding emission lines from the light source. The corresponding full width at half maximum of each filter as measured by the manufacturer is 9.98nm, 10.35nm, 11.48nm, 11.11nm, and 11.40nm, respectively. The operational parameters of the UV light source are listed in Table 1. For a given wavelength, the light intensity at the surface of the sample was measured (using a calibrated power meter), and the photon flux (number/s·cm²) was determined from the measured intensity. Different illumination times were used during the deposition process such that the total incident photon exposure on the sample was ~2×10¹⁸ /cm² for all of the above band gap wavelengths. After the UV exposure, the sample was immersed in deionized water for 1 min, blown try with nitrogen, and imaged using intermittent mode AFM in ambient environment.
using a non-conducting probe (PPP-NCH, Nanosensors, \( k = 42 \) N/m, 1\textsuperscript{st} order resonance frequency \( \sim 300\text{kHz} \)). The same photo-induced process was employed for the oxygen implanted surfaces.

4.2.3 Analysis

The Ag nanoparticle size and density were determined from visual analysis of the AFM images. To obtain the particle density, three different regions with area of 400nm\( \times \)400nm were selected in each domain, and the particles were visually counted. Features (particles) that visually appeared much smaller than the average size were excluded. For example, particles with height < 2nm were excluded. To determine the average particle size on the boundary and domain surfaces, 20 isolated particles were visually selected along the boundary nanowire structure and on the negative domain surface while 40 isolated particles are selected on the positive domains. Then a cross section profile across the center of each selected particle is obtained using the AFM software. Particle diameter and height are determined from the cross section profile. The average size (volume) is calculated based on the volume of a section of a sphere using

\[ v = \frac{1}{6} \pi h \left( \frac{3}{4} D^2 + h^2 \right), \]

in which \( D \) presents the diameter and \( h \) is the height. The uncertainty is the root-mean-square deviation of the volume of the 20 or 40 particles. For photo-induced deposition using the shortest wavelengths, coalescence of adjoining particles was observed, and in some cases it was difficult to identify and select isolated particles. This analysis was also limited by the fact that nanoparticles smaller than the tip
diameter are not accurately represented. While we made every effort to minimize
this effect (by using sharp tips) it seems likely that the smaller particles are not
accurately reflected.

The deposition for each wavelength has been repeated several times to
minimize errors and obtain consistent results. For every repeated experiment, the
visual inspection identified the same phenomena, and the quantitative analysis
was consistent. The small variance in the absolute value of silver particle size and
density did not change the interpretation of the experimental results.

4.3 Results

4.3.1 Ag deposition on congruent PPLN surfaces

AFM images of the undoped congruent PPLN surfaces after the photo-
induced deposition process are displayed in Figure 4.3. Noting again, all surfaces
were prepared the same way, and the UV exposure time was calibrated such that
the total photon exposure was the same for each wavelength (with the exception
of the below bandgap 365 nm exposure). The Figure includes a low resolution
image of the positive and negative domains, a higher resolution image near a
domain boundary, and a line scan across the domain boundary that displays the
relative height of the features.

Figure 4.3(a) displays the topography of the undoped congruent PPLN surface
after Ag photo-induced deposition with 254nm light. This is the shortest
wavelength employed in this study, and it is evident that nanowire-like structures
assemble along the boundaries of the positive and negative domains. However,
the higher magnification image (Fig. 4.3(b)) reveals that the ‘nanowires’ are formed from a series of ~100 nm rounded islands, some of which are separated by gaps of ~10nm. The surfaces of the positive and negative domains were also both densely covered by smaller sized nanoparticles (25~50nm).

Fig. 4.3(c-j) displays the results for photo-induced Ag depositions using longer wavelengths of 291nm, 302nm and 314nm. The periodic domain patterns and their boundaries are evident for all of these above band gap wavelengths. Upon analysis of the corresponding 2μm×2μm images, we find that the positive domains exhibit a higher density of Ag nanoparticles than the negative domains, and that larger nanoparticles are densely aligned along the boundaries forming nanowire-like structures.

Figure 4.4 presents a quantitative analysis of the Ag nanoparticle size (volume) and density. The response to the different excitation wavelengths is summarized in the following:

1) Domain boundary structures: for all above band gap excitation, the domain boundaries are decorated with larger Ag clusters which form nanowire-like structures. The nanowire width is ~85nm; the height is ~27nm for 254nm exposure (Fig. 4.3(b)), ~60nm width and ~ 16nm height for 291nm exposure (Fig. 4.3(d)), ~55nm width and ~15nm height for 302nm exposure (Fig. 4.3(f)) and ~15nm width and ~4nm height for 314nm exposure (Fig. 4.3(h)). It is evident that the size of the domain boundary nanoparticles decreases with increasing wavelength.
2) Selectivity on domain surfaces: for the shortest wavelength 254nm exposure, Ag nanoparticles are formed on both positive and negative domains with a similar density. However, for 302nm, 291nm and 314nm exposure, the nanoparticle density on the positive domains is enhanced over that formed on the negative domains. Overall, the relative difference of the particle density on the positive and negative domains increases with increasing wavelength.

3) Nanoparticle size: for all above band gap wavelength exposures, Ag nanoparticles on the domain boundary are larger than nanoparticles on the domain surfaces. The size ratio of boundary nanoparticles over domain surface nanoparticles decreases with increasing wavelength.

4) Below band gap excitation: For 365nm exposure, nanoparticle formation was not detected in the AFM images when the same integrated photon flux was used. However, if a longer exposure was employed, Ag deposition was observed which was predominantly on the positive domain surface. The results are shown in Figure 4.3 (i) and (j). It is evident that the distribution of Ag nanoparticles is very sparse, and there is no evidence of enhanced deposition at the domain boundary. This below band gap deposition may be due to defects and/or weak above band gap illumination due to the band pass function of the filter.

4.3.2 Ag deposition on oxygen implanted PPLN surfaces

AFM images of Ag deposition on the oxygen implanted PPLN surfaces with the lower dose of $\sim6 \times 10^{14}/\text{cm}^2$ are displayed in Figure 4.5(a, b) for 254nm...
exposure and Figure 4.5(c, d) for 314nm exposure. The Ag nanoparticles are evident on both the positive and negative domain surfaces, and there is also evidence of enhanced deposition at the boundary. The boundary nanowire-like structures are suppressed compared to those that form on the un-implanted PPLN surfaces. AFM images of Ag deposition on PPLN implanted with the higher dose of $\sim 2 \times 10^{15}/\text{cm}^2$ are displayed in Figure 4.5(e, f) for 254nm and Figure 4.5(g, h) for 314nm. As displayed in the images, the density and average height of Ag nanoparticles on the negative domains is less than on the positive domains, the combination of these effects results in a $\sim 2$nm increase in the average height on the positive domains. This difference is clearly evident in the lower magnification scans. However, the boundary nanowire-like structures are hardly evident. This implantation process is repeatable and the same experimental results are found under the same implanting energy and dose level. These results are in many ways similar to the results for photo-induced deposition of Ag on PZT, where it has been proposed that internal screening leads to significant band bending and internal fields that drive the photoexcited electrons towards the positive domain surfaces [15-17].

4.4 Discussion

The photo-induced deposition process involves illumination with above bandgap light ($\sim 3.9$ eV or 318nm) to produce electron-hole pairs near the surface. Free electrons can be separated by the presence of an internal field or through diffusion. The electrons can migrate towards (or away from) the surface due to the
electric field or through thermal diffusion to/from the surface. With the 0.001M AgNO₃ solution the flux of Ag ions \((10^{19-20}/s\cdot cm^2)\) to the surface is significantly greater than the photon flux \((10^{15-16}/s\cdot cm^2)\). Consequently, the deposition process is limited by the availability of electrons at the surface. The presence of the nanoparticles indicates that nucleation limits the process, and that growth apparently occurs due to reduction of the Ag on the nucleated particles. The presence of the large nanoparticles at the boundary suggests that the electron distribution in response to the internal electric field determines the growth pattern. Presumably, the free electrons migrate or diffuse towards the surface, collect on nucleated nanoparticles and further growth proceeds through reduction of Ag ions at the nanoparticle surface.

In order to explain the wavelength dependence of the Ag deposition process and the differences of Ag deposition on original PPLN and implanted PPLN, we consider three aspects which are addressed in the following subsections.

4.4.1 Surface charge screening and electric field distribution

Based on the deposition model described above the photo-induced deposition pattern will depend on the electric field distribution in the ferroelectric material that arises from the internal or external screening of the polarization and the domain pattern. Consequently, the density of photo-generated carriers near the surface will differ substantially at different regions of the surface. Moreover, for similar polarization domain patterns, the screening mechanism can lead to significantly different electric field distributions. For doped materials or materials
with a high density of charged defects, internal screening will become important, and the electric field due to the polarization bound charge and charged defects (or dopants) leads to significant band bending. Studies have determined the electric field distribution with the assumption of complete internal screening [19, 22]. The results indicate significant electric fields near the domain surfaces which drive electron migration towards the positive domain surfaces. These studies do not indicate a significantly enhanced electric field along the domain boundary. Thus the deposition on these templates showed uniform coverage predominantly on the positive domain surfaces without evidence of enhanced deposition along the domain boundaries [15-17].

In order to explain the nanowire-like structure along the PPLN domain boundaries, the electric field distribution has also been calculated near the surface of domain boundaries of lithium niobate [6, 19] with the assumption of complete external screening. The results indicated a nonuniform field distribution with a strong $E_z$ component of the electric field in the vicinity of the 180° domain boundaries. Away from the boundary, the field due to the polarization and screening decreases rapidly. It is expected that the photo excited electrons in the vicinity of the boundaries will migrate under the influence of the strong boundary electric field. Consequently, enhanced Ag deposition is observed along the domain boundary and nanowire-like structures are observed. In Figure 4.6, a sequence of images for above band gap 314nm illumination displays the accumulation of Ag nanoparticles on the surface over a time period of 4 mins. It is evident that the formation is most rapid at the boundaries followed by the positive
domains and then the negative domains. Or in other words, more electrons are available at the boundaries than on the domain surfaces during the same irradiation time. Thus the Ag deposition at the boundaries reflects predominantly the effect of the field induced migration, while the deposition on the domain surfaces is due to both diffusion and field induced migration (due to the relatively weak field).

The experiments related to the ion implanted PPLN surfaces were designed to explore the effects due to a change in screening mechanism while preserving the other properties of the materials to the extent possible. The oxygen implantation introduces defects into the PPLN which can contribute to the screening of the polarization bound charge. The presumption is that the defects are within the band gap and can screen both positive and negative polarization charges consequently enhancing band bending in both positive and negative domains. Depending on the implantation level, the surface of the PPLN changes from external screening, low defect density and weak band bending (<0.1eV from XPS measurements) for un-implanted surfaces to enhanced internal screening, high defect density and stronger band bending. The latter case is similar to the expected screening for PZT, and the resulting Ag deposition structures were expected to also be similar. This was indeed confirmed by the Ag deposition results shown in Figure 4.5. The results showed that the boundary deposition was substantially reduced for the lower dose implantation and was essentially completely suppressed in the higher dose implantation. There was more deposition on the positive surfaces indicating the effects of the field induced migration.
4.4.2 Illumination penetration depth

A significant effect related to the wavelength is that the illumination generates carriers at different depths from the surface and that the carrier density near the surface will also depend on the wavelength. Table 4.1 lists the absorption coefficient and depth for the different illumination wavelengths.

As the illumination photon energy decreases to the bandgap, an increasing fraction of electrons are generated relatively deep in the sample, and these electrons will have a lower probability of diffusing or migrating to the surface before recombination or trapping. Consider first the size of the boundary nanoparticles where the size of these particles increases monotonically with increasing illumination photon energy (Figure 4.4(a)). A similar effect is observed for the deposition on the positive and negative domains (figure 4.4(b)). The difference in the deposition on the positive and negative domains is ascribed to the relative effects of field induced migration. It is evident that as the wavelength decreases, the field induced migration becomes relatively less significant compared to diffusion.

For 254nm illumination the diffusion effect is most evident. The photons are strongly absorbed within a depth of ~100nm. The electrons generated in both the positive and negative domains have a high probability of diffusing to the surface, and field induced migration is less significant. Consequently, Ag nanoparticles are formed at a similar density on the positive and negative domain surfaces.

4.4.3 Photo-reduction and photoelectric deposition
As noted in the introduction, recent research on photo-induced deposition on lithium niobate has suggested that photo-electron emission processes could be significant in the process [21, 23]. The effect would be important for the negative domains where the 0.7 eV electron affinity and 3.9 eV band gap would lead to a threshold of 4.6 eV for photo electron emission while on the positive domain the threshold is anticipated at 6.2 eV [5, 22]. All wavelengths employed in our experiment are significantly below 6.2 eV, thus the photo-induced reduction process would not involve photo-electron emission. However, the 4.9 eV photon energy of the 254 nm illumination is above the anticipated photo threshold of 4.6 eV of the negative domains. However, we do not observe a significant difference in the deposition rate on the negative domains for this excitation suggesting that the effect is less significant for these PPLN surfaces as compared to those of references 22 and 23. The most evident difference between the results reported here and those of ref. 22 and 23 is that they employed an illumination source with higher photon energies (cutoff at 200nm) which would enhance the photo electron emission. In addition, if the screening is different between the materials of the two studies, then the photo-threshold would be affected. Band bending and internal screening could also enhance the photo-electric effect or limit its observation.

4.5. Conclusion

We have investigated the wavelength and screening dependences of a liquid-based photo-induced deposition process for the synthesis of Ag nanostructures on a periodically poled lithium niobate template. The observed variation of
deposition rate and domain/boundary location was explained by consideration of the polarization screening mechanism and the resultant electric field distribution, the penetration depth of illumination, and the photo-chemical and photo-electric emission deposition mechanisms. The results establish that shorter wavelength illumination enhances the role of carrier diffusion over field induced migration. It is shown that implantation can be employed to tune the polarization screening between external and internal screening mechanisms which substantially affects the internal electric field distribution. The results also support the photo-induced deposition model where the process is limited by carrier generation and the cation reduction occurs at the surface. This study provides quantitative results and analysis of the physics of polarization screening and the photo-induced Ag nanostructure formation process on ferroelectric materials. The results provide a foundation to employ ferroelectric templates for assembly and patterning of inorganic, organic, biological and integrated structures.
REFERENCES


Table 4.1 UV light exposure parameters.

<table>
<thead>
<tr>
<th>wavelength (nm)</th>
<th>254</th>
<th>291</th>
<th>302</th>
<th>314</th>
<th>365</th>
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<tr>
<td><strong>photon energy (eV)</strong></td>
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<td>4.26</td>
<td>4.11</td>
<td>3.95</td>
<td>3.40</td>
</tr>
<tr>
<td><strong>intensity (mW/cm²)</strong></td>
<td>1.8</td>
<td>5.5</td>
<td>13.4</td>
<td>13.5</td>
<td>39.0</td>
</tr>
<tr>
<td><strong>photon flux (×10¹⁵ /s·cm²)</strong></td>
<td>~2.30</td>
<td>~8.00</td>
<td>~20.36</td>
<td>~21.32</td>
<td>~71.60</td>
</tr>
<tr>
<td><strong>Illumination time (min)</strong></td>
<td>~13</td>
<td>~4</td>
<td>~1.5</td>
<td>~1.5</td>
<td>~60</td>
</tr>
<tr>
<td><strong>absorption coefficient (cm⁻¹)</strong></td>
<td>&gt;10⁴</td>
<td>~3000</td>
<td>~800</td>
<td>~90</td>
<td>&lt;10</td>
</tr>
<tr>
<td><strong>penetration depth (μm)</strong></td>
<td>&lt;1</td>
<td>3.33</td>
<td>12.5</td>
<td>111</td>
<td>&gt;1000</td>
</tr>
</tbody>
</table>
Figure 4.1 Band schematics for negative (a) and positive (b) domains for a material with internal screening (i.e. PZT) and band schematics for negative (c) and positive (d) domains for a material with external screening (i.e. lithium niobate). Internal screening leads to strong band bending due to a high concentration of charged states near the surface. Lithium niobate has a smaller concentration of defect states and exhibits external screening, thus, the band bending that occurs at the surface is smaller and depletion width is longer than for PZT.
Figure 4.2 AFM topography image of as-received PPLN (a), PFM phase image of the same region (b), and PFM phase image of the oxygen implanted PPLN (c). The PPLN shows a featureless image in AFM topography, however, the periodic structure of the positive and negative domains are evident in the PFM phase image.
Figure 4.3 AFM topographic images of a PPLN surface after Ag photo-induced deposition using 254nm (a, b), 291nm (c, d), 302nm (e, f), 314nm (g, h) and 365nm (i, j) illumination. (a), (c), (e), (g) and (i) are 40µm×40µm scans and (b), (d), (f), (h) and (j) are 2µm×2µm higher magnification images (insets: heights profiles of the higher magnification images).
Figure 4.4 Average Ag nanoparticle size (volume) (a, b) and density (c) vs. wavelength. The lines are from point to point and are not fits to the data.
Figure 4.5 AFM topographic images of the oxygen ion implanted PPLN surfaces after Ag deposition: (a ~ d) low dose implant (~6×10^{14}/cm^2) and (e ~ h) higher dose implant (~2×10^{15}/cm^2). For each dose level, photo induced deposition with two UV illumination wavelengths is used: 254nm (a, b, e & f) and 314nm (c, d, g & h). The scan sizes are 25µm×25µm for the left images and 2µm×2µm for the right higher magnification images.
Figure 4.6 AFM images after Ag photo induced deposition on PPLN using 314nm illumination for 60 sec (left), 100 sec(middle) and 240 sec (right). The scan size is 2µm×2µm for all three images.
Chapter 5

PHOTOINDUCED Ag DEPOSITION ON PERIODICALLY POLED LITHIUM NIOBATE: CONCENTRATION AND INTENSITY DEPENDENCE

5.1 Introduction

The use of ferroelectric materials as templates for ‘growth’ of patterns of nanoparticles and nanowires has gained interest due to its potential application for bio-chemical sensors or reconfigurable electronics [1, 2, 3]. Moreover, as researchers have come to better understand the physics behind this process, it has become evident that aspects of this research could influence other technologies.

Essential to this process is the use of ferroelectric crystals, which exhibit spontaneous and reversible polarization. Consequently, these materials can be patterned with an alternating, external, electric field to create a periodically poled substrate and thus obtain a template with a pattern of regions with alternating surface charge. These areas of surface charge are referred to as domains, whereby the negatively- and positively-charged domains present different properties such as work function, electron affinity, and surface potential [4]. Moreover, to obtain an energetically stable state, the surface charges undergo external and/or internal screening. Internal screening is distinguished by the formation of a space-charge layer near the surface, while external screening is identified by the absorption of charged molecules, or surface states due to the surface layer. These processes can modify the electron affinity as well as band bending [5]. For example, a positively polarized surface is screened by free electrons, negative ionized defects, negatively charged surface states and/or the absorption of negative ions from the
atmosphere. (The same is true for a negatively polarized surface except the screening is by holes or positively charged defects, surface states or molecules.) This intrinsic screening gives rise to an internal electric field and thus band bending near the surface region [7]. These unique properties of ferroelectric surfaces have been utilized in several processes including localized chemical reactions, nanopatterned surface functionalization [7~11], and electrowetting [12, 13].

These characteristics are also important to the photo-induced formation of metallic nanostructures on the surface of ferroelectrics, as they allow the ferroelectric to be used as a template [14, 15, 16]. The photo-induced deposition process on these materials typically results in preferential deposition along the grain boundary domain wall and dispersed deposition on the domain surfaces, where the positive domains exhibit a higher density of metallic particles than the negative. In our research, congruent periodically poled lithium niobate (PPLN) is used as the deposition template. The PPLN template has a band gap of ~3.9 eV [4]. When the ferroelectric sample is immersed in a chemical solution and exposed to light with photon energy higher than the ferroelectric band gap (>3.9eV or <318nm), the photon absorption process produces electron-hole pairs near the surface. The electrons or holes potentially migrate or diffuse to the surface where reduction of metallic cations from the solution can occur on the surface of the ferroelectric. Then the reduced atoms nucleate and the later growth occurs due to reduction of the Ag on the nucleated particles to form larger clusters and particles [17].
The subsequent deposition pattern of these nanostructures depends on the following four factors at room temperature: photon energy, surface polarization charge screening, flux of photo generated electrons, and flux of metallic cations, \( J_b \). Our previous work investigated how the photo-induced deposition process depended on the photon energy and surface polarization charge screening [18]. The results showed enhanced deposition along the domain boundary and preferential deposition on the positive domain surface. The overall deposition rates decreased with increasing wavelength (decreasing photon energy). The enhanced boundary nanowire formation was suppressed on surfaces that had been modified by oxygen ion implantation. The preferential deposition along the boundary was attributed to the external screening of the surface polarization charge and the resulting strong electric field in the direction of the polar axis near the domain walls. It was therefore expected that migration of the photo-generated electrons would be accelerated by the strong electric field and thus enhanced deposition occurs along the boundary. Conversely, the suppression of boundary nanowire formation for oxygen implanted surfaces was attributed to the transition from surface external to bulk internal screening of the polarization charge.

In this study, PPLN surfaces were illuminated with 254nm light (photon energy 4.9eV), and the effects of the intensity dependent electrons flux, \( J_e \) and the flux of metallic cations, \( J_b \) were investigated. The electrons flux reaching the template surface is mainly determined by the UV-light intensity and the corresponding photon flux. The metallic cation flux depends on the concentration and mass of the solute. For Ag deposition, the chemical solution concentration
determines the metallic cation flux. By varying the concentration of the solution and intensity of the light, we are able to observe the relative effects of the \( \text{Ag}^+ \) cation flux and the electron flux. It is hypothesized that the relationship between these two fluxes can account for the variations in the relative deposition on the domain boundaries and surfaces of the ferroelectric template. Through varying the relative values of these two fluxes, different deposition patterns of boundary enhanced nanowire formation or domain surface Ag nanoparticle coverage on \(+c\) and \(-c\) surfaces are expected even without changing the external screening to bulk internal screening. The Stern layer at the ferroelectric surface and the Ag nanoparticle nucleation and growth mechanism are also considered in explaining of the observed results.

5.2 Experiment

This study employs congruent, single crystal lithium niobate as the ferroelectric template. At room temperature, lithium niobate is characterized by hexagonal symmetry with polarization along the \( c \) axis. As a result, there are only two possible domain orientations with 180° domain boundaries. In this experiment, 6mm x 4mm x 0.5 mm plane-parallel plates cut normal to the polar axis were used. The PPLN is periodically patterned with ~15\( \mu \)m positive and negative striped domains divided by 180° domain boundaries. The positive or negative domains (+c or -c) have a positive or negative surface charge of (+ or -) 71\( \mu \)c/cm\(^2\) (4.44\( \times \)10\(^{14}\)e/cm\(^2\)) [19]. PPLN displays a low density of defects near the
surface, which results in predominantly external screening and nearly flat bands near the surface [5].

Immediately prior to the photo-induced deposition, the lithium niobate template was sonicated in acetone and methanol for approximately 20 minutes each. After the cleaning process, the sample was immersed into an aqueous solution of AgNO₃. The thickness of aqueous solution above lithium niobate template is ~2mm. The solution concentrations were varied from ~10⁻³ to ~10⁻⁷ M. The surfaces were illuminated by UV light with a high intensity of 1400 μW/cm² and a low intensity of 25 μW/cm² in order to investigate the effect of intensity on the deposition pattern. The light source is a 100 W Hg lamp with a 254 nm band pass filter. The different intensity is achieved by tuning the focus of the lamp or by changing the distance between the lithium niobate template and the lamp. The full width at half maximum of the filter as measured by the manufacturer is ~10 nm.

After numerous preliminary photo induced deposition experiments we selected four different combinations of solution concentration and UV intensity to be presented here which are listed in Table 1. For each case, the corresponding metallic cation flux and photon flux are estimated. The flux of electrons reaching the template surface is mainly determined by the UV-light intensity and the corresponding photon flux. The photon flux is given by

\[ J_e = \frac{w \cdot \lambda}{h \cdot c} \quad (5.1) \]

where \( w \) is the UV intensity, \( \lambda \) is the wavelength, \( h \) is Planck’s constant and \( c \) is
the speed of light. The chemical flux density of a solute is given by

\[ J_b = v_o C_b \]  \hspace{1cm} (5.2)

where the average velocity of a particle in solution toward or near a surface is denoted by \( v_o \), and the concentration of the particles is given by \( C_b \). Classical kinetic theory suggests that \( v_o \) can be approximated as

\[ v_o = \sqrt{\frac{kT}{2\pi m}} \]  \hspace{1cm} (5.3)

where \( k \) is Boltzmann constant, \( T \) is temperature in Kelvin, and \( m \) is the mass of the particle in the solution. This suggests that the chemical flux of metallic cations is proportional to the concentration and inverse square root of the solute mass [20].

After UV exposure, the sample was immersed in deionized water for 1 min, blown dry with nitrogen, and imaged using intermittent mode AFM in ambient environment using a non-conducting probe (PPP-NCH, Nanosensors, \( k = 42 \) N/m, 1st order resonance frequency \( \sim 300\)kHz). The Ag nanoparticle size was determined from visual analysis of the AFM images. Features (particles) that visually appeared much smaller than the average size were excluded. To determine the average particle size on the boundary and domain surfaces, 20 isolated particles were visually selected along the boundary nanowire structure while 40 isolated particles are selected on the domains. The same statistical calculation described in chapter 4 applied here to determine the average particle size on domain boundaries and domain surfaces, respectively.

5.3 Results
The PPLN was immersed in solutions of various concentrations of AgNO₃ and illuminated with two different intensities as summarized in Table 5.1. For case 1, the Ag⁺ flux, \( J_b \) was \( \sim 10^{21}/\text{cm}^2\cdot\text{sec} \) and the photon flux, \( J_e \) was \( \sim 10^{15}/\text{cm}^2\cdot\text{sec} \). Thus, the Ag⁺ flux, \( J_b \) is six orders of magnitude greater than the photon flux, \( J_e \). The resulting deposition pattern is displayed in Figure 5.1(a, b). The images show preferential deposition along the domain boundary and a distribution of smaller particles on the positive and the negative domain surfaces. The Ag boundary nanoparticle size is \( \sim 20 \) times larger than that on the domain surfaces.

Next, the same growth was repeated but with a lower (~10⁻⁵M) concentration of AgNO₃ under the same high illumination intensity of 1400 μW/cm². In this case, the Ag⁺ flux, \( J_b \), is only four orders of magnitude greater than the photon flux, \( J_e \). The deposition results are shown in Figure 5.1(c, d). The particle density is similar to the previous results; however, the Ag nanoparticle size along the boundary is decreased to \( \sim 10 \) times larger than the Ag particles on the domain surfaces demonstrating that the domain boundary growth is reduced in comparison to the high concentration deposition.

The photo induced deposition was repeated using a reduced concentration of 10⁻⁵M, while also reducing the UV intensity to \( \sim 25 \) μW/cm². This deposition condition restores the ratio of the Ag⁺ to photon flux, \( J_b/J_e \), back to 10⁶ as employed in the first case. Figure 5.1(e, f) shows that the deposition pattern with preferential deposition along the boundary is restored, and the size ratio of the Ag particles on the boundary in comparison to that on the domain increases to \( \sim 21 \).
Finally, the experiment was repeated using the low UV intensity, 25μW/cm² and further decreasing the solution concentration to 10⁻⁷M. The ratio between the Ag⁺ to photon flux, \( J_b / J_e \), is thus decreased to 10⁴, which is the same as in the second case. As shown in Figure 5.1 (g, h), the boundary growth is again suppressed and a uniform pattern is observed on the surfaces. Here the size ratio of boundary to surface particles is decreased to ~5.

5.4 Discussion

The electric field distribution has been calculated near the surface of domain boundaries on lithium niobate with the assumption of complete external screening [21]. The results indicated a non-uniform distribution with a strong \( E_z \) electric field in the vicinity of the 180° domain boundaries. Away from the boundary, the field due to the polarization and screening decreases rapidly. Figure 5.2(a) shows \( E_z \), the normal component of electric field, at a distance of 50nm under the surface. The value of normal component amplitude at the boundary varies with distance below the lithium niobate surface, and Figure 5.2(b) plots this variation. The calculation indicates that the boundary normal electric field decreases with distance into the bulk while the domain surface normal electric field is \(~0.17\times10^4\) V/m and varies little with distance into the bulk. The boundary normal component electric field is roughly 10-30 times larger than that at the domain surface as shown in Figure 5.2(b). It is estimated that the photo-excited electron-hole pairs have a recombination time of the orders of 100ps [22]. The mobility of electrons of congruent lithium niobate is \(~0.8\text{m}^2/\text{V·sec}\) [23]. Photo-generated electrons
migrate to the surface under the influence of the electric field distribution profile. Within a 100ps recombination time, it is straightforward to show that electrons generated around the domain boundary region would migrate to the surface from a depth of ~40nm while the on the domains, electron generated using the same analysis indicates that electrons generated within <2nm would migrate to the surface. Thus although the photon flux is uniform across the surface, the photo generated electrons at the surface are not uniformly distributed. It follows that the distribution of electrons will be the same as the electric field.

In order to simplify our analysis, we assume that one Ag\(^0\) atom is generated when one electron combines with one Ag\(^+\) cation, and that the process is 100% efficient when both an electron and Ag\(^+\) cation are present at the surface.

For case 1 and case 3, the presence of the enhanced nanowire boundary formation suggests that the electron distribution in response to the internal electric field determines the Ag deposition pattern. The domain boundary particles are ~20 times larger than the particle on the domain surface, which is similar to the ratio of the electric field at the domain boundary and surface. As shown in table 5.1, for case 1 and 3, the Ag\(^+\) flux, \(J_b\), is projected to be six orders greater than the photon flux, \(J_e\), which means for each electron migrating to the surface, there is one Ag\(^+\) ion available to combine with and produce a Ag\(^0\) atom. The consequence is that the resulting Ag\(^0\) atom distribution, is the same as the electron distribution as determined by the electric field distribution. Since there are more Ag\(^+\) ions and fewer electrons, the efficiency of Ag\(^+\) ion reduction is reduced under the
conditions for case 1 and case 3. In fact, the efficiency of Ag$^+$ ion reduction essentially determines the pattern on the surface.

Although the Ag$^0$ atom deposition reflects the electric field distribution for case 1 and 3, when the ratio between the Ag$^+$ ion flux and photon flux, $J_b / J_e$, is decreased to $10^4$ as for cases 2 and 4, the formation of boundary nanowire-like structures is suppressed (Figure 5.1c, d) and a more uniform pattern of nano-islands is observed (Figure 5.1g, h). This transition of patterns suggests that the Ag$^0$ atom deposition is not only determined by the electron distribution. The other component in the Ag$^+ + e^-\rightarrow$Ag$^0$ reaction is the Ag$^+$ flux. Here we presume that the Ag$^+$ ions flux is the same for the positive domains, negative domain, and domain boundaries. Although the calculated Ag$^+$ ion flux is 4 orders of magnitude greater than the photon flux for cases 2 and 4, later we will suggest factors that could reduce the Ag$^+$ ion flux impinging the surface to be less than the electron flux. Then for each Ag$^+$ ion impinging on the surface, there always a supply of electrons available to produce a Ag$^0$ atom. Conversely, for each electron migrating to the surface, there may not be one Ag$^+$ ion available. Thus, in this situation, the Ag$^0$ atom distribution is determined by the Ag$^+$ ion flux which is uniform over the lithium niobate surface.

It is evident that there is a delicate balance that determines the deposition pattern. Moreover, due to the low solution concentration and/or low UV-light intensity for cases 3 and 4, it is necessary to lengthen the time of the deposition process as indicated in Table 5.1.

Two possibilities are considered for reducing the effective Ag$^+$ flux. The first
is the Ag particle growth mechanism. The presence of the nanoparticles in the AFM image indicates that nucleation limits the process. Photo-excited electrons from regions around the nucleation site are collected at the nucleation sites. The particles grow due to reduction of the Ag which deposits on the nucleated particles. The flux of Ag$^+$ ions impinging onto available nucleation sites is less than the total flux impinging surface as calculated from equation 5.2. The second effect is the Stern layer at the ferroelectric surface. Due to the surface charge and surface potential of ferroelectric materials, a Stern layer is formed at the surface which contributes to the external screening [24]. In an aqueous AgNO$_3$ solution, the layer will consist of NO$_3$ ions and polarized H$_2$O molecules. In order for Ag$^+$ cations outside the Stern layer to reach the lithium niobate surface, there must be a disturbance in the Stern layer such that the screening molecules will be desorbed from the surface. When electrons are generated by UV photons and migrate to the surface, the surface potential is changed and the Stern layer is disturbed, and thus the NO$_3$ ions and polarized H$_2$O molecules disassociate from the surface enabling transport of the Ag$^+$ ions to the surface which allows reduction by the available electrons. This process of disturbing the Stern layer to enable Ag$^+$ ions transport effectively decreases the Ag$^+$ flux at the surface. As a result, the actual flux of the Ag ions is much smaller than the calculated value. Our experimental results suggest that the combined effect of the nucleation limited growth mechanism and the Stern layer will reduce the effective Ag$^+$ flux by a factor of $\sim 10^4$ from the calculated value.

From the above analysis of the role of the Stern layer, it is also evident that
regions of enhanced electrons accumulation will lead to a greater disturbance of the Stern layer and thus more efficient Ag deposition. In comparing the deposition parameters of case 2 and case 4, although they have the same Ag\(^+\) ion flux and vs. photon flux ratio of \(\sim 10^4\), the nanowire structures are still evident in case 2 but are not distinct in case 4. We suggest that this difference stems from the effect of the enhanced photon flux which leads to enhanced electron accumulation at the surface. For case 2, the photon flux is 100 times larger than that for case 4, and the greater density of photo-excited electrons at the surface more effectively disturbs the Stern layer. Consequently, due to Stern layer the Ag\(^+\) ion flux is reduced more effectively in case 4. The result is that in case 2, the nanowire structures are still evident.

5.5 Conclusion

We have investigated the solution concentration and UV-light intensity dependences of a liquid-based photo-induced deposition process for the synthesis of Ag nanostructures on a periodically poled lithium niobate template. The observed variation of boundary-enhanced or boundary-depressed deposition is explained by consideration of the electric field distribution and the ratio between the Ag\(^+\) ion and photon flux. The results establish that the ratio can be controlled by tuning the solution concentration and UV-light intensity to generate enhanced nanowire-like structures along the domain boundary or a more uniform deposition pattern over the positive and negative domain surfaces. This can be better understood by considering the Ag\(^+\)/photon flux ratio, where the nucleation
limited growth mechanism and the Stern layer on the lithium niobate surface are responsible for decreasing the effective Ag+ ion flux near the surface. These results also support the photo-induced deposition model where the process is limited by carrier generation, and the cation reduction occurs at the surface. These findings will hopefully provide a foundation to employ ferroelectric templates for assembly and patterning of inorganic, organic, biological, and integrated structures.
REFERENCES


Table 5.1 Solution, UV light, and Ag particle size parameters

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<th>4</th>
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<td>$10^{-5}$</td>
<td>$10^{-5}$</td>
<td>$10^{-7}$</td>
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<td>$10^{19}$</td>
<td>$10^{19}$</td>
<td>$10^{17}$</td>
</tr>
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<td>UV intensity ($\mu$W/cm$^2$)</td>
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<td>1400</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>Photon flux $J_e$ (1/cm$^2$·sec)</td>
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<td>$10^{15}$</td>
<td>$10^{13}$</td>
<td>$10^{13}$</td>
</tr>
<tr>
<td>Flux Ratio ($J_b/J_e$)</td>
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<td>$10^4$</td>
<td>$10^6$</td>
<td>$10^4$</td>
</tr>
<tr>
<td>Deposition time (minutes)</td>
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<td>8</td>
<td>100</td>
<td>160</td>
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<td>Size Ratio (boundary /domain)</td>
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<td>9.0</td>
<td>21.2</td>
<td>4.5</td>
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</table>
Figure 5.1 AFM images of Ag deposition patterns on PPLN using 254nm UV light for the following solution concentrations and UV-light intensities: (a, b) $10^{-3}$M and 1400μW/cm²; (c, d) $10^{-5}$M and 1400μW/cm²; (e, f) $10^{-5}$M and 25μW/cm²; and (h, g) $10^{-7}$M and 25μW/cm².
Figure 5.2 (a) Theoretical simulation of normal component of electric field $E_z$ at a distance 50nm below LiNbO$_3$ surface. (b) Domain boundary electric field $E_z$ (left scale) and the ratio between $E_z$ at domain boundary and $E_z$ at the center of domain surface (right scale) vs. distance below LiNbO$_3$ surface.
Chapter 6

CONDUCTANCE OF PE-ALD DEPOSITED ZnO THIN FILM ON
POSITIVELY AND NEGATIVELY POLED LITHIUM NIOBATE

6.1 Introduction

Ferroelectric materials have been considered for dielectric layers in switchable, non-volatile field-effect transistors due to their switchable polarizations [1~5]. Ferroelectric field effect transistor (Fe-FET) structures have been fabricated and tested with a number of ferroelectric layers including bismuth tantalate SrBi$_2$Ta$_2$O$_9$ [6, 7, 8], lead zirconate titanate (PZT) [3, 9] [10] and ferroelectric polymers such as Polyvinylidene Fluoride (PVDF) [11]. Among the different ferroelectric materials, LiNbO$_3$ has a large spontaneous polarization and low defects density, which make it an ideal substrate for epitaxial thin film growth. However, LiNbO$_3$ as a dielectric layer in Fe-FET has attracted less attention may due to the high field required for polarization switching, the external screening of the polarization surface charge and the relatively smaller dielectric constant. In this chapter, the interface properties of semiconducting zinc oxide deposited on LiNbO$_3$ is investigated. Here ZnO can be considered as the semiconductor channel layer in a Fe-FET device [12, 13]. As deposited ZnO is typically a n-type semiconductor with a wide band gap (3.37eV) [14]. The reason for the n-type property is still under investigation, but researchers have attributed the n-type character to defects such as oxygen vacancies, zinc interstitials and hydrogen shallow donors [14].
In this chapter, the growth and properties of ZnO thin films on single crystal LiNbO$_3$ substrates are investigated. Specifically, ZnO thin films are grown on positive and negative domain surfaces of lithium niobate (LiNbO$_3$, LN) substrates by plasma enhanced atomic layer deposition (PE-ALD). After growth, ZnO thin films are characterized by XPS, XRD and RBS in order to obtain the chemical components, crystal orientation and film thickness. The electrical properties are determined from temperature dependent I-V curves of the grown ZnO thin films on different domains of LN. The results display different temperature dependent conductance for films on the different domains. Analysis of experimental results gives us a better understanding of how lithium niobate polarization charge screening affects the interface properties and electrical properties.

6.2 Experimental Details

Positive and negative polarity, congruent lithium niobate (LiNbO$_3$) substrates were cleaned with acetone and methanol and loaded into the ALD chamber. Prior to growth the substrates were annealed at the growth temperature of 175°C for 30min. The base pressure of the ALD chamber is $\sim$7×10$^{-8}$ Torr. Dimethylzinc Zn(CH$_3$)$_3$ was used as the zinc precursor and a remote oxygen plasma was employed for the oxidation steps. The dimethylzinc bubbler was cooled to -17.2°C and delivered to the growth chamber with Ar carrier gas (flow rate 40sccm). The pulse time for the dimethylzinc step was 0.12, and the pressure in the chamber reached $\sim$100 mTorr. Dimethylzinc molecules which did not attach on the surface were then purged to turbo pump by N$_2$ gas. Dimethylzinc
molecules remaining on the sample surface were oxidized by the following oxygen plasma step to form the ZnO film. The oxygen plasma was generated in a quartz tube positioned about 25 cm above the sample surface. The plasma was excited 200 W of RF power to a copper coil around the outside of the quartz tube. The O plasma step was for 8 seconds per growth cycle with a 35 sccm O\textsuperscript{2} flow rate, and a chamber pressure reached 100 mTorr when the oxygen plasma is generated. The ZnO films were grown with 75 ALD cycles.

After ZnO ALD growth, XPS, XRD and RBS data was collected for characterizing the film components, crystal structure and thickness, respectively. Then ~20 nm Au electrode was sputtered on ZnO surface with a shadow mask having 1 mm diameter round holes and 2 mm distance between holes. The schematic drawing after the Au electrode deposition is shown in Figure 6.1. Atomic Force Microscopy (AFM) permits imaging of the ZnO surface topography deposited on the positive and negative cut LiNbO\textsubscript{3} surfaces. The AFM was operated in intermittent mode using a non-conducting probe (PPP-NCH, Nanosensors, k=42 N/m, 1st order resonance frequency ~300 kHz). Current vs. voltage curve was measured between Au electrodes using Keithley 237 probe station on the positive and negative cut sample at room temperature, 70°C and 125°C, respectively.

6.3 Experimental results

The AFM topography images of the ~40 nm films on positive and negative domains are shown in Figure 6.2 (a, b), respectively. The RMS roughness is
~0.9nm on both the positive and negative domains indicating smooth surfaces.

Figure 6.3 presents the XPS data for the Zn\textsuperscript{2+} and O\textsubscript{2-} related core levels. The Zn 2p\textsubscript{3/2} and 2p\textsubscript{1/2}, peaks with binding energies of 1021.7eV and 1044.9eV are attributed to the ZnO deposited on the molybdenum sample holder plate. The peaks at 1026.4eV (2p\textsubscript{3/2}) and 1049.6eV (2p\textsubscript{1/2}) are attributed to ZnO deposited on the LiNbO\textsubscript{3} surface. The 4.7eV binding energy difference between the ZnO on Molybdenum plate and ZnO on LiNbO\textsubscript{3} surface is attributed largely to charging effect since LiNbO\textsubscript{3} is an insulator with a room temperature dark conductivity $<10^{-18}\Omega^{-1}\text{cm}^{-1}$ [15]. Figure 6.3 (b) presents the XPS data for the O 1s core level peak. The data is fit with a Gaussian peak shape. The peaks at 530.7eV and 532.5eV are attributed to ZnO film deposited on the molybdenum sample holder plate, and the peaks at 535.1eV and 536.9eV are attributed to ZnO deposited on the LiNbO\textsubscript{3} surface. The 4.6eV difference is again largely attributed to charging effects on the LiNbO\textsubscript{3}. The lower binding energy components at 530.7eV and 535.1eV are attributed to oxygen bonded to zinc [16, 17]. The components at higher binding energy, 532.5eV and 536.9eV, are usually attributed to the O-H groups on the surface of the ZnO films [18, 19, 20].

Thicker films deposited with 200 PE-ALD cycles were used for XRD measurements. Wurtzite ZnO has a hexagonal structure with lattice constants $a = 0.325$ nm and $c = 0.521$ nm while the LiNbO\textsubscript{3} hexagonal unit cell has lattice constants $a = 0.515$ nm and $c = 1.386$. Figure 6.4 displays the XRD data of ZnO films on the positive and negative lithium niobate domains, and the similar XRD spectra, indicates that the crystal structure is not domain orientation dependent.
The strong peak at 34.44 degrees indicates the dominant (002) orientation of the PE-ALD ZnO growth. No other ZnO related peaks were detected. The peak at 38.1 degrees is from the Au electrode while the two weaker peaks at 38.9 and 39 degrees are from the lithium niobate substrate. Previous work has shown that PE-ALD ZnO films grown higher temperatures (~200°C) were polycrystalline wurtzite structure with dominant (002) orientation while films grown at lower temperature (<150°C) exhibited small grains without a preferred orientation [21]. The single peak (002) indicates the strong texture c-axis of our ZnO films.

A 75 cycle ZnO film was used for RBS/channeling measurements to determine the thickness of the film. The result shown in Figure 6.5 indicates a coverage $1.70 \times 10^{17}$ Zn atoms/cm$^2$. Based on the known density of ZnO, the film thickness is calculated to be $\sim 36\pm 5$nm.

I-V curve measurements of the $\sim 36$nm ZnO films on positive and negative domains are shown in Figure 6.6. Here, $V_{ds}$ is the voltage bias between two adjacent Au electrodes. On the positive domain surface, the ZnO conductance is $2.780 \times 10^{-7}$A/V at room temperature but decreases to $1.621 \times 10^{-7}$A/V at 70°C and $0.337 \times 10^{-7}$A/V at 125°C. While on the negative domain surface, ZnO conductance increases from $0.432 \times 10^{-8}$A/V at room temperature to $1.435 \times 10^{-8}$A/V at 70°C and $2.522 \times 10^{-8}$A/V at 125°C.

6.4 Discussion

LiNbO$_3$ is a ferroelectric crystal which belongs to the class of pyroelectric solids. A pyroelectric solid exhibits a linear change in spontaneous polarization as
a function of temperature which can be written as $\Delta P_s = p_3 \Delta T$ [22] where $p_3$ is the pyroelectric tensor. For LiNbO$_3$ crystal, the only non-zero component is $p_3 = -6.8 \times 10^{-3} \, \mu\text{C/K}\cdot\text{cm}^2$ [23]. The negative value indicates that heating the crystal will results in a decrease of the spontaneous polarization. The spontaneous polarization at room temperature is $P_s = 70.0 \pm 3 \, \mu\text{C/cm}^2$ ($P_s = \pm 5e/4$ per surface unit cell). At $70^\circ\text{C}$ and $125^\circ\text{C}$, the spontaneous polarization decreases to $\sim 69.5 \, \mu\text{C/cm}^2$ and $\sim 69.2 \, \mu\text{C/cm}^2$, respectively. To obtain a stable surface it is necessary to screen the polarization surface charge. As noted in chapter 2, we apply the screening model proposed by the authors of reference [24] to analyze our experimental observations. The authors of [24] conclude that the positive surface is compensated by an extra Li atom and the negative surface is compensated by an O-Li pair. This reduces the uncompensated charge to $\pm e/4$ per unit cell, which is passivated by mobile carriers or by a submonolayer coverage of adsorbed ions and molecules. A rough calculation shows that this is $\sim 14 \mu\text{C/cm}^2$ at room temperature, $\sim 13.5 \mu\text{C/cm}^2$ at $70^\circ\text{C}$ and $\sim 13.2 \mu\text{C/cm}^2$ at $125^\circ\text{C}$, respectively. Then the remaining unscreened charge is listed in table 5.2.

In order to simplify the model, the screening from external molecules and ions is assumed to be completely removed by the oxygen plasma or by annealing at the PE-ALD growth temperature of 175°. Then the $\pm e/4$/unit cell polarization charge is assumed to be screened by the charges originating from interface defects and traps or free carriers accumulated at the ZnO/LN interface. In order to obtain an estimate of the conductance at different temperature and on different domain

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surfaces, we simply assume the screening arises from accumulation or depletion of free carriers from ZnO bulk to ZnO/LN interface.

On the positive domains, the unscreened positive polarization charge will generate a strong surface electric field. When the ZnO film is deposited on the LN surface, the unscreened polarization charge and surface electric field will generate strong downward band bending in the ZnO film (Figure 6.7 (a)). The band bending potential change, \( \phi_s \), may be described using

\[
\phi_s = \frac{qN_D}{2\varepsilon_o\varepsilon_{ZnO}}w^2
\]  

(6.1)

where \( q \) is the electron charge = \( 1.6 \times 10^{-19} \) coulomb, \( N_D \) is the doping level and is estimated to be \( \sim 10^{18}/\text{cm}^3 \) [26, 27], \( \varepsilon_o \) is the vacuum permittivity, \( \varepsilon_{ZnO} \) is the ZnO relative permittivity \( (\varepsilon_{ZnO} = 8.12 [28]) \), and \( w \) is the depletion width. Through a straight forward calculation, the depletion width can be represented as

\[
w = \frac{\sigma \cdot \varepsilon_{ZnO}}{\left(\varepsilon_{ZnO} + \varepsilon_{LNO}\right)qN_D}
\]  

(6.2)

where \( \sigma \) is the unscreened charge density, \( \varepsilon_{LNO} \) is the LiNbO\(_3\) substrate relative permittivity and \( (\varepsilon_{LNO} = 29) \). By substituting equation (6.2) into equation (6.1), the band bending is represented by

\[
\phi_s = \frac{\sigma^2 \cdot \varepsilon_{ZnO}}{2\varepsilon_o\left(\varepsilon_{ZnO} + \varepsilon_{LNO}\right)^2qN_D}
\]  

(6.3)

Using this expression the temperature dependence of the values of the downward band bending is estimated in table 6.2. These values are much larger than the real values at the interface, since in our analysis the interface charges
originating from interface defects, traps and dangling bonds are not considered. These charges will also screen the polarization charges and reduce the band bending in the film [29]. The degree of interface charge screening from these contributions is not readily determined and thus this effect is excluded in our analysis of the experimental results.

The downward band bending will lead to accumulation of free electrons at the ZnO/LN interface and the formation of a conductive channel. The free carrier concentration at the interface depends on the band bending and can be described as follows

$$n_x = n_i e^{\frac{q(\phi_s - \phi_{Fn})}{k_B T}}$$  \hspace{1cm} (6.4)

where \( n_i \) is the intrinsic free carrier density, \( \phi_s \) is the band bending at the interface, \( \phi_{Fn} \) is the difference between the Fermi level and the mid-band-gap level, \( k_B \) is Boltzmann’s constant and \( T \) is the temperature. According to prior measurements of similar films, the Fermi level of ALD deposited ZnO film is ~0.05eV below the conduction band [14]. The band gap of ZnO film is ~3.37eV, thus \( \phi_{Fn} \) is 1.64eV. The intrinsic free carrier concentration \( n_i \) is not known since undoped ZnO films are typically n-type as discussed in the introduction. At the same time, the actual band bending is not known, either. Consequently, the value of free carrier concentration accumulated at the interface is unknown. However, we can see from equation 6.4 that larger band bending will induce higher free carrier concentration. The higher the free electron concentration, the larger the
conductance is expected. Thus the conductance of the ZnO film deposited on positive domains of LiNbO3 decreases with increasing temperature.

For the ZnO film grown on the negative LiNbO3 domain, the unscreened polarization charge is negative, and the electric field is directed toward the surface. When the ZnO film is deposited on the negative domain surface, the polarization charge will induce upward band bending within the ZnO film at the interface (Figure 6.7(b)). The upward band bending causes a depletion of electrons in the ZnO and thus decreases the conductivity compared to that of ZnO grown on the positive domains. When the temperature increases, the polarization charge decreases resulting in decreased upward band bending at the interface. The reduced upward band bending leads to an enhanced concentration of free electrons, and for the ZnO film deposited on negative domains, the observed conductance increases with increasing temperature.

At room temperature, the ratio of conductance between positive domain and negative domain is only 64 while this ratio becomes smaller at elevated temperature (Table 6.1). This is due to the naturally high carrier concentration of ZnO films grown by PE-ALD. ZnO films grown by PE-ALD exhibit generally a high carrier concentration (~10^{18} \text{cm}^{-3}) [15]. High carrier concentrations in the channel layer usually induce an undesirable drain-to-source current in the absence of applied gate voltage. Thus the conductance on negative domain is too large in our experiment. For making a Fe-FET device with LiNbO3 as the dielectric layer, higher on/off ration on positive and negative domain is desired. Further
improvement might comes from a optimization of PE-ALD growth condition like temperature or using buffer layer between ZnO film and LiNbO3 substrate.

6.5 Conclusions

ZnO films were grown on positive and negative domain of ferroelectric LiNbO3 substrates at 175°C using oxygen plasma ALD. The XPS results confirmed the deposition of ZnO film and also showed O-H groups on the surface of the deposited film. The roughness is similar on both positive and negative domain surfaces as given by AFM images. The I-V measurements of ZnO films grown on positive and negative domains gave substantially different conductance values at room temperature where the ZnO film conductance on positive domains is almost 2 orders of magnitude greater than that on the negative domain. The conductance on the positive domain was found to decrease with increasing temperature while that on the negative domain increased with increasing temperature. The dependence of the conductance on domain polarization and temperature was analyzed in terms of the unscreened polarization charge and the induced band bending at the ZnO/LN interface. Since this simplified model excludes the contribution interface defects and trapped charges, the deduced band bending is larger than the actual situation and the resulting ratios between carrier concentrations at different temperatures are also larger. In order to understand the interface structure, defects and electric potential, future work is proposed in Chapter 7 for possible FeFET device application.
REFERENCES


Table 6.1 ZnO conductance on positive domain (+c) and negative domain (-c)

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<tr>
<th>Temperature</th>
<th>Conductance on (+c) (A/V)</th>
<th>Conductance on (-c) (A/V)</th>
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<td>~11</td>
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<tr>
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Table 6.2 Theoretical calculation of LN and ZnO electric properties

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<td>125°C (400K)</td>
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Figure 6.1 Schematic drawing of PE-ALD grown ZnO film on positive and negative domain surfaces of LiNbO$_3$ substrate showing Au electrodes sputtered on the ZnO film surface.
Figure 6.2 AFM topography images of PE-ALD grown ZnO film on positive (a) and negative (b) domain surfaces of LiNbO$_3$ substrates. The RMS roughness is ~0.9nm in both cases.
Figure 6.3 XPS scans of Zn₂⁺ (a) and O₂⁻ (b). In (a), the peaks at 1021.7eV and 1044.9eV are ascribed to the Zn 2p₃/₂ and 2p₁/₂ core levels, respectively. These peaks are attributed to the ZnO deposited on the molybdenum sample holder plate. The peaks at 1026.4eV (Zn 2p₃/₂) and 1049.6eV (Zn 2p₁/₂) are attributed to ZnO deposited on the LiNbO₃ surface. In (b) the XPS O (1s) scan is shown along with a Gaussian fit. The peaks at 530.7eV and 532.5eV are attributed to ZnO film deposited on the molybdenum sample holder plate and the peaks at 535.1eV and 536.9eV are attributed to ZnO film deposited on the LiNbO₃ surface.
Figure 6.4 XRD scans of PE-ALD ZnO thin film grown at 175°C on positive and negative polarity lithium niobate surfaces.
Figure 6.5 RBS/channeling spectra of PE-ALD ZnO thin film grown at 175°C.
Figure 6.6 I-V measurements on positive (a) and negative domains (b) at room temperature (black), 70°C (red) and 125°C (blue), respectively. $V_{ds}$ is the voltage bias between two Au electrodes and $I_{ds}$ is the measured current.
Figure 6.7 Schematic drawing of the band schematics at the ZnO/LN interface for the positive (a) and negative domains (b). Downward band bending in the ZnO film is induced by the positive polarization charge on positive domains and upward band bending is induced by the negative polarization charge on negative domains.
Chapter 7

SUMMARY AND FUTURE WORK

7.1 Summary

Understanding the ferroelectric polarization surface charge and charge screening is important for application of ferroelectric material as template or substrate materials. In chapter 2, the basic concepts and properties of ferroelectrics are introduced. SPM characterization techniques are presented in chapter 3 with focused discussion of PFM, which is designed for ferroelectric domain visualization.

In chapter 4 and 5, ferroelectric lithium niobate (LN) are used as a template to direct the assembly of metallic nanostructures via photo-induced reduction reaction. The photo-induced deposition involves ultraviolet light illumination of polarity patterned lithium niobate while immersed in a AgNO₃ solution. The results focus on the differences of the Ag nanostructure formation process on the positive and negative domains and the domain boundaries. The effects of four factors including UV wavelength, intensity, polarization screening and chemical concentration are studied. The results showed that for all above gap excitation wavelengths, deposition occurs on both polarity surfaces and at the domain boundaries. The density is greatest at the domain boundaries and reduced densities of smaller nanostructures are observed to form on both the positive and negative domains. The deposition on the domain surfaces is greatest for the shortest wavelengths while the domain selectivity is increased for wavelengths just above the band gap. The results are attributed to external screening of the
polarization surface charge, surface electric field distribution and penetration depth of photon. In chapter 5 we also investigated the relationship between the Ag$^+$ ion flux due to chemical diffusion and the electron flux initiated by the UV exposure of the ferroelectric surface in chapter 5. The subsequent results suggest that this relationship is responsible for the different deposition patterns. The observed variation of boundary-enhanced or boundary-depressed deposition is explained by consideration of the electric field distribution and the ratio between the Ag$^+$ ion and photon flux. The results establish that the ratio can be controlled by tuning the solution concentration and UV-light intensity to generate enhanced nanowire-like structures along the domain boundary or a more uniform deposition pattern over the positive and negative surface.

In chapter 6, zinc oxide (ZnO) thin films were grown by plasma enhanced atomic layer deposition (PE-ALD) on lithium niobate (LiNbO$_3$) crystalline substrates. The films grown on positive and negative polarity lithium niobate substrate are display different conductance and temperature dependence. The conductance on positive domains decreases with increasing temperature, while the conductance on negative domains increases with increasing temperature. At room temperature, the conductance on positive domain is 64 times greater than that on negative domain. The experimental results are discussed in terms of downward or upward band bending at the ZnO/LiNbO$_3$ interface induced by the ferroelectric polarization charges.
7.2 Future work

7.2.1 Au depositions

In chapter 3 and 4, Ag nanoparticle photo-induced deposition using AgNO₃ solution was quantitatively studied and patterns were explained in terms of wavelength, intensity and solution concentration. Other than Ag deposition, Au and Cu deposition are also investigated in our experiments and significantly different deposition patterns are observed under the same UV light wavelength, intensity and concentration conditions.

In other studies Au nanoparticle deposition using HAuCl₄ as the reduction chemical solution on PZT has been investigated [1] and results showed dominant deposition on the positive domains. We repeated the Au deposition using HAuCl₄ as the reduction chemical solution, and followed the explored the same effects studied for Ag deposition. However, there is no Au reduced on the lithium niobate surface with chemical solution concentration $\geq 10^{-3}$ M which was attributed to the strong absorption of UV photons in the chemical solution. Then the chemical concentration is chosen to be as low as $10^{-5}$ M while the UV intensity is varied. According to the theory concluded from Ag deposition, boundary enhanced deposition are expected. However, only uniform Au nanoparticle deposition pattern is obtained. The physics of the photo-induced Au deposition needs further investigation to understand the photo-induced reduction process at the liquid/LN interface. The possible reasons for the different reduction potential of Au include the low pH value of HAuCl₄ solution [2]; the effect of the Stern layer at the Au particle and lithium niobate surfaces [3], and the larger diffusion energy at of the
AuCl₄ negative ions. Cu nanoparticles were also deposited on PPLN template from a metallic organic chemical solution Cua(acac)₂ dissolved in hexane, however, the results only showed boundary nanowires deposition pattern. The might be due to the UV light absorption in the chemical solution, which reduces the effective photon flux absorbed by PPLN.

7.2.2 ZnO thin film PE-ALD deposition and characterization

In chapter 7, the use of ferroelectric lithium niobate as a substrate for ZnO deposition at 175°C is reported. The results showed good crystalline quality of the ZnO films. However, the carrier concentration of the deposited film is unknown. In order to understand the conductivity, the carrier concentration of the ZnO film has to be measured. At the same time, although ZnO films on positive and negative domains display different conductivity behavior, the on/off ratio (~64) is not sufficiently large for ideal memory devices (an on/off ratio of 1000 is desired for device application). This may be due to the high free carrier concentration for the PE-ALD growth. Researchers have investigated the carrier concentration vs. growth temperature and found a lower carrier concentration is related to lower growth temperature [5] for PE-ALD. To improve the on/off ratio, we suggest PE-ALD deposition at lower temperature (~100°C).

In chapter 7, the ZnO film is only deposited on bulk congruent lithium niobate crystalline substrates. The properties of ZnO deposited on thin film lithium niobate have to be investigated for possible device applications. Thin film
stoichoimetric lithium niobate having switchable polarization within $\pm 10V_{pp}$ is more promising for device application and higher on/off ratio.
REFERENCES


Figure 7.1 AFM topographic images of Au nanoparticle deposition on PPLN surface. (a) and (b) are deposited with $10^{-5}$ M HAuCl$_4$ solution and UV intensity 1400 $\mu$W/cm$^2$. (c) and (d) are deposited with $10^{-5}$ M HAuCl$_4$ solution and UV intensity 25 $\mu$W/cm$^2$. Although the contrasted between positive and negative domains are observed in (c) and (d), the results are less repeatable.