Development of High Capacitance Films for Electrical Energy Storage
Using Electrophoretic Deposition of BaTiO$_3$ on Ultrasonically Etched Ni

by

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Abstract

High capacitance devices were developed using rapid electrophoretic deposition (EPD) of barium titanate (BaTiO$_3$) on ultrasonically etched nickel (Ni) substrates. The microstructural and electrical properties of films with varying thicknesses, sintering temperatures and substrate etching times were investigated to study their effect on the capacitance. Although increasing the capacitance was the primary goal, decreasing manufacturing costs and reducing environmental impact was also considered.

After confirming the tetragonality and particle size of a 0.2 $\mu$m hydrothermal powder, it was dispersed in an aqueous-organic mixture of ethanol, acetone and water. A zeta potential of 50 mV was observed at the EPD pH level (6.8). Flocculation or coagulation was not likely in this situation. Therefore, mixing water with an organic solution was an effective method for reducing environmental impact while maintaining deposition quality.

The presence of BaCO$_3$ in the films was proven using X-ray diffraction. Other impurities such as TiO$_2$ and NiO were not detected. A significant variation in the average grain size was not observed for films with different thicknesses whereas films sintered at different temperatures displayed greater variation. A bimodal pore size distribution in the samples suggested that the powder was agglomerated after deposition due to a high deposition voltage (20 V). Rapid deposition times of 2 to 8 seconds offered a potential for cost reduction compared to longer deposition times implemented in industry. Therefore the increased porosity was accepted.

The dielectric constant of the films increased from 2900 to 6730 as the thickness increased from 17.75 $\mu$m to 47.5 $\mu$m. The dissipation factor decreased from 0.27 to 0.06 with increasing thickness. This behavior was attributed to a low dielectric constant interfacial layer and a higher dielectric leakage current at smaller thicknesses. The dielectric constant increased from 1700 to 6350 and the dissipation factor decreased from 0.23 to 0.04 as the sintering temperature increased from 1150°C to 1300°C. This was attributed to an increase in tetragonality with grain
size and a decrease in porosity with sintering temperature. Finally, etching a substrate for 60 seconds increased its capacitance by 27.47% and using ultrasonic agitation further increased the capacitance by 8.75%.
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I dedicate this thesis to my mother, father and brother for their love and support.

We have wandered the world together and no matter where we settle—If we settle—our journey will never end.
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Nomenclature

$E_g$  Band gap
$ar{p}$  Dipole moment
$Q$  Charge
$d$  Charge separation
$\alpha$  Polarizability
$\bar{E}$  Applied electric field
$\bar{P}$  Sum of dipole moments
$N$  Number of dipoles in a cubic meter
$\varepsilon_0$  Electric permittivity of a vacuum (8.854 × 10$^{-12}$ F/m)
$\chi$  Dielectric susceptibility
$\varepsilon_r$  Relative permittivity or dielectric constant
$\bar{D}$  Electric flux density or dielectric displacement
$Q_0$  Free charge on plates
$A$  Area
$Q_p$  Polarization charge on plates
$C$  Capacitance
$V$  Voltage
$d$  Distance between electrodes
$\varepsilon$  Permittivity of a material
$\varepsilon^*$  Complex ac permittivity
$\varepsilon'_r$  Real portion of permittivity
$\varepsilon''_r$  Imaginary portion of permittivity
$DF$  Dissipation factor
\( QF \) Quality factor

\( T_0 \) Curie temperature

\( T \) Temperature

\( \tilde{E} \) Local electric field

\( V_{\text{Total}} \) Total interaction energy function

\( V_R \) Electrical double layer repulsive force

\( V_A \) Van der Waals attractive force

\( \varepsilon_s \) Suspension liquid’s dielectric constant

\( a \) Particle radius

\( \psi_\delta \) Zeta potential of particle

\( \kappa \) Double layer thickness reciprocal

\( D \) Separation distance between two particles

\( A_{131} \) Hamaker constant for particle media 1 in a suspension media 3

\( A_{11} \) Hamaker constant for particle media 1 in a vacuum

\( A_{33} \) Hamaker constant for suspension media 3 in a vacuum

\( f(P) \) Retardation factor

\( P \) Particle separation distance

\( F_p \) Force experienced by a particle

\( q_p \) Particle charge

\( E_{\text{cell}} \) Electric field applied in cell

\( F_f \) Frictional force caused by liquid

\( \eta \) Viscosity of liquid

\( d_p \) Particle diameter

\( v \) Terminal velocity
\( G \)  \hspace{1em} \text{Gibb’s free energy}
\( \gamma_i \)  \hspace{1em} \text{Interfacial energy}
\( A_i \)  \hspace{1em} \text{Interfacial area}
\( \theta_d \)  \hspace{1em} \text{Dihedral angle}
\( \gamma_{ss} \)  \hspace{1em} \text{Solid-solid interfacial energy}
\( \gamma_{sv} \)  \hspace{1em} \text{Solid-vapor interfacial energy}
\( \Delta P \)  \hspace{1em} \text{Pressure difference between interior and exterior}
\( \gamma \)  \hspace{1em} \text{Surface energy}
\( r \)  \hspace{1em} \text{Radius of curvature of sphere}
\( \Delta G \)  \hspace{1em} \text{Difference in free energy}
\( V_m \)  \hspace{1em} \text{Molar volume}
\( x \)  \hspace{1em} \text{Distance from center for necking to tip}
\( a^3 \)  \hspace{1em} \text{Diffusing vacancy volume}
\( D^* \)  \hspace{1em} \text{Self-diffusion coefficient}
\( k \)  \hspace{1em} \text{Boltzmann’s constant}
\( t \)  \hspace{1em} \text{Time}
\( V_{m0} \)  \hspace{1em} \text{Initial molar volume}
\( L \)  \hspace{1em} \text{Current central distance between two particles}
\( L_{0} \)  \hspace{1em} \text{Initial central distance between two particles}
\( K \)  \hspace{1em} \text{Apparent dielectric constant}
\( K_m \)  \hspace{1em} \text{Dielectric constant of matrix phase}
\( \nu_p \)  \hspace{1em} \text{Porosity}
\( K_r \)  \hspace{1em} \text{Room temperature dielectric constant}
\( RI_r \)  \hspace{1em} \text{Relative refractive index}
$RI_p$ Refractive index of particle

$RI_d$ Refractive index of dispersant

$ZP$ Zeta potential

$EM$ Electrophoretic mobility

$SC$ Specific conductance

$TDS$ Total dissolved solids

$d_i$ Inter-planar distance between lattice planes

$\theta$ Scattering angle

$n$ Equation order

$\lambda$ Wavelength

$Z'$ Real component of impedance

$Z''$ Imaginary component of impedance

$j$ Square root of -1

$\omega$ Frequency
Chapter 1

Introduction

Due to the increasing demand for energy storage and its transport, there is a need for a new generation of materials capable of storing large quantities of electrical energy without problems associated with disposal and environmental contamination. The slow charging times, performance degradation and toxicity of acid-based batteries is leading researchers to develop alternative devices with improved energy densities. One very promising device is the capacitor. The capacitor has been around for hundreds of years but its primary role has been as a pulse power device that is charged periodically from an external energy source such as a battery [1]. Its low energy density has limited its use to electronic components in telecommunication devices and personal computers. The trend towards miniaturization, low electric power consumption and cost reduction has become increasingly prominent and the multilayer ceramic capacitor (MLCC) has been at the forefront of these advances due to its high capacitance with small size, high reliability, and excellent high-frequency characteristics [2].

Of all the dielectric materials used in MLCCs, barium titanate (BaTiO$_3$) is the most widely studied due to its perovskite structure and high dielectric constant [2, 3]. Cathodic electrophoretic deposition (EPD) is a cost-effective technique to prepare homogenous BaTiO$_3$ films on various substrates and there are a number of studies that examine the microstructural and dielectric properties of these films [3, 4]. However, to the best of the author’s knowledge similar studies on etched surfaces do not exist and electrophoretic deposition on ultrasonically etched nickel is a whole new concept altogether. Previous reports on aluminum foils point out that it is an effective method to increase etching efficiency and capacitance [5].
In addition to ultrasonic etching of nickel, another new procedure demonstrated in this study is rapid EPD whereby uniform BaTiO$_3$ films are deposited onto nickel substrates in 2 to 8 seconds compared to longer deposition times used in industry. Using an aqueous-organic suspension during EPD is also a new concept. Aqueous suspensions lead to oxygen and hydrogen evolution due to electrolysis, however due to economic and environmental reasons they can be favored. Organic suspensions offer a wide range of vapor pressures and thus evaporation rates and yield higher quality depositions but they are more expensive and may affect the environment negatively if used in high quantities. Therefore, using an aqueous-organic suspension balances the positive and negative effects of each suspension medium.

The aim of this study is to develop a new generation of high capacitance devices using rapid electrophoretic deposition of pure BaTiO$_3$ on ultrasonically etched nickel electrodes. The microstructural and electrical properties of films with varying thicknesses, sintering temperatures and substrate etching times are investigated. High capacitance is achieved by maximizing the dielectric constant, which is considered to be a material factor, and the interfacial surface area, which is considered to be a geometric factor. Figure 1.1 displays a flow chart of the experimental procedure followed in this study. Each step is explained in detail in Chapter 3.
Figure 1.1: Flow chart of the experimental procedure.
2.1 Dielectrics and Ferroelectricity

Dielectric materials are insulators where all of the electrons are bound in atomic orbitals and cannot move freely. These materials consist of positively and negatively charged particles whose charges balance each other in the absence of an external electric field, giving rise to overall charge neutrality. When an electric field is applied the balance is disturbed due to electronic, atomic, orientation or space charge polarization [6]. This behavior is illustrated in Figure 2.1. An important characteristic of dielectric materials is that they have a low density of charge carriers ($<10^6$ e$^-$/m$^3$) and a large band gap ($E_g > 2.5$eV) [7], which causes very low electrical conduction.

![Figure 2.1](image)

Figure 2.1: The effect of an external electric field on a dielectric material.
Under the influence of an electric field electronic polarization arises from the displacement of electrons with respect to atomic nuclei. Atomic polarization occurs due to a change in dipole moment accompanying the stretching of chemical bonds between different atoms in a molecule. Orientation (or dipole) polarization arises from the orientation of molecules with permanent dipole moments caused by an asymmetric charge distribution. Space charge (or interfacial) polarization occurs when charge carriers that can travel significant distances through the dielectric material are trapped and cannot discharge at the electrode. This is the only type of polarization that is accompanied by macroscopic charge transport.

When a dielectric material is placed in an electric field generated by two parallel capacitor plates the charge storage ability per unit voltage increases by a factor of $\varepsilon_r$. This value is called the relative permittivity or dielectric constant. The increase in this value is caused by the charges at the electrode surface being neutralized. The material between the electrodes responds to the electric field by creating dipoles with dipole moments. The equation for a dipole moment $\bar{p}$ is as follows:

$$\bar{p} = Q\bar{d} \tag{2.1}$$

where $Q$ is the charge and $\bar{d}$ is the charge separation. The ability of a particle to become polarized is represented by the polarizability $\alpha$, which is given by:

$$\alpha = \frac{\bar{p}}{E} \tag{2.2}$$
where $\vec{E}$ is the applied electric field. The polarization $\bar{P}$ is represented as the sum of all the dipole moments and is given by:

$$\bar{P} = N\vec{p}$$

(2.3)

where $N$ is the number of dipoles in a cubic meter. The effect of the electric field on the polarization is seen in the following equation:

$$\bar{P} = \chi\varepsilon_0\vec{E}$$

(2.4)

where $\varepsilon_0$ is the electric permittivity of a vacuum and has a value of $8.854 \times 10^{-12}$ F/m. The dielectric susceptibility $\chi$ is written as follows:

$$\chi = \varepsilon_r - 1$$

(2.5)

where $\varepsilon_r$ is the relative permittivity or dielectric constant. The electric flux density or dielectric displacement is a measure of the electric field strength generated by a free electric charge $Q_0$ corresponding to the number of electric lines of force passing through a certain area $A$. The flux density is expressed in the following equation:

$$\vec{D} = \frac{Q_0}{A} = \varepsilon_0\vec{E}$$

(2.6)
The free charge $Q_0$ on the plates form when there is no dielectric material between them. The presence of a dielectric material increases the value of the charge by adding a polarization charge component $Q_p$ so that the final free charge on the plates is the sum of these two values. The electric flux density becomes:

$$
\bar{D} = \varepsilon_0 \bar{E} = \bar{P}
$$

(2.7)

The main characteristic of a capacitor is that an electric charge can be stored [8]. In a parallel plate capacitor the capacitance $C$ is directly proportional to the area of the conductor plates and inversely proportional to the distance between them. The capacitance is related to the charge $Q$ and the voltage $V$ by the following equation:

$$
C = \frac{Q}{V}
$$

(2.8)

Figure 2.2 shows a parallel plate capacitor connected to a power supply.

![Parallel plate capacitor](image)

Figure 2.2: Parallel plate capacitor.
The capacitance in a parallel plate capacitor is affected by both a geometric and a material factor:

\[ C = \varepsilon_r \varepsilon_0 \frac{A}{d} \quad (2.9) \]

The geometric factor is represented by the area \( A \) divided by the distance between the electrodes \( d \) while the material factor is represented by the relative permittivity \( \varepsilon_r \) multiplied by the permittivity of a vacuum \( \varepsilon_0 \). The relative permittivity (or dielectric constant) is the ratio of the amount of electrical energy stored in a material (or permittivity of the material \( \varepsilon \)) relative to that stored in a vacuum:

\[ \varepsilon_r = \frac{\varepsilon}{\varepsilon_0} \quad (2.10) \]

Table 2.1 displays dielectric constants of various ceramics for comparative purposes. Titanate ceramics have significantly higher values. This is due to their crystal structure, which will be discussed later.

<table>
<thead>
<tr>
<th>Material</th>
<th>Dielectric Constant at 1 MHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titanate Ceramics</td>
<td>15-10,000</td>
</tr>
<tr>
<td>Mica</td>
<td>5.4-8.7</td>
</tr>
<tr>
<td>Steatite (MgO-SiO₂)</td>
<td>5.5-7.5</td>
</tr>
<tr>
<td>Soda-Lime Glass</td>
<td>6.9</td>
</tr>
<tr>
<td>Porcelain</td>
<td>6.0</td>
</tr>
<tr>
<td>Fused Silica</td>
<td>3.8</td>
</tr>
</tbody>
</table>
When an ac voltage in sinusoidal form is applied across a capacitor the dielectric polarizes and leads to a complex ac permittivity $\varepsilon^*$:

$$\varepsilon^* = \varepsilon'_r - i\varepsilon''_r$$  \hspace{1cm} (2.11)

This equation consists of a real and imaginary portion. The real part is represented by $\varepsilon'_r$ and corresponds to polarization due to an applied electric field. The imaginary part is represented by $\varepsilon''_r$ and corresponds to the energy loss due to polarization. This value is termed the loss tangent and is written as follows:

$$\tan \delta = \frac{\varepsilon''_r}{\varepsilon'_r}$$  \hspace{1cm} (2.12)

In the case of conductors the angle between the real and imaginary component is 0° and for insulating materials it is 90°. These values are never achieved in real capacitors; a phase angle between 0° and 90° is usually observed. Dissipation factor is another common term used to describe the rate of electrical energy loss in a system. Although dissipation factor and loss tangent are often used synonymously, they take slightly different meanings. The term dissipation factor $DF$ is used at low frequencies, whereas loss tangent $\tan \delta$ is more accurate for high frequency readings. The quality factor $QF$ is the ratio of the energy stored to that dissipated per cycle and is related to the dissipation factor by the following equation:

$$\tan \delta = DF = \frac{1}{QF}$$  \hspace{1cm} (2.13)
Both the dielectric constant and the loss tangent are dependant on frequency. The behavior of the frequency curve depends on the polarization mechanism within a certain range as seen in Figure 2.3.

![Frequency Dependence of the Real and Imaginary Parts of the Dielectric Constant](image)

Figure 2.3: Frequency dependence of the real and imaginary parts of the dielectric constant in the presence of interfacial, orientation, ionic and electronic polarization (adapted from [10]).

The electric charge in an ideal capacitor rapidly adjusts itself to any change in voltage. However, in reality, there is inertia-to-charge movement that shows up as a relaxation time for charge transport. Both electronic and ionic polarizations are similar to simple harmonic motion where the driving force is the vibrating electric field and the restoring force is the coulombic attraction between the species. Electronic polarization is very rapid and follows alternative fields in the visible part of the spectrum; due to this, the index of refraction is dependant on it. Ionic polarization follows an applied high-frequency field and affects the dielectric constant up to the infrared region of the spectrum. The relaxation times for orientation and space charge polarization only play a role at lower frequency values.
Ferroelectricity is the spontaneous alignment of electric dipoles by their mutual interaction [11]. This process is similar to the alignment of magnetic dipoles in ferromagnetism however in ferroelectricity the spontaneous polarization due to an electric field can be reversed. The ferroelectric phase in a material occurs due to a structural transition from a high symmetry phase to a phase that has low symmetry. The term Curie point is given to the temperature at which this transition happens. Above the Curie point there is a dependence of the dielectric constant on the temperature. The Curie-Weiss law represents this dependence as follows:

\[ \varepsilon_r = \varepsilon_0 + \frac{C}{T - T_0} \]  

(2.14)

where \( C \) is the Curie constant, \( T_0 \) is the Curie temperature and \( T \) is the temperature at which the dielectric constant is being measured. When the temperature is above the Curie point, the crystal is non-polar and has no net dipole. Below the Curie point ferroelectric phase transition occurs and the material becomes spontaneously polarized. The source of spontaneous polarization is seen in the equation for polarization:

\[ \vec{P} = N\alpha\vec{E}' \]  

(2.15)

where \( \vec{E}' \) is the local field and represents the microscopic electric field felt by the polarizing atom. This parameter can be written as:

\[ \vec{E}' = \vec{E} + \frac{\vec{P}}{3\varepsilon_0} \]  

(2.16)
Combining Equations 2.4 and 2.5 and substituting Equation 2.16 into 2.15 creates the following relationship:

\[
\varepsilon_r = \frac{1 + \frac{2N\alpha}{3\varepsilon_0}}{1 - \frac{N\alpha}{3\varepsilon_0}} \tag{2.17}
\]

Equation 2.17 shows that the relative permittivity approaches infinity when \( N\alpha \approx 3\varepsilon_0 \). This implies that the material can polarize in the absence of an electric field. Not taking the ionic and electronic mechanisms into account and only using dipolar polarizability the relative permittivity can be written as follows:

\[
\varepsilon_r \approx \frac{C}{T - T_0} \tag{2.18}
\]

This equation implies that as \( T \) approaches \( T_0 \) the relative permittivity becomes infinite, destabilizing the system and prompting phase transition.

The direction of polarization in dielectric materials is not always uniform and the dipole moments in unit cells are aligned into separate ferroelectric domains with uniform polarization. In order to make the direction of polarization uniform an external electric field is applied in the paraelectric state while cooling the material down. The polarization occurs parallel to the electric field and the domains reorient themselves accordingly. Materials with different phases yield domain walls of different orientations. In the rhombohedral perovskite phase polarization results in 71°, 109° and 180° domain walls while the tetragonal phase produces 90° and 180° domain
walls as seen in Figure 2.4. Although the 180° domain wall is purely ferroelectric, the 90° domain wall has a ferroelastic component due to increased strain [7].

Figure 2.4: 90° and 180° domain walls.

The polarization of a material can be represented as a function of electric field in a hysteresis loop as seen in Figure 2.5. Hysteresis occurs from the energy required to reorient dipoles during a cycle. A material in the paraelectric state displays a non-linear response with no hysteresis due to the absence of domains. Formation of 90° domain walls is common in polycrystalline materials due to the presence of stresses that need to be relieved. The saturation point in a loop occurs when the polarization increases due to an electric field and the domains orient themselves parallel to the field. As the electric field strength decreases some domains switch back leaving the material with a net polarization and when the field is applied in the opposite direction the polarization eventually disappears.
Figure 2.5: Ferroelectric (single crystal, polycrystalline) and paraelectric hysteresis loops.
Dielectric losses in ferroelectric materials are caused by extrinsic and intrinsic factors. The domain wall movement is the primary contributor in the extrinsic case. Internal friction arises due to the domain walls interacting with their surroundings. The interaction of impurities and charged defects with the electric field also causes dielectric losses. These losses are caused due to an increase in conductivity in the material and due to the restriction of domain wall motion. This restriction is caused by the presence of defects such as oxygen vacancies and trapped electrons around the domain wall region. There are no domains in the paraelectric state and therefore the losses are significantly lower. The dielectric losses increase with permittivity and measured frequency in the intrinsic case. These losses are caused by the interaction between the electric field and the lattice vibrations [7, 12].

2.2 Perovskite Structure

It is well known that BaTiO$_3$ has a perovskite structure [2]. The name perovskite is derived from the CaTiO$_3$ perovskite mineral. Perovskite is a ternary compound with a formula of ABO$_3$ where A and B cations differ in size. The larger A cation and oxygen make up a face-centered cubic (FCC) lattice and the smaller B cation takes up the octahedral interstitial sites in the array. A network of corner-linked oxygen octahedra makes up the structure. The large cations fill the dodecahedral holes while the small ones fill the octahedral holes. Figure 2.6 illustrates a cubic BaTiO$_3$ perovskite structure. The coordination number of A (Ba$^{2+}$ Barium) is 12 while that for B (Ti$^{4+}$ Titanium) is 6. The coordination number represents the number of an atom’s nearest neighbours. Fluorides, chlorides, hydrides… etc. are all considered perovskites because having an anion that is oxygen is not necessary and a slight distortion in the oxygen octahedral is not a problem.
The perovskite structure has many substitution possibilities of cations A and B as well as anions as long as a charge balance is maintained and the sizes are kept within a certain coordination number. The physical properties of the crystal are profoundly affected by structural distortion and the small displacement of atoms. The crystallographic dimensions of the perovskite lattice are affected by temperature. Above its Curie point of ~120°C BaTiO$_3$ has a paraelectric cubic phase. Between 0°C and 120°C a ferroelectric tetragonal phase is present. The spontaneous polarization in this phase is along one of the [001] directions of the centrosymmetric cubic structure. Between 0°C and -90°C a ferroelectric orthorhombic phase is present. The polarization...

Figure 2.6: Perovskite structure of BaTiO$_3$ (adapted from [13]).
in this phase is along one of the [110] directions of the cubic structure. Below -90°C a ferroelectric rhombohedral phase is present. The polarization is along one of the [111] directions of the cubic structure. The spontaneous polarization below the Curie temperature occurs because of changes in the crystal structure of the material. The crystallographic dimension changes in BaTiO$_3$ are shown in Figure 2.7.

![Diagram showing lattice parameters as a function of temperature for BaTiO$_3$.](image)

**Figure 2.7:** Lattice parameters as a function of temperature for BaTiO$_3$ (adapted from [14]).

The paraelectric cubic phase is stable above 120°C. Cooling below the Curie temperature leads to the development of a tetragonal structure where the Ba$^{2+}$ and Ti$^{4+}$ ions are displaced relative to O$^{2-}$ ions. This causes the formation of electric dipoles. The effect of temperature on the relative permittivity of BaTiO$_3$ is shown in Figure 2.8 with the reversible phase transitions corresponding to each temperature range. The relative permittivity maximum at the Curie point is used for materials with high capacitances (Y5V ceramics). Unfortunately these materials display
inferior temperature stability. The region below the Curie point is used for materials with lower capacitances (X7R ceramics). These materials display higher temperature stability. The tetragonal and cubic phases of BaTiO$_3$ are very important in the microelectronics industry. The ferroelectric properties of the tetragonal phase make it ideal for electronic device applications. Although the cubic phase is not ferroelectric its high dielectric constant makes it suitable for capacitor applications.

Figure 2.8: Relative permittivity as a function of temperature depicting crystallographic changes of BaTiO$_3$ [15].

2.3 Synthesis of BaTiO$_3$ Powder

There are numerous methods for making BaTiO$_3$ powder some of which include Solid-state synthesis, oxalate synthesis, hydrothermal synthesis and alkoxide synthesis. Solid-state
synthesis involves a reaction between BaCO\textsubscript{3} and TiO\textsubscript{2} above 1100°C. The reaction for BaTiO\textsubscript{3} formation is represented as follows:

\[ \text{BaCO}_3 + \text{TiO}_2 \rightarrow \text{BaTiO}_3 + \text{CO}_2 \] \hspace{1cm} (2.19)

High calcination temperatures lead to numerous disadvantages such as wide size distribution and large particle size. Using mechanically activated powders can decrease the calcination temperature because the activation energy of BaTiO\textsubscript{3} decreases by milling the powder. The barium ion diffusion through the BaTiO\textsubscript{3} layer is also improved [16].

Oxalate synthesis involves reacting BaCl\textsubscript{2}, TiCl\textsubscript{4} and C\textsubscript{2}O\textsubscript{4}H\textsubscript{2}. Drop-wise addition of a NH\textsubscript{4}OH solution is performed to maintain a constant pH of 6 during the precipitation of oxalate species from a hot oxalic acid solution. The precipitation is heated at 750-1100°C to form the oxide product [17]. The precipitation and calcination are highly controllable enhancing stoichiometry, purity and particle size control. The reaction is described as follows:

\[ \text{BaCl}_2 + \text{TiCl}_4 + \text{oxalic acid} (\text{C}_2\text{O}_4\text{H}_2) \rightarrow \text{BaTi oxalate hydrate} + \text{HCl} \] \hspace{1cm} (2.20)

Alkoxide synthesis involves using Ti isopropoxide. Spin coating is used to coat a gel on a substrate, which decomposes into BaTiO\textsubscript{3} after heat-treating. Layers below 2 microns can be formed using this method. The reaction is represented as follows:

\[ \text{Ba(OH)}_2 + \text{Ti alkoxide} \rightarrow \text{BaTiO}_3 + \text{alcohol} \] \hspace{1cm} (2.21)
Hydrothermal synthesis requires temperatures around 200°C and several atmospheres of pressure. Calcination at around 600°C is done to remove hydroxyl groups to improve crystallinity. The hydrothermal reaction is described as follows:

$$Ba(OH)_2 + TiO_2 \rightarrow BaTiO_3 + H_2O \hspace{1cm} (2.21)$$

At low temperatures, the interface-diffusion growth mechanism is kinetically restricted. High pH levels during hydrothermal synthesis causes hydroxide defects that are incorporated into the particle lattice. Defects affect the densification and sintering behavior of the material. This is why calcination is performed after synthesis. Some advantages of using the hydrothermal method include high purity, homogenization of the chemical composition, small particle size and tolerable particle size distribution. The disadvantages include the formation of agglomerates and corrosion issues related to chloride salt.

### 2.4 Particle Suspension and Zeta Potential

Particles in dispersion have a tendency to stick together and form aggregates. These aggregates eventually settle down due to the effect of gravity. This process is called flocculation. Coagulation occurs if the aggregate transforms into a denser phase. Separation of an aggregate occurs by sedimentation or creaming if it is more or less dense than the surrounding phase. The main difference between flocculation and coagulation is that flocculation is reversible whereas coagulation is not. Figure 2.9 illustrates the different mechanisms that cause a loss in stability. It is clear that flocculation and coagulation can occur before or after sedimentation.
The formation of films on substrates using electrophoretic deposition requires suspensions to have a number of qualities. The particle surfaces need to be charged to promote migration by an electric field. The particles need to be well dispersed and not coagulate to increase the density of the deposited film. The suspensions need to contain excess ions because ions other than the charged particles cause the transport number of the particles to decrease reducing the stability of the slurry. The particles also need to have high adhesion to the substrate to prevent peeling when it is taken out of the solution. Colloidal processes usually involve using aqueous solvents due to environmental reasons and their low cost. However, using aqueous solvents cause gas evolution, which leads to pore formation in the deposited body. This is due to
the electrolysis of water. Stable suspensions in aqueous-organic solutions of acetone, ethanol and water are prepared by adding particles to the solvent and stirring. Adding acids or bases controls the charges of the particles. BaTiO$_3$ particles adsorb hydroxyl groups on their surfaces and acids or bases are added to the solution to cause these groups to either gain or lose protons changing the particles charges accordingly. Although it is beneficial to use acids and bases to alter the particle charge the unadsorbed ions compress the electric double layers ruining the degree of dispersion of the suspension. Excess ions also significantly reduce the transport number of the charged particles and fewer particles are deposited on the surface of the electrode [18]. In order to improve the particle adhesion cationic, anionic or nonionic polymer binders are used. The amount of binder is critical and too much of it can promote non-uniform film deposition and decreased density. If a binder is added to a solution it must be removed during sintering by heating to ~500°C.

The electric double layer is a region that exists around a particle. The net charge at the surface of the particle affects the distribution of ions in this interfacial region. There are two parts to the liquid layer around the particle. An inner part called the stern layer where the ions are closely packed and a diffuse outer layer where the ions are more distributed. When a particle is in motion the ions inside the boundary layer move it whereas the ions outside the layer stay with the solution. The potential at this boundary layer is called the zeta potential. Figure 2.10 displays the double layer around a particle along with the zeta potential as a function of the distance from the surface. The value of the zeta potential indicates whether or not a colloidal system is stable. If the absolute value of the zeta potential is high the particles in a solution do not clump together and the stability is improved. If the absolute value of the zeta potential is low flocculation occurs. Particles with zeta potentials higher than ±30 mV are considered stable as seen in Table 2.2.
Figure 2.10: Diagram representing electric double layer and zeta potential.

Table 2.2 – Colloidal behavior at different zeta potentials.

<table>
<thead>
<tr>
<th>Zeta potential (mV)</th>
<th>Stability of colloid</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 to ±5</td>
<td>Rapid coagulation / flocculation</td>
</tr>
<tr>
<td>±10 to ±30</td>
<td>Minor instability</td>
</tr>
<tr>
<td>±30 to ±40</td>
<td>Moderate stability</td>
</tr>
<tr>
<td>±40 to ±60</td>
<td>Good stability</td>
</tr>
<tr>
<td>&gt; ±61</td>
<td>Excellent stability</td>
</tr>
</tbody>
</table>
There are three factors that affect the zeta potential of a system. The pH level, conductivity and the presence of contaminants. The pH of the solution plays a significant role in changing the zeta potential. When alkali is added to a suspension with a negative zeta potential the particles gain more negative charge. When acid is added to the suspension the charge slowly becomes neutralized and eventually a build up of positive charge occurs. The point where the curve intersects the y-axis at a zeta potential of zero is called the isoelectric point. This is the point where the suspension is least stable. The double layer thickness of particles depends on the ionic strength of the solution. The lower the ionic strength, the less compressed the double layer becomes. The valency of the ions also affects the double layer thickness. Trivalent ions for example have a higher compressive effect than monovalent ions [19]. Ions interact with the particle surface through non-specific ion adsorption or specific ion adsorption. Non-specific ion adsorption does not affect the isoelectric point whereas specific ion adsorption does. Charge reversal often occurs in the latter case. Understanding the influence of contaminants on the zeta potential is also critical and flocculation can be avoided if the solution is prepared properly.

The relationship between the stability of a suspension and the interparticle forces and energies of interactions between particles is described by the DLVO theory, which was developed by Derjaguin, Landau, Verwey and Overbeek [20, 21]. The suspension liquid is stationary in this model and particle collisions happen due to Brownian translational motion. The stability of a colloidal system is related to the total energy of interaction and is given by:

\[ V_{\text{total}} = V_R + V_A \]  

(2.22)
where $V_{total}$ is the total interaction energy function, $V_R$ is electrical double layer repulsive force and $V_A$ is the van der Waals attractive forces between particles. The electrical double layer repulsive force $V_R$ can be written as follows:

$$V_R = \frac{\varepsilon_a \psi_\delta}{2} \ln \left[ 1 + \exp \left( -\kappa D \right) \right]$$  \hspace{1cm} (2.23)

where $\varepsilon_s$ is the suspension liquid’s dielectric constant, $a$ is the particle radius, $\psi_\delta$ is the zeta potential of the particle, $\kappa$ is the double layer thickness reciprocal and $D$ is the separation distance between two particles. The van der Waals attractive forces $V_A$ is given as follows:

$$V_A = \frac{a A_{31}}{2D} f(P)$$  \hspace{1cm} (2.24)

where $A_{31}$ is the Hamaker constant for media 1 of which the particles are composed and separated in a suspension media 3:

$$A_{31} = \left( A_{11}^{1/2} - A_{33}^{1/2} \right)^2$$  \hspace{1cm} (2.25)

where $A_{11}$ and $A_{33}$ represent the interaction of 1 and 3 in a vacuum. Equations 2.26 and 2.27 give the retardation factor $f(P)$ displayed in Equation 2.24.
The van der Waals forces dominate at small and large particle separation distances whereas the ionic strength plays a more prominent role at intermediate separation distances. Figure 2.11 displays the curves for the total potential energy as a function of interparticle distance. Large deviations in stability are apparent where curve A represents spontaneous dispersion of particles, curve B represents no primary coagulation due to a high energy barrier \( E_a \), curves C and D represent weak secondary minimum coagulation and curve E represents fast coagulation (unstable system).

![Figure 2.11: Potential energy versus interparticle distance curve [22.]](image)

\[
f(P) = \frac{1}{1 + 1.77P} \quad \text{for } P \leq 0.5
\]

\[
f(P) = \frac{2.45}{5P} - \frac{2.17}{15P^2} + \frac{0.59}{5P^3} \quad \text{for } P > 0.5
\]
2.5 Electrophoretic Deposition Process

Electrophoretic deposition (EPD) is a colloidal forming process that is widely used in industry to produce ceramic films on various substrates. It has numerous advantages over other colloidal forming techniques such as short formation time, flexibility on the shape of the formation, use of cheap equipment and easy control of the thickness and morphology of the film. Electrophoretic deposition involves applying a DC electric field onto particles that are suspended in a solution causing them to migrate and settle onto a conductive substrate of opposite charge. When the particles are positively charged they migrate towards a cathode as seen in Figure 2.12.

![Electrophoretic deposition cell with positive particles moving towards cathode](image)

Figure 2.12: Electrophoretic deposition cell with positive particles moving towards cathode [23].
Unlike electrolytic deposition, which is a suspension of ionic species, electrophoretic deposition is based on the suspension of particles in a solvent. These particles do not react with the electrode and they do not lose their charge after being deposited. Part of the electrical current is carried by free ions in the suspension but this current is usually negligible because very few free-ions exist in organic solutions. However, the accumulation of these ionic charges at the electrodes may reduce the deposition rate [20].

The deposition rate is also affected by the time of deposition for a fixed electric field. The deposition is initially linear but as the duration is increased the rate decreases and reaches a plateau. This occurs because the electric field’s influence decreases as the thickness of the deposited film increases. The applied voltage also affects the deposition. As the potential increases so does the amount of deposited material on the electrode. Although the speed at which the particles migrate towards the electrode increases with voltage the quality of the film suffers. This is true because the particles do not form a very close-packed structure as their speed increases. The concentration of solids in a suspension also affects the electrophoretic deposition process. These solids can deposit at different rates depending on their volume fraction in the solution. High volume fractions lead to equal deposition rates whereas low volume fractions cause different particles to be deposited at different rates according to their mobility. The conductivity of the substrate also influences the deposition process. The higher the conductivity the more uniform the deposited green film and the faster the deposition process.

An understanding of the kinetics of electrophoretic deposition is necessary to control the deposition rate and film microstructure. The amount of the deposition is related to the suspension concentration, surface area, time of deposition and strength of the electric field. Figure 2.13 represents the deposited weight versus time for four conditions (A to D).
Figure 2.13: Kinetics of electrophoretic deposition [24].

Line A represents a constant current and concentration, curve B represents a constant current with a decreasing concentration, curve C represents a constant voltage and suspension, and curve D represents a constant voltage with a decreasing concentration. The deposition rate in line A is linear whereas in the other curves it decreases gradually with time. Decreasing the suspension concentration decreases the final deposited weight since curves B and D both have lower weights than line A and curve D. By comparing line A and curve C it is clear that the deposition rate decreases with time when a constant voltage is applied. This is due to a decrease in particle velocity as time goes by caused by the growth of the green film which reduces the driving force through the solution. The force experienced by a particle $F_p$ is represented in Equation 2.28 [25].
where \( q_p \) is the particle charge and \( E_{cell} \) is the electric field applied in the cell. In addition to the particle experiencing a force that attracts it to the electrode it also experiences a frictional force \( F_f \) in the opposite direction caused by the liquid. This force is written as follows according to Stokes’ law:

\[
F_f = 6\pi \eta d_p v
\]  

(2.29)

where \( \eta \) is the viscosity of the liquid, \( d_p \) is the particle diameter and \( v \) is the terminal velocity.

The terminal velocity is written as follows:

\[
v = \frac{q_p E_{cell}}{3\pi \eta d_p}
\]

(2.30)

In terms of mobility \( \mu \) the equation becomes:

\[
\mu = \frac{v}{E_{cell}} = \frac{q}{3\pi \eta d_p}
\]

(2.31)
Organic suspension liquids such as acetone and ethanol are preferred over water during the electrophoretic deposition process. Significantly higher electric field strengths can be employed because electrochemical reaction of the electrodes, electrolytic gas evolution and joule heating do not exist. The high density, low conductivity and chemical stability of these liquids are highly sought after. The low dielectric constant in these liquids leads to low dissociating power, which limits the charges of the particles. Higher potentials need to be applied through organic liquids to move the particles. Other disadvantages include higher cost and toxicity compared to aqueous suspensions. Flammability is also a problem that needs to be taken into account. Organic liquids usually contain residual water but this water is not removed in industry due to high costs. According to potentiometric titration experiments and comparing charging to the sign of the electrophoretic mobility of a reference solution the particle charging behavior in aqueous and non-aqueous solutions are similar. The small amounts of water present in non-aqueous solutions generate $\text{H}^+$ and $\text{OH}^-$ ions due to electrolytic dissociation [26] and the further addition of water enhances ion production. The presence of water leads to gas evolution at the electrodes caused by electrolysis at very low voltages. $\text{O}_2$ and $\text{H}_2$ gases are produced at the anode and cathode respectively according to the decomposition reactions represented in Equations 2.32 and 2.33. The overall cell reaction is also given below in Equation 2.34:

$$\text{Anode: } 4\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4e^- \quad (2.32)$$

$$\text{Cathode: } 4\text{H}_2\text{O} + 4e^- \rightarrow 2\text{H}_2 + 4\text{OH}^- \quad (2.33)$$

$$2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{O}_2 \quad (2.34)$$
The volume of $H_2$ gas that is generated from these reactions is twice the volume of $O_2$ gas. Bubble formation at the electrodes negatively affects the electrophoretic deposition process and often leads to the development of a porous structure as seen in Figure 2.14.

![Figure 2.14: Photograph of alumina deposited on a nickel substrate at 20 V (adapted from [27]).](image)

In order to prevent bubble formation due to the electrolysis of water the deposition can be performed at low voltages below the room temperature decomposition voltage of water, which is 1.23 V. These voltages are not high enough to yield uniform deposition and film formation. A microporous membrane can also be placed in front of the electrode to prevent gas evolution [28, 29]. This method generates films with very low densities and the shrinkage increases during sintering.

Anodic deposition is another way to prevent bubbles, however, the main drawback of this method is metal cation contamination [30, 31]. Adding hydroquinone (HQ) to the suspension during deposition causes $O_2$ to be consumed by chemical oxidation of HQ to quinone at high pH levels, which makes it possible to create bubble-free deposits [32]. All of these methods are mainly used in aqueous solutions where the water content is high. Suspending the particles in an aqueous-organic liquid ensures very low water content and minimizes the adverse effects of gas evolution at the electrodes.
2.6 Surface Chemistry of BaTiO$_3$

Organic liquids such as ethanol are hygroscopic and absorb water from the surrounding air. Commercial acetone also contains residual water. The water content of these liquids is a common occurrence even in laboratory grade products [33]. The measured water content of an ethanol/acetone solvent system with a ratio of 2:1 is ~0.05 wt% [34]. Although this is a small amount the dissolution of BaTiO$_3$ in water still occurs and needs to be taken into consideration when studying the surface chemistry of the powder in organic suspensions. When water is added to the liquid this behavior becomes unavoidable. The dissolution of BaTiO$_3$ in room temperature due to poor thermodynamic stability results in Ba$^{2+}$ leaching. The reaction at the surface of BaTiO$_3$ is represented in regular and acidic conditions in Equations 2.34 and 2.35 respectively.

\[
\text{BaTiO}_3 + H_2O \rightarrow \text{Ba}^{2+} + \text{TiO}_2 + 2\text{OH}^- \quad (2.34)
\]

\[
\text{BaTiO}_3 + 2\text{H}^+ \rightarrow \text{Ba}^{2+} + \text{TiO}_2 + \text{H}_2\text{O} \quad (2.35)
\]

The thermodynamic solubility of Ba$^{2+}$ is greater than 1 M at pH levels below 10.2 [35]. Solid concentration and particle surface area both affect the amount of Ba$^{2+}$ dissolved in the solution. The dissolution is greatest at pH levels below 6. The solubility is caused due to the kinetically limited diffusion through a growing surface depletion layer with passivation [36] and it depends on the available surface area in a unit of volume. Higher surface areas lead to more dissolved Ba$^{2+}$ in the solution. The stoichiometry of the powder also affects the amount of Ba$^{2+}$ in the solution. Ba-rich powders correspond to more dissolution. Figure 2.15 displays the stability of BaTiO$_3$ according to the pH of the solution.
The reaction of BaTiO$_3$ with dissolved CO$_2$ in the liquid also needs to be considered when studying the surface chemistry of the powder. CO$_2$ is absorbed by the solution from the surrounding air and creates H$_2$CO$_3$. The dissolved Ba$^{2+}$ reacts with CO$_3^{2-}$ and forms BaCO$_3$, which may redeposit on the BaTiO$_3$ surface and prevent leaching of Ba$^{2+}$. This behavior is depicted in Equations 2.36 and 2.37.
\[ \text{Ba}^{2+} + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{BaCO}_3 + 2\text{H}^+ \]  

(2.36)

\[ 2\text{H}^+ + \text{CO}_3^{2-} + \text{BaTiO}_3 \rightarrow \text{BaCO}_3 + \text{TiO}_2 + \text{H}_2\text{O} \]  

(2.37)

The formation of BaCO\(_3\) is undesirable when sintering the powder and its evolution occurs at temperatures where closed porosity is present. At high temperatures localized de-sintering and lower densification is caused by CO\(_2\) formation in the pores. The contamination of BaTiO\(_3\) significantly affects the microstructure of the deposited film. Milling the powder at various pH levels affects exaggerated grain growth. The presence of BaCO\(_3\) is necessary for exaggerated grain growth to occur. In order to avoid Ba\(^{2+}\) dissolution and aggregation the powder can be synthesized in the presence of a surfactant. However, this method is too expensive for use in industry. The stability of the powder can be improved by surface passivation where a barrier to dissolution is formed around the BaTiO\(_3\) particle. The required parameters for a passivation agent include low solubility in the solution and the formation of a good diffusion barrier.

### 2.7 Microstructure of BaTiO\(_3\) Film

The dielectric properties of BaTiO\(_3\) ceramics can only be taken advantage of after thermal consolidation produces adequate densification in their structure. The microstructure of BaTiO\(_3\) films is heavily dependant on drying and sintering, which is why it is important to gain a better understanding of these concepts. Drying of the film gets rid of the solution and binder on the surface after electrophoretic deposition. Internal stresses are generated due to capillary forces and often lead to cracking. Cracking can be prevented by reducing capillary stresses by using a low
surface tension solvent or decreasing the porosity of the coating [38]. The evaporation rate of the solvents used needs to be controlled to prevent cracking. A mixture of acetone and ethanol is an ideal suspension for BaTiO$_3$. Acetone has small surface tension but it evaporates quickly. This high evaporation rate causes the green films to crack when they are taken out of the solution. Ethanol does not evaporate as quickly as Acetone but it has large surface tension. This surface tension causes the BaTiO$_3$ particles to peel off the substrate when taken out of the solution. That is why it is necessary to mix the two liquids to yield uniform deposits. Sintering the films after electrophoretic deposition may also lead to cracking. Usually 10-15% linear shrinkage is witnessed during sintering. The shrinkage of the film can be different from the shrinkage of the substrate. This behavior can lead to tensile and compressive stresses in the material. Figure 2.16 displays three possibilities where the shrinkage of the film is greater than the substrate causing tension (a), the shrinkage of the substrate is greater than the film causing compression (c) and the shrinkage of the film and substrate are identical (b).

![Figure 2.16](image_url)  
**Figure 2.16**: Cross-section of a sample showing three possible shrinkage scenarios [38].
There are several methods that can reduce cracking due to linear shrinkage such as liquid phase sintering using glass enamel, matching the thermal expansion coefficient of the substrate with the film and by using a reaction-bonding technique [39]. These methods can be difficult to reproduce and they affect the dielectric properties of the material therefore understanding the thermal consolidation behavior of powders is crucial.

Sintering involves heating a sample to approximately two-thirds of its melting temperature and holding for a certain period of time. Densification occurs when the thermodynamic driving force minimizes the Gibb’s free energy of the system. Atoms travel to lower energy positions to decrease the total free energy of the system. This total energy takes up the form of extra pore surface and interfacial energy. The driving force for sintering is represented as follows:

\[ dG = \sum \gamma_i \cdot dA_i \]  

(2.38)

where \( G \) is the Gibb’s free energy, \( \gamma_i \) is the interfacial energy and \( A_i \) is the interfacial area. The chemical potential and powder interfacial area decreases during sintering due to the material transport in the system. The thermodynamics of the system plays a vital role in determining the size of the grains and pores as well as the degree of densification. Grain growth and pore shrinkage is caused by material transport. In the initial stages of sintering necking occurs between the particles and grain boundaries develop. Pore formation occurs at these boundaries and at the final stages of sintering these pores close to form a fully dense material. Sintering causes impurities in the material to move towards the grain boundaries. These impurities affect the densification, slow down grain growth or generate a grain boundary phase that is different from
the rest of the material [40, 41]. Solid-state, liquid-phase and viscous sintering are the three types of thermal consolidation techniques known in the ceramics industry. BaTiO$_3$ powder is sintered through the solid-state route. This route requires high temperatures and long holding times to achieve adequate densities. Dopants are often used to promote sintering at lower temperatures and to control grain growth. The dihedral angle is used to study the microstructure of a material sintered by the solid-state route:

\[ \theta_d = 2 \cos^{-1} \left( \frac{\gamma_{sv}}{\gamma_{ss}} \right) \]  

(2.39)

where \( \theta_d \) is the dihedral angle formed at the pore-grain boundary junction, \( \gamma_{ss} \) is the solid-solid interfacial energy and \( \gamma_{sv} \) is the solid-vapor interfacial energy. A high dihedral angle assists in densification and pore elimination but pore elimination becomes impossible above a certain pore size due to thermodynamic reasons.

\[ \gamma_{ss} \]

\[ \gamma_{sv} \]

\[ \theta_d \]

\[ \text{Pore} \]

\[ \text{Grain 1} \]

\[ \text{Grain 2} \]

Figure 2.17: Pore-grain boundary with dihedral angle and interfacial energies [42].
As heat is applied into a system curved surfaces tend to become flat due to a force wanting to reduce the area of the surface. This force acts on a certain area of the surface and dividing it by the area gives the pressure. The pressure difference $\Delta P$ between the interior and exterior of a surface is represented as follows:

$$\Delta P = \frac{2\gamma}{r}$$

(2.40)

where $\gamma$ is the surface energy and $r$ is the radius of curvature of the sphere. The surface energy in this equation is isotropic. A two-sphere model seen in Figure 2.18 represents the joining of two particles and the transport paths around them. The particles are seen to move closer to each other after neck formation.

Figure 2.18: Two-sphere model showing necking and densification [43].
The transport mechanisms during sintering that are illustrated in Figure 2.18 occur in three different locations: At the surface, grain boundary and dislocation. These mechanisms are given below in Table 2.3.

Table 2.3 – Transport mechanisms during sintering.

<table>
<thead>
<tr>
<th>Source</th>
<th>Mechanism</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface</td>
<td>- Surface Diffusion (SD)</td>
</tr>
<tr>
<td></td>
<td>- Volume Diffusion (VD)</td>
</tr>
<tr>
<td></td>
<td>- Evaporation-Condensation (E-C)</td>
</tr>
<tr>
<td>Grain Boundary</td>
<td>- Grain Boundary Diffusion (GB)</td>
</tr>
<tr>
<td></td>
<td>- Volume Diffusion (VD)</td>
</tr>
<tr>
<td>Dislocation</td>
<td>- Plastic Flow (PF)</td>
</tr>
</tbody>
</table>

When ceramics are heated at elevated temperatures aggregates of fine-grained crystals increase in grain size. This increase is eventually followed by the shrinkage and disappearance of neighboring grains. This behavior can be explained by studying the grain-boundary curvature as seen in Figure 2.19.

Figure 2.19: Grains with three to eight boundaries [43].
When a grain has three boundaries the grain boundary junctions have an angle of 120° and the grain is considered to be at equilibrium. Six boundaries give a metastable structure with flat grain boundaries. When the number of grain boundaries is less than six they concave inwards and cause the grain to shrink during sintering while grains with more than six grain boundaries grow. A difference in free energy $\Delta G$ is developed due to a pressure difference caused by a curved grain boundary. This value causes the grain to either grow or shrink and is given below, where $V_m$ is the molar volume.

$$
\Delta G = 2\gamma \frac{V_m}{r}
$$

(2.41)

When the grains grow the porosity of the material decreases due to densification and the transfer of matter into the pores. This transfer occurs from the grain itself, the grain boundaries, or the exterior of the particles. The grain boundary diffusion is represented by the following equation:

$$
\frac{x}{r} = \left( \frac{40\gamma a^3 D^*}{kT} \right)^{\frac{1}{5}} r^{-\frac{3}{5}} t^{\frac{1}{5}}
$$

(2.42)

where $x$ is the distance from the center for necking to the tip, $a^3$ is the diffusing vacancy volume, $D^*$ is the self-diffusion coefficient, $k$ is Boltzmann’s constant, $T$ is temperature and $t$ is time. Equation 2.42 represents the rate of neck area growth while Equation 2.43 represents the rate of particle centers moving towards each other.
\[
\frac{\Delta V_m}{V_{m0}} = \frac{3\Delta L}{L_0} = \left(\frac{20\gamma a^3 D^*}{\sqrt{2kT}}\right)^{\frac{3}{2}} r^{-\frac{7}{4}} t^{\frac{7}{4}}
\]  

(2.43)

In Equation 2.43, \( V_{m0} \) is the initial molar volume, \( L_0 \) is the initial central distance between two particles and \( L \) is the current central distance between the same particles. The densification in a material slows down with sintering time and a final value is reached at which increases in sintering time do not affect densification. Considering the structure of a boundary seen in Figure 2.20, the overall rate of the process is determined by the rate at which atoms pass the interface and the change in energy when this occurs is also seen in Figure 2.20. It is clear that not all atoms move in the same direction. In fact, some may have paths that are normal to others and some may not move due to other atoms blocking their way.

Figure 2.20: Structure of boundary and energy change for atom passage [43].
The basal surfaces of BaTiO$_3$ particles may join parallel to one another to form single crystals or twinned crystals. The grain boundaries of the twinned crystals tend to have low energy values. If the grains are rotated away from the twin positions dislocations will form in the new interfaces leading to secondary recrystallization and exaggerated grain growth. This process occurs when a number of grains in a material grow at an unusually fast rate consuming neighboring grains that are smaller in size. These larger grains have more sides than their neighbors and hence increased curvature. This curvature leads to nucleation and increased grain growth. Primary recrystallization occurs when strain-free grains nucleate and grow. Secondary recrystallization occurs when general grain growth is slowed down due to the presence of pores or impurities and the grains with increased curvatures are the only ones able to expand. This type of recrystallization is common in BaTiO$_3$ where grain growth is inhibited by the presence of second phases and pores. Secondary recrystallization significantly affects the mechanical and dielectric properties of these materials.

On a microstructural level the dielectric properties of BaTiO$_3$ are affected by the particle size, grain size, structure of agglomerates, grain boundaries and domains [44]. In BaTiO$_3$ powders the domain structure changes as the particle size is decreased. If the particle size passes a certain minimum value the paraelectric phase at high temperatures stabilizes. The lattice elastic energy and polarization energy are decreased in large particles due to twinning. This causes 90° and 180° domain walls to form. The surplus elastic energy of the particles is released because the surface of the particles is stress-free. The curved surface of small particles causes the number of domains to decrease and at a certain size the particles consist of only one domain [45]. As the particle size decreases further a tetragonal to cubic phase change occurs. The amount of agglomeration and shape of the particle influence the size at which this phase transformation
occurs [46]. The synthesis method affects the degree of agglomeration and shape of the particles. Agglomeration becomes more of a problem as the particle size decreases. As clusters start forming the internal stress of the material increases and the particles start to display grain-like properties.

In addition to internal stresses (caused by micro-strains), sintering may lead to external residual stresses (caused by macro-strains) due to differences in the shrinkage, thermal expansion and lattice mismatch between the dielectric and electrode. These residual stresses are complex in nature and consist of compressive stresses parallel to the electrode and tensile stresses perpendicular to the electrode. Residual stresses have an effect on the dielectric constant but their relationship is unknown.

The degree of tetragonality is an important concept that affects the electrical properties of BaTiO$_3$. It represents the relative ratio of the lattice parameter of the c-axis to the a-axis (c/a) as seen in Figure 2.21.

![Figure 2.21: Tetragonal phase of BaTiO$_3$ where a = b ≠ c (adapted from [13]).](image)
The tetragonality of BaTiO$_3$ increases with grain size as the film is sintered [47]. The lower tetragonality at smaller grains is attributed to the effects of internal stresses on the crystal structure. Larger grains allow the formation of banded domain structures. These structures provide a three dimensional compensation for homogenous stress. When the grain size is small domain twinning does not occur and therefore the internal stresses throughout the grain increases. These stresses reduce the tetragonal distortion of the lattice.

Powder forming techniques such as electrophoretic deposition always result in some amount of porosity after thermal consolidation. Therefore, it is important to understand the behavior of pores in BaTiO$_3$ films and their effect on the electrical properties. Pores coalesce like particles during sintering. The driving force is also similar and involves the reduction of the total energy by reducing the total interfacial area. However, in order to shrink, pores nucleate a vacancy first and the vacancy diffuses through the lattice along a dislocation or interface. The sintering process causes grain boundary and bulk diffusion to the neck around a pore, which contributes to the densification of the material. It also causes evaporation-condensation and surface diffusion, which do not contribute to the densification of the material. Pores are considered volume defects that contain gas. The gas is trapped when sintering in reducing atmosphere. Pores can be present inside grains or at the grain boundaries and junctions. The pore size, porosity distribution and amount of porosity all affect the ceramic’s properties. The shape of the pores does not play a significant role. The strength of the ceramic is reduced due to the presence of pores. Pores reduce the cross-sectional area over which a load is applied and they also act as stress concentrators. When a critical level of stress is reached crack formation occurs. These cracks propagate through the material until fracture occurs [49].
BaTiO$_3$ films with small pores display lower dielectric constants than films with large pores when the porosity is the same. The decrease of dielectric constant with porosity is seen in Figure 2.22. A single mixing rule curve cannot be used to represent the data points. Two linear regions are present for both small pores and large pores. These regions represent closed pores below 26% or 30% porosity and open pores above these values.

![Dielectric constant vs. porosity](image)

**Figure 2.22**: Dielectric constant as a function of porosity for BaTiO$_3$ [50].

When the pores are isolated and small they are regarded as closed pores and Wiener’s mixing rule can be used to determine the apparent dielectric constant $K$ [51]:

$$K = \frac{2K_m(1-v_p)}{2+v_p} \tag{2.44}$$

where $K_m$ is the dielectric constant of the matrix phase and $v_p$ is the porosity.
When pores connect to one another and form continuous paths they are considered open pores. The dielectric constant experiences a steeper drop as porosity increases in this region. The apparent dielectric constant can be represented by Niesel’s equation [52]:

\[
K = \frac{K_m(9 - 14\nu_p)}{9 + \nu_p}
\]  

(2.45)

Increased porosity in BaTiO₃ does not only affect the dielectric constant. It also increases the dissipation factor, especially when air with a small amount of water vapor is present in the pores. When there is an excess of Ba in the material its limited solubility in the BaTiO₃ lattice causes it to segregate as Ba₂TiO₄ and makes it vulnerable to react with water [53].

### 2.8 Ni Electrode Properties

Ni is a material commonly used as an electrode in capacitors due to its superior electrical conductivity and low cost. Heating Ni at high temperatures and in reducing atmospheres causes it to diffuse into the dielectric film [54, 55]. Diffusion can occur up to 500 nm into the film when samples are sintered at 1250°C in a pO₂ of 10⁻¹⁰ to 10⁻¹³ atm. The interfacial region between the film and the electrode does not contain intermediate or secondary phases. The O₂ vacancy concentration is increased and the Curie point is lowered due to the substitution of Ni into BaTiO₃. When sintering temperatures and holding times are increased the solubility limit of Ni in BaTiO₃ is reached; if this solubility limit is exceeded NiO forms [56]. The solubility limit of NiO in BaTiO₃ is 0.6 to 1.0 wt% [57, 58, 59]. The valence state of Ni ions in the BaTiO₃ lattice is represented as Ni²⁺ [58, 60]. These ions may occupy the Ba²⁺ sites or Ti⁴⁺ sites [60, 61].
The presence of NiO affects the dielectric properties of the film. The room temperature dielectric constant $K_r$ slightly decreases as the NiO content increases when the content is below the solubility limit as seen in Figure 2.23. The dielectric constant increases drastically as the NiO content approaches the solubility limit. Beyond the solubility limit the dielectric constant decreases as NiO inclusions increase.

![Figure 2.23: Room temperature dielectric constant of BaTiO$_3$ as a function of NiO content [62].](image)

The dependence of the dielectric constant on grain size is shown in Figure 2.24. When the grain size is larger than 20 µm the dielectric constant remains relatively constant. As the grain size approaches 2 µm the dielectric constant steadily increases. This is due to the decrease of 90° domain widths.

48
Figure 2.24: Room temperature dielectric constant of BaTiO$_3$ as a function of grain size [62].

The size of the BaTiO$_3$ grains is drastically reduced with an increase in NiO content as seen in Figure 2.25. The 90° domain width in NiO-doped BaTiO$_3$ is also decreased due to the solubility of Ni in BaTiO$_3$. The increase in the dielectric constant (seen in the right of Figure 2.24) is due to the decrease of the 90° domain width. The decrease of the dielectric constant with grain size for doped BaTiO$_3$ (seen in the left of Figure 2.24) is due to the low dielectric constant of the NiO phase. It is known that the room temperature dissipation factor increases with porosity due to the adsorption of moisture on the pore surface [52]. The dissipation factor also increases as the NiO content increases. This is due to the dissipation factor of non-ferroelectric NiO phase being high.
2.9 Ultrasonic Assisted Wet Etching

The process of wet etching involves using liquid chemicals to remove material from a substrate. These chemicals consist of oxidizers, acids or bases and dilution media. One or more chemical reactions are involved in consuming the original reactants and producing new species. The basic wet etching process consists of three steps: (1) Diffusion of the etchant to the surface of the substrate for removal; (2) Reaction between the etchant and substrate; and (3) Diffusion of the byproducts from the surface of the substrate. Reduction-oxidation reactions occur during wet etching where an oxide of the material (in this case NiO from Ni) is formed. This oxide is then dissolved leading to the formation of a new oxide, which is also dissolved. This process continues until the material is consumed.
Wet etching is considered isotropic and it consumes the material at an equal rate in all directions. Dry etching is another technique used in the electronics industry. This technique is anisotropic and involves using ion bombardment or chemically reactive gases and plasma. A comparison between these two techniques is displayed in Table 2.4.

Table 2.4 – Comparison between wet etching and dry etching technique [63].

<table>
<thead>
<tr>
<th></th>
<th><strong>Wet Etching</strong></th>
<th><strong>Dry Etching</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Method</strong></td>
<td>Chemical solutions</td>
<td>- Ion bombardment</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Chemically reactive gases and plasma</td>
</tr>
<tr>
<td><strong>Environment and Equipment</strong></td>
<td>Atmosphere, Bath</td>
<td>Vacuum Chamber</td>
</tr>
<tr>
<td><strong>Advantage</strong></td>
<td>- Low cost, easy to implement</td>
<td>- Capable of defining small feature size (&lt; 100 nm)</td>
</tr>
<tr>
<td></td>
<td>- High etching rate</td>
<td></td>
</tr>
<tr>
<td></td>
<td>- Good selectivity for materials</td>
<td></td>
</tr>
<tr>
<td><strong>Disadvantage</strong></td>
<td>- Inadequate for defining feature size &lt; 1 µm</td>
<td>- High cost, difficult to implement</td>
</tr>
<tr>
<td></td>
<td>- Potential of chemical handling hazards</td>
<td>- Low throughput</td>
</tr>
<tr>
<td></td>
<td>- Substrate contamination</td>
<td>- Poor selectivity</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Potential radiation damage</td>
</tr>
<tr>
<td><strong>Directionality</strong></td>
<td>Isotropic (Except for crystalline materials)</td>
<td>Anisotropic</td>
</tr>
</tbody>
</table>
etchant may lead to dead spots. These regions may also be caused by the solution becoming saturated in certain areas. This leads to non-uniformity and a decrease in the etching action in these areas. One way to increase local concentration is to increase the overall etchant concentration. This, however, does not solve the problem of non-uniformity and may significantly increase the etching rate in some regions leading to over-etching. Another approach is to use magnetic stirring during the etching process. This process produces vortices and enhances the macroscopic mixing of the solution but does not improve the microscopic uniformity therefore the dead spots still exist and continue to degrade the electrical storage properties of the capacitor.

Ultrasonic-assisted etching is a reliable method for causing microscopic stirring and preventing dead spots [5]. The term “ultrasound” refers to sound possessing a frequency above 20 kHz, which is the upper limit for human hearing. Ultrasound is generally used to increase the chemical reaction rates and yields of products through cavitation. Cavitation is the process of bubble formation and collapse in a solution. In the case of wet etching, applying ultrasonic stirring causes agitation by means of acoustic streaming and cavitation. As an ultrasound wave propagates through the solution, the liquid is agitated leading to enhanced mass transfer. The boundary layer between the etchant and the substrate is affected and the concentration polarization is reduced leading to increased etching efficiency. The power applied to the ultrasonic bath affects the etching rate and efficiency. The increased etching efficiency and uniformity of concentration of the solution leads to an increase in the surface area of the electrode in contact with the dielectric material. This leads to increased charge storage and improved capacitance.
Chapter 3

Experimental Procedure

3.1 Powder Characteristics and Particle Size Analysis

The BaTiO₃ powder used throughout this study was supplied by Inframat® Advanced Materials™. The process of hydrothermally synthesizing the powder involved using thawed hydrated titanium oxide gel. The thawing process was done to cause the solid and aqueous phases of the gel to separate giving it low viscosity and allowing it to be fed into a reaction chamber without the need for dilution. The thawed hydrated titanium oxide gel was then mixed with barium hydroxide octahydrate. The temperature of the hydrothermal reaction mixture was raised to promote a reaction between the titanium oxide and barium hydroxide octahydrate, which caused a suspension of barium titanate to form. The resulting aqueous slurry was finally washed and gradually cooled to room temperature [65].

The stoichiometric ratio (Ba/Ti) of the resulting powder was given as 0.99 to 1.01. The BET specific surface area (using gas adsorption) was given as 4±0.5 m²/g and the average primary particle size (using BET and SEM) was given as 0.2 µm. In order to confirm the particle size a laser scattering method was used. Laser diffraction based particle size analysis relies on the fact that particles passing through a laser beam scatter light at angles that are related to their size. The scattering angle increases logarithmically with a decrease in particle size. The intensity of the scattered beam decreases as the particle volume increases. Therefore, large particles scatter light at narrower angles and higher intensities than small particles, which scatter light at wider angles and lower intensities. Figure 3.1 illustrates the change in scattering angle with particle size.
During the analysis process a dilute colloidal powder suspension is bombarded with a short wavelength He-Ne 1 mW laser for small particle analysis and a monochromatic light from a 50 W tungsten lamp for the analysis of particles greater than 1 µm. A silicon photo-diode array is used to detect the scattered light. Computer software then processes this information using an iterative deconvolution method and generates a particle size distribution diagram.

In this experiment the particle size distribution of advanced BaTiO$_3$ powder was determined using an LA-910 Horiba Laser Scattering Particle Size Analyzer. 0.1 g of the powder was mixed in 60 ml of deionized water and the suspension was stirred for 3 hours using a Branson 220 Ultrasonic Cleaner with a power of 125 Watts. A few drops of the mixture were added to the sample chamber of the analyzer, which contained approximately 300 ml of circulating deionized water. The Relative Refractive Index $RI_r$ of the mixture was imputed into the computer before the analysis procedure. Its value was determined using Equation 3.1. With
the Refractive Index of BaTiO$_3$ ($RI_p$) and the dispersant ($RI_d$) taken as 2.4 and 1.333 respectively. A value of approximately 1.80 was calculated.

$$RI_r = \frac{RI_p}{RI_d}$$ (3.1)

The mixture was diluted by adding one drop at a time to 75-95% light transmission as indicated by the photo-diode array. Mechanical stirring was applied to the solution with a mixer rotating at 400 RPM coupled with ultrasonic agitation to improve the distribution of the particles prior to taking measurements.

3.2 Zeta Potential Measurements

Zeta potential measurements are carried out using a microelectrophoresis method. A stereoscopic microscope is used to observe colloidal particles inside an electrophoresis cell. An electric field is generated by a power supply connected to two electrodes, one in each side of the cell. The suspended particles become charged and move inside the cell and their zeta potential is determined from their velocity and direction. The electrophoretic mobility is expressed as microns per second over volts per centimeter. The first term represents a velocity measurement and the second term represents the electrical field strength. Mobility represents the physical effect of the potential and not the colloidal motion itself, which is why zeta potential is a more accurate way of measuring a system. A Zeta-Meter 3.0 unit was used in this study to calculate the zeta potential values. This unit automatically calculates the zeta potential for aqueous systems. However for an aqueous-organic suspension of ethanol, acetone and water it is recommended that the electrophoretic mobility values outputted from the device be used to manually calculate the
zeta potential using the Smoluchowski Equation. This formula shows a relationship between the zeta potential \( ZP \) (millivolts) and electrophoretic mobility \( EM \) (microns/second per volts/centimeter) [67].

\[
ZP = 113,000 \frac{\eta}{\varepsilon_s} \times EM \tag{3.2}
\]

where \( \eta \) and \( \varepsilon_s \) are the viscosity of the suspending liquid (poise) and dielectric constant respectively. The Zeta-Meter 3.0 unit used to calculate the electrophoretic mobility in this study is seen in Figure 3.2 below.

![Figure 3.2: Schematic of Zeta-Meter 3.0 unit with labeled components [68].](image)

A power supply provides stable DC power at voltages varying from 0 to 300 V. Data is entered into the system by tracking a colloid from the beginning of a division to the end by
looking at the monitor. The elapsed time is recorded by the system and combined with the tracking voltage and ocular micrometer tracking distance to calculate the electrophoretic mobility. Once a value is calculated the device saves it in its memory and as numerous measurements are made an average value is displayed along with the number of colloids tracked and the standard deviation. The appropriate tracking voltage (maximum allowable voltage) is selected to limit problems with thermal overturn where convection in the liquid causes the colloids to travel in a helical path. The tracking voltage is selected by calculating the specific conductance of the sample using Equation 3.3.

\[
SC = \frac{TDS}{0.65}
\]  

(3.3)

where \(TDS\) is the total dissolved solids (mg/L) and \(SC\) is the specific conductance (micromhos/cm). The calculated specific conductance is compared to predetermined maximum specific conductance values and an appropriate voltage is selected from Table 3.1.

<table>
<thead>
<tr>
<th>Voltage (V)</th>
<th>Maximum allowable specific conductance (micromhos/cm)</th>
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<tbody>
<tr>
<td>300</td>
<td>300</td>
</tr>
<tr>
<td>200</td>
<td>700</td>
</tr>
<tr>
<td>150</td>
<td>1,200</td>
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<tr>
<td>100</td>
<td>3,000</td>
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<tr>
<td>75</td>
<td>5,000</td>
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<td>50</td>
<td>10,000</td>
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<tr>
<td>40</td>
<td>20,000</td>
</tr>
<tr>
<td>30</td>
<td>30,000</td>
</tr>
<tr>
<td>20</td>
<td>60,000</td>
</tr>
</tbody>
</table>
In this experiment the voltage across the electrophoresis cell caused the evolution of gases at each electrode due to electrolysis of water molecules. Hydrogen gas evolved at the cathode and oxygen evolved at the anode. The cathode side was open and allowed the hydrogen gas to escape however the anode side was closed therefore an opening was made to prevent oxygen gas from displacing the liquid and causing false motion. Using a molybdenum anode that combined with the oxygen molecules as they evolved prevented this false motion further. In order to record accurate values for the electrophoretic mobility the colloidal motion had to be seen and since the concentration of colloids in the solution was high, dilution was necessary. High concentrations of dissolved ions leads to a phenomenon known as “salting out” whereby the electrophoretic mobility and zeta potential are significantly reduced. Diluting the solution significantly reduces this problem. Although a diluted sample does not represent the original system it can be used for comparative purposes. In this study, 4 g of BaTiO$_3$ powder was ultrasonically mixed in a 40 ml aqueous-organic suspension medium of ethanol, acetone and water with a 2:1:1 ratio for 3 hours. The suspension was diluted from 100 g/L to $6.67 \times 10^{-3}$ g/L to accurately monitor the change in potential at different pH levels. HCl and NaOH were added to the solution and 15 measurements were taken at 6 different pH levels. The pH of the solution was determined using an Oakton® pH 110 handheld pH meter. A zeta potential plot was generated and the stability of the colloidal system was verified.

3.3 Substrate Preparation

Twelve substrates (3 cm × 1.5 cm) were cut out from nickel foil (Aldrich® Chemistry, ≥99.9%). The thickness of the foil was 125 µm. Nine samples were ultrasonically etched in a solution containing nitric acid (HNO$_3$), acetic acid (CH$_3$COOH) and acetone (CH$_3$COCH$_3$) with
equal ratios for 60 seconds. One sample was etched in the same solution without ultrasonic agitation for 60 seconds. Another sample was ultrasonically etched for 120 seconds and the final sample was left unetched. The ultrasonic etching was performed using a Branson 220 Ultrasonic Cleaner with a power of 125 Watts. The nickel foil before etching is shown in Figure 3.3.

Figure 3.3: Substrate preparation from Ni foil (3 cm × 1.5 cm).

Etching is an electrochemical process that involves electron transfer as part of the surface reactions. Oxidation is the process of electron loss and reduction is the process of electron gain. Redox reactions are composed of oxidation of species and simultaneous reduction of others. The wet etching process in this study involved using an oxidizer (HNO$_3$) and diluting media (CH$_3$COOH) to transport the reactants and products. The use of acetic acid was preferred over water because its dielectric constant was significantly lower (6.15 compared to 81). This low dielectric constant produced less dissociation of the nitric acid and yielded a higher oxidation power for etching. Acetic acid also helped in achieving proper wetting of slightly hydrophobic areas due to its low polarity.
3.4 Electrophoretic Deposition Setup

The solution used for the electrophoretic deposition process was prepared by ultrasonically mixing 4 g of BaTiO$_3$ powder in a 40 ml suspension of ethanol, acetone and water with a 2:1:1 ratio for 3 hours. The solution was kept in a 40 ml Pyrex beaker and cathodic electrophoretic deposition was conducted by applying a potential of 20 V using a Hewlett Packard Harrison 6206B DC Power Supply. The exact voltage was measured using an Agilent 34401A digital multimeter. The anode was platinum and the distance between the anode and cathode (Ni substrate) was kept at 3 mm as seen in Figure 3.4. The deposition was performed at room temperature for varying amounts of time. Nine substrates were deposited on for 2 seconds and the remaining three were deposited on for 4, 6 and 8 seconds.

![Cathodic electrophoretic deposition setup](image)

Figure 3.4: Cathodic electrophoretic deposition setup.
After the constant voltage application the samples were slowly pulled out of the solution in a vertical manner to prevent liquid loading on the green films. Excess deposition on the back of the substrates was scraped off to prevent interference with the dielectric measurements. The sides of the samples were also cleaned to eliminate cracking due to a difference in thermal expansion of the film and substrate during sintering. The samples were air-dried at room temperature for 24 hours then weighed before and after the deposition process using a Sartorius BP 221S analytical balance with a precision of 0.1 mg. This was done to determine the effect of deposition time on film thickness.

3.5 Sample Firing in Reducing Atmosphere

The samples were dried at 140°C for 30 minutes and sintered in a Lindberg Eurotherm 2404 programmable tube furnace with a reducing atmosphere of nitrogen + 5% hydrogen at temperatures between 1150°C and 1300°C for 60 minutes. The heating and cooling rate was set at 5°C per minute. Nine samples were sintered at 1200°C and the rest were sintered at 1150°C, 1250°C and 1300°C. A mullite tube was used due to its high temperature resistance. The tube was evacuated by pumping the air out using a vacuum prior to filling it with the gas mixture. This ensured that no oxygen was present in the tube during sintering. The cylinder valve was opened and a steady stream of gas was let into the chamber. The gas escaped through an outlet, which was connected, to a bubbler to visually regulate the flow rate. The furnace was also used to cure a silver paste (DuPont 4922N) applied on the films at 140°C for 60 minutes. The heating and cooling rates for this process were set at 10°C per minute. Figures 3.6 and 3.7 represent the sintering and curing temperature variation with time and Figure 3.7 illustrates the tube furnace setup.
Figure 3.6: Sintering procedure (not to scale).

Figure 3.7: Curing silver paste (not to scale).
3.6 X-Ray Diffraction

X-ray diffraction was conducted before the paste application and curing processes to prevent interference. A Rigaku CN2005 Miniflex diffractometer was used with a copper source and a nickel filter, providing an incident CuK wavelength of 0.1542 nm. X-rays were generated in a cathode ray tube by heating a filament to produce electrons and accelerating the electrons towards the copper source by applying a voltage. The electrons then bombarded the target and dislodged the inner shell electrons of the copper material producing characteristic X-ray spectra. These X-rays were then made monochromatic using a nickel filter and directed onto the sample. The intensity of the reflected X-rays was recorded as the sample and detector rotated. When the geometry of the incident X-rays impinging the sample satisfied Equation 3.4 (The Bragg Equation), constructive interference and a peak in intensity occurred. A detector processed this information and converted it to a count rate, which was outputted to a data box and computer.
This data was plotted as intensity as a function of $2\theta$. The sample rotated in the path of the collimated X-ray beam at an angle of $\theta$ while the detector rotated at an angle of $2\theta$. Sample rotation was performed using a goniometer. The Bragg equation describing the defraction is seen below:

$$2d_i\sin\theta = n\lambda$$

(3.4)

where $d_i$ is the inter-planar distance between the lattice planes, $\theta$ is the scattering angle, $n$ is an integer determined by the order given and $\lambda$ is the wavelength. In this study powder X-ray diffraction was performed on the 0.2 $\mu$m BaTiO$_3$ material to verify its composition and determine whether the present phase was tetragonal or cubic. The sample was scanned between a $2\theta$ angle of 10° and 80° with a step size of 0.05°. The powder was compacted onto a glass substrate and diffraction was performed. The diffraction data was compared to published values from the American Mineralogist Crystal Structure Database (AMCSD).

Thick film X-ray diffraction was conducted on eight BaTiO$_3$ samples that were sintered to identify contaminants (BaCO$_3$, TiO$_2$ and NiO). Four samples were of varying thickness while the other four were of varying sintering temperature. All of the samples were scanned between a $2\theta$ angle of 10° and 80° with a step size of 0.05°. The solid samples were attached to an aluminum holder using putty and diffraction was performed. The data was compared to published values from the AMCSD. Although other impurities may have been acquired from milling the powder at the manufacturer they were not studied due to their minor influence on electrical properties and lack of information on the employed milling media.
3.7 Dielectric Measurements

The room temperature dielectric constant, dissipation factor and capacitance of all the samples was determined using impedance measurements made by a Solartron 1260 Impedance Analyzer with a Solartron 1296 Dielectric Interface. The measuring voltage was kept at a small value (1 V RMS) to prevent non-180° domain reorientations from contributing to the measurements. The capacitance $C$ and loss tangent $\tan\delta$ were internally calculated from the real and imaginary components of the impedance over a frequency of 1 Hz to 1 MHz using Equations 3.5 and 3.6:

\begin{equation}
C = \frac{1}{Z'j\omega}
\end{equation}

\begin{equation}
\tan\delta = \frac{Z'}{Z''}
\end{equation}

where $Z'$ and $Z''$ are the real and imaginary components of impedance, $j$ is the square root of -1 and $\omega$ is frequency. The dielectric constant was calculated from the capacitance using Equation 2.9 with the permittivity of a vacuum being $8.854 \times 10^{-12}$ F/m and the film thickness determined optically as will be discussed later. Silver paste was applied and cured before conducting dielectric measurements. This paste acted as the second electrode for the BaTiO$_3$ film and increased the metal-ceramic contact area and charge storage capacity. Figures 3.6 to 3.8 display the samples used for dielectric measurements with a penny for reference. Tables 3.2 to 3.4 present the etching, deposition and sintering procedure for each set of samples. Although applying silver paste increased measurement uncertainty the study was appropriate for comparative purposes.
Figure 3.6: Samples with different deposition times after applying paste.

Table 3.2 – Etching, deposition and sintering procedure for first set of samples.

<table>
<thead>
<tr>
<th></th>
<th>Sample 1</th>
<th>Sample 2</th>
<th>Sample 3</th>
<th>Sample 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Etching</td>
<td>Ultrasonic for 60 seconds</td>
<td>Ultrasonic for 60 seconds</td>
<td>Ultrasonic for 60 seconds</td>
<td>Ultrasonic for 60 seconds</td>
</tr>
<tr>
<td>Deposition</td>
<td>20 V for 2 seconds</td>
<td>20 V for 4 seconds</td>
<td>20 V for 6 seconds</td>
<td>20 V for 8 seconds</td>
</tr>
<tr>
<td>Sintering</td>
<td>1200°C for 1 hour</td>
<td>1200°C for 1 hour</td>
<td>1200°C for 1 hour</td>
<td>1200°C for 1 hour</td>
</tr>
</tbody>
</table>
Figure 3.7: Samples with different sintering temperatures after applying paste.

Table 3.3 – Etching, deposition and sintering procedure for second set of samples.

<table>
<thead>
<tr>
<th></th>
<th>Sample 1'</th>
<th>Sample 2'</th>
<th>Sample 3'</th>
<th>Sample 4'</th>
</tr>
</thead>
<tbody>
<tr>
<td>Etching</td>
<td>Ultrasonic for 60 seconds</td>
<td>Ultrasonic for 60 seconds</td>
<td>Ultrasonic for 60 seconds</td>
<td>Ultrasonic for 60 seconds</td>
</tr>
<tr>
<td>Deposition</td>
<td>20 V for 2 seconds</td>
<td>20 V for 2 seconds</td>
<td>20 V for 2 seconds</td>
<td>20 V for 2 seconds</td>
</tr>
<tr>
<td>Sintering</td>
<td>1150°C for 1 hour</td>
<td>1200°C for 1 hour</td>
<td>1250°C for 1 hour</td>
<td>1300°C for 1 hour</td>
</tr>
</tbody>
</table>
Figure 3.8: Samples with different etching times after applying paste.

Table 3.4 – Etching, deposition and sintering procedure for third set of samples.

<table>
<thead>
<tr>
<th></th>
<th>Sample 1&quot;</th>
<th>Sample 2&quot;</th>
<th>Sample 3&quot;</th>
<th>Sample 4&quot;</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Etching</strong></td>
<td>Not etched</td>
<td>60 seconds</td>
<td>Ultrasonic for 60 seconds</td>
<td>Ultrasonic for 120 seconds</td>
</tr>
<tr>
<td><strong>Deposition</strong></td>
<td>20 V for 2 seconds</td>
<td>20 V for 2 seconds</td>
<td>20 V for 2 seconds</td>
<td>20 V for 2 seconds</td>
</tr>
<tr>
<td><strong>Sintering</strong></td>
<td>1200°C for 1 hour</td>
<td>1200°C for 1 hour</td>
<td>1200°C for 1 hour</td>
<td>1200°C for 1 hour</td>
</tr>
</tbody>
</table>
3.8 Scanning Electron Microscopy

The scanning electron microscopy study was performed using a JEOL JSM-840 microscope working at an accelerating voltage of 10 kV and a probe current of $6 \times 10^{-10}$ amp. An electron gun produced a stream of monochromatic electrons that were initially condensed by a lens. A second lens further condensed the electrons into a thin coherent beam and a set of coils scanned the beam dwelling on points for a certain amount of time. A third lens called the objective was used to focus the beam on a particular point on a sample resulting in the emission of secondary electrons. A portion of these secondary electrons reached a detector and the brightness of the generated image was determined by the quantity of electrons that hit the detector.

Studies of the Ni substrates, BaTiO$_3$ green film and sintered films were conducted. Four substrates with different etching procedures were studied to understand the influence of surface roughness and pitting on capacitance. The ceramic films were gold plated to make them conductive using a Hummer 6-A sputtering system (Anatech Ltd.) with a plate DC setting and a voltage of 8 V for 3 minutes. A particle size measurement of a BaTiO$_3$ green film was conducted by taking an average of 15 particle diameter readings. This was done for comparison purposes to the laser scattering method discussed in Chapter 3.1. Due to the increased porosity of the sintered films their grain size could not be determined using conventional methods therefore 15 grain size measurements were made using a point to point distance tool in Flamenco-Acquisition software (Oxford Instruments plc) and their average was taken. These surface measurements gave a good approximation of grain size along the Ni-BaTiO$_3$ interface according to cross-sectional studies. The percent area fraction of pores of the sintered films was determined using ImageJ software. SEM images with a magnification of 15,000× were converted into an 8-bit binary format. The
isolated pixels outside the pores were removed by using an erode and dilate function. Since the erosion eliminated objects that were one pixel thick, no pixels were left to dilate while the pixels close to porous regions returned to their original size. The total surface area of the image and surface area of the pores (in pixels) were determined and used in Equation 3.7 to calculate the percent area of pores. Bare outline images were generated and used to provide a visual indicator of the porosity of the films with different thicknesses and sintered at different temperatures.

\[
\text{% Area of pores} = 100 \times \left( \frac{\text{Surface area of pores}}{\text{Total surface area}} \right)
\]  

(3.7)

3.9 Thickness Determination

The thickness of the BaTiO₃ films with different deposition times was determined using optical microscopy. Two samples at a time were clamped down inside a cylindrical shell using plastic mounting clips (MetLab Corporation). The shell was filled with a mixture of 105 epoxy resin and 206 slow hardener (WEST SYSTEM®) and left to solidify for 24 hours. The shell was carefully removed and the surface in contact with the samples was successively hand ground using SiC abrasive paper with a grit size of 220, 320, 400 and 600. Water was used as the lubricant. The samples were then polished using a rotor with a 1 µm diamond paste and lubricant mixture. Figure 3.9 shows a sample used for optical measurements. An Olympus BH2-UMA optical microscope with a magnification set at 200× was used to measure the minimum and maximum thicknesses of the films along the 3 cm side. The average of these measurements were taken due to the lack of uniformity of the films.
Figure 3.9: Two samples encased in epoxy ready for optical measurements.
Chapter 4

Results and Discussion

4.1 Powder Characterization and Suspension of BaTiO₃

4.1.1 Composition and Particle Size

Powder X-ray diffraction was performed on hydrothermal BaTiO₃ (InfraMat® Advanced Materials™) to verify its composition and determine the present phase. The diffraction data was compared to published values from the AMCSD to ensure the relative purity of the powder and the tetragonality was studied to gain a preliminary understanding of its dielectric behavior [69]. Figure 4.1 displays the diffraction pattern along with the reflection lines and proves that the prominent peaks perfectly match the $2\theta$ locations for pure BaTiO$_3$. The transition from cubic to tetragonal structure is evident from the evolution of double peaks (002) and (200) from a single (200)-type peak at $2\theta = 44^\circ$ - $46^\circ$. The intensity ratio of the (002) and (200) peaks ($I_{002}/I_{200}$) was calculated as 0.497 which is equivalent to the expected intensity ratio of a tetragonal BaTiO$_3$ powder ($I_{002}/I_{200} = 0.5$) [70]. The low symmetric tetragonal phase occurred due to the Ba$^{2+}$ and Ti$^{4+}$ ions becoming displaced relative to O$^{2-}$ ions. The presence of this phase proved the powder was a ferroelectric and capable of forming 90° and 180° domain walls through spontaneous polarization. The tetragonality of the powder needed to be increased through grain growth caused by sintering at high temperatures with the grain size being increased to a point where twinning relieved the internal stresses in the material. The eradication of these stresses was desirable because they reduced the tetragonal distortion of the BaTiO$_3$ lattice.
The particle size of the powder was determined using an LA-910 Horiba Laser Scattering Particle Size Analyzer as outlined in Chapter 3.1. The mean particle size was found to be 0.943 µm with a standard deviation of 0.351 µm as seen in Figure 4.2 and Appendix A. This value was significantly larger than the particle size measured by the manufacturer (0.2 µm). A particle size measurement using SEM had to be made since the results obtained from the laser scattering method did not match the manufacturer’s specifications. A green film of BaTiO₃ was deposited on a Ni substrate and 15 particle diameter readings were made resulting in an average particle size of 0.209 µm. This was a more accurate estimate and proved that the ultrasonic agitation of the particles prior to laser scattering was not sufficient to deagglomerate groups of particles. In fact, the laser scattering analyzer was including the size of clumps of particles in the measurements. An important observation made by the SEM analysis was the large variation in particle size ranging from ~0.5 µm to ~0.1 µm as seen in Figure 4.3.
Figure 4.2: Particle size distribution of ultrasonically stirred BaTiO₃ in deionized water.
Figure 4.3: SEM image of BaTiO$_3$ green film deposited on Ni.
4.1.2 Effect of pH on Zeta Potential

The stability of the aqueous-organic solution containing BaTiO$_3$ used during EPD was investigated by finding the zeta potential. This was done to prevent flocculation and coagulation of the particles in the suspension, which can cause heterogeneities upon sintering the dielectric. HCl and NaOH were added to a diluted solution containing BaTiO$_3$. Although diluting a solution does not represent the original system it was used for comparative purposes. A tracking voltage of 300 V was selected by using Equation 3.3 and the zeta potential values were calculated from the average electrophoretic mobility at each pH level using Equation 3.2. The average zeta potential measurements and plot can be seen in Table 4.1 and Figure 4.4. It is important to note that the standard deviations were included in Table 4.1 to give a better idea of the errors involved.

A maximum zeta potential of ~55 mV was observed at pH levels below 6. The pH of the solution used for preparing the samples was 6.8. This value corresponded to a zeta potential of 50 mV and was considered appropriate (according to Table 2.2) therefore further acidification of the solution was unnecessary. At acidic values (below pH 5) the formation of oxide-rich TiO$_2$ leads to the development of large positive surface potential. When the solution is made basic, carbonates and hydroxides appear on the BaTiO$_3$ surface [71]. These impurities modify the interfacial properties and surface potential of the powder leading to lower dielectric properties. Although it can be beneficial to use acids and bases to alter the particle charge the unadsorbed ions compress the electric double layers ruining the degree of dispersion of the suspension. Excess ions also significantly reduce the transport number of the charged particles and fewer particles are deposited on the surface of the electrode. A balance of high zeta potential and low adsorption/precipitation of Ba$^{2+}$ was achieved by keeping the pH at 6.8 during the electrophoretic deposition process.
Table 4.1 – Average zeta potential measurements at different pH values with standard deviation.

<table>
<thead>
<tr>
<th>Measurement</th>
<th>pH</th>
<th>Average zeta potential</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>55.68</td>
<td>3.52</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>55.21</td>
<td>2.87</td>
</tr>
<tr>
<td>3</td>
<td>6</td>
<td>50.17</td>
<td>4.31</td>
</tr>
<tr>
<td>4</td>
<td>8</td>
<td>45.43</td>
<td>5.65</td>
</tr>
<tr>
<td>5</td>
<td>11</td>
<td>-4</td>
<td>3.29</td>
</tr>
<tr>
<td>6</td>
<td>14</td>
<td>-10</td>
<td>4.37</td>
</tr>
</tbody>
</table>

Figure 4.4: Average Zeta potential as a function of pH of the suspension.
The isoelectric point (IEP) in Figure 4.4 is the point where the curve intersects the x-axis at a zeta potential of zero. This is the point where the suspension is least stable and in this experiment it was at a pH of 10.8. At this pH level the electrostatic repulsion between the double layers of the particles is eliminated and the attractive van der Waals forces are the only contributors to the potential energy of the system causing flocculation. The IEP values for BaTiO$_3$ reported in literature vary widely from acidic (4.3) to alkaline (10.2) as seen in Table 4.2. This variation is largely due to different experimental conditions and powders used proving that a large degree of uncertainty exists in zeta potential measurements.

Table 4.2 – Reported IEP values for BaTiO$_3$.

<table>
<thead>
<tr>
<th>IEP</th>
<th>Ba/Ti ratio</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.3</td>
<td>0.991</td>
<td>[72]</td>
</tr>
<tr>
<td>4.7</td>
<td>1.0</td>
<td>[73]</td>
</tr>
<tr>
<td>6.0</td>
<td>1.0</td>
<td>[74]</td>
</tr>
<tr>
<td>7.7</td>
<td>0.99</td>
<td>[75]</td>
</tr>
<tr>
<td>8.5</td>
<td>1.07</td>
<td>[76]</td>
</tr>
<tr>
<td>10.2</td>
<td>1.1</td>
<td>[77]</td>
</tr>
</tbody>
</table>

4.2 Surface Chemistry and Contamination of BaTiO$_3$

4.2.1 BaCO$_3$ Identification

The formation of orthorhombic BaCO$_3$ (Witherite mineral) was possible during the hydrothermal synthesis of the powder, its suspension in the aqueous-organic solution prior to and throughout electrophoretic deposition or during the drying and sintering steps. It was important to identify this contaminant in the prepared films because it was known to contain < 10 ppm by weight metallic impurities and result in the formation of thin conductive layers at grain
boundaries thereby increasing the dielectric losses. Its presence was also known to cause exaggerated grain growth, which could result in a lower dielectric constant [78].

X-ray diffraction analysis of four films sintered at different temperatures and four films deposited for different amounts of time was performed (Figures 4.5 and 4.6). A weak signal at $2\theta = 24^\circ$ proved the presence of BaCO$_3$ at sintering temperatures of 1250°C and 1300°C. The intensity of the signal slightly increases at 1300°C as seen in Figure 4.6. During the hydrothermal synthesis procedure where Ba(OH)$_2$ reacted with TiO$_2$ at high pH levels it was possible for BaCO$_3$ to occur as a byproduct due to atmospheric absorption of CO$_2$. Atmospheric absorption of CO$_2$ may have also occurred during electrophoretic deposition. In this case the dissolved Ba$^{2+}$ may have reacted with CO$_3^{2-}$ and formed BaCO$_3$. The lack of O$_2$ purging during electrophoretic deposition increased the odds of CO$_2$ being present in the solution. During the drying and sintering steps CO$_2$ may have been trapped inside closed pores in the films and reacted with Ba$^{2+}$ to add to the BaCO$_3$ content. Although some BaCO$_3$ was identified, X-ray diffraction did not prove to be an overly accurate method of detecting the contaminant because the formation of a very thin partially amorphous BaCO$_3$ layer between crystalline BaTiO$_3$ did not stand out very well in Figures 4.5 and 4.6.
Figure 4.5: X-ray diffraction of BaTiO$_3$ films deposited for different amounts of time with BaCO$_3$ reflection lines.
Figure 4.6: X-ray diffraction of BaTiO$_3$ films sintered at different temperatures with BaCO$_3$ reflection lines.
4.2.2 TiO$_2$ Identification

The presence of TiO$_2$ (Rutile mineral) in BaTiO$_3$ films was studied. This contaminant may have been present due to the excess of Ti in the powder, usually due to exposure to an acidic environment. Since the stoichiometric ratio (Ba/Ti) of the powder was 0.99 to 1.01 it was not likely that large quantities of Ti existed. An X-ray diffraction study was conducted nevertheless due to the significant effect of TiO$_2$ on the dielectric properties. Small amounts of TiO$_2$ can react with BaTiO$_3$ to form Ba$_6$Ti$_{17}$O$_{40}$, which forms a eutectic melt at high temperatures. This liquid phase promotes densification and grain growth of BaTiO$_3$ and lowers the onset sintering temperature, which can affect the dielectric properties [79, 80]. X-ray diffraction analysis of four films sintered at different temperatures and four films deposited for different amounts of time was performed (Figures 4.7 and 4.8). As expected, no TiO$_2$ phase was observed, which proved that the solution pH of 6.8 was not acidic enough to allow the formation of TiO$_2$ and the stoichiometry reported by the manufacturer was accurate.
Figure 4.7: X-ray diffraction of BaTiO$_3$ films deposited for different amounts of time with TiO$_2$ reflection lines.
Figure 4.8: X-ray diffraction of BaTiO$_3$ films sintered at different temperatures with TiO$_2$ reflection lines.
4.2.3 NiO Identification

The formation of cubic NiO (Bunsenite mineral) may have occurred in the samples due to the diffusion of Ni into the dielectric films caused by sintering at high temperatures. If the solubility limit of Ni in BaTiO$_3$ was exceeded NiO should have been able to be identified using X-ray diffraction. The presence of NiO was studied because it had the potential to significantly degrade the dielectric constant of the samples. This was possible due to the formation of a thin layer of NiO between the Ni substrate and BaTiO$_3$ film acting as the primary dielectric layer, and since the dielectric constant of NiO is significantly lower than BaTiO$_3$ this was not desirable. The presence of NiO in a sample sintered in air was visually identified as being green in color as seen in Figure 4.9. X-ray diffraction analysis of four films sintered in reducing atmosphere at different temperatures and four films deposited for different amounts of time was performed (Figures 4.10 and 4.11). No NiO content was observed proving that the solubility limit of NiO in BaTiO$_3$ (0.6 - 1.0 wt%) was not reached and the reducing atmosphere of nitrogen + 5% hydrogen was sufficient to prevent contamination.

Figure 4.9: Formation of NiO after sintering at 1200°C in air.
Figure 4.10: X-ray diffraction of BaTiO$_3$ films deposited for different amounts of time with NiO reflection lines.
Figure 4.11: X-ray diffraction of BaTiO$_3$ films sintered at different temperatures with NiO reflection lines.
4.3 Film Weight and Thickness

The weight of the BaTiO$_3$ green films deposited on the Ni substrates for 2, 4, 6 and 8 seconds was measured using a Sartorius BP 221S analytical balance. This was done by first weighing the etched Ni substrates then weighing them again after depositing the films. The weight of the BaTiO$_3$ films was calculated by subtracting the weight of the substrates from the weight of the substrates with the deposited films as seen in Table 4.3. The purpose of this study was to understand the behavior of the deposition rate during the EPD procedure. Figure 4.12 proved that the deposition rate decreased with time when a constant voltage was applied. This occurred because the electric field’s influence decreased as the thickness of the deposited BaTiO$_3$ film increased. The increase in film thickness reduced the driving force of the particles in the solution and decreased their velocity. Although the films were deposited within a very short period of time, a high voltage (20 V) caused the decrease in deposition rate with increasing time to be noticeable. Since two measurements were taken to determine the weight of the BaTiO$_3$ films at each deposition time (one of the substrate and another of the substrate with the film) the precision of the analytical balance (0.1 mg) yielded an uncertainty of ±0.2 mg. This low value along with several trials confirmed that the results were reproducible.

Table 4.3 – Variation of film weight with deposition time.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Dep. Time (sec)</th>
<th>Ni</th>
<th>Ni + BaTiO$_3$</th>
<th>BaTiO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>0.414</td>
<td>0.423</td>
<td>0.009</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>0.4176</td>
<td>0.4464</td>
<td>0.0288</td>
</tr>
<tr>
<td>3</td>
<td>6</td>
<td>0.3985</td>
<td>0.438</td>
<td>0.0395</td>
</tr>
<tr>
<td>4</td>
<td>8</td>
<td>0.4135</td>
<td>0.461</td>
<td>0.0475</td>
</tr>
</tbody>
</table>
The thickness of the films was determined to understand its effect on the electrical properties of BaTiO$_3$. It was also used to calculate the dielectric constant as will be discussed in Chapter 4.6. An Olympus BH2-UMA optical microscope with a magnification set at 200× was used to measure the minimum and maximum thicknesses of the films along the longer side of the samples. The average of these measurements were taken due to the lack of uniformity of the films. It is clear from Table 4.4 that the thickness did not increase linearly with deposition time. In fact, its behavior was similar to that of the deposition weight.

Table 4.4 – Variation of film thickness with deposition time.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Dep. Time (sec)</th>
<th>Minimum</th>
<th>Maximum</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>16.5</td>
<td>19</td>
<td>17.75</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>28</td>
<td>34.5</td>
<td>31.25</td>
</tr>
<tr>
<td>3</td>
<td>6</td>
<td>35</td>
<td>44</td>
<td>39.5</td>
</tr>
<tr>
<td>4</td>
<td>8</td>
<td>42.5</td>
<td>52.5</td>
<td>47.5</td>
</tr>
</tbody>
</table>
4.4 Grain Size at Different Thicknesses and Sintering Temperatures

An average of 15 SEM grain size measurements were taken for the films deposited for different amounts of time and for the films sintered at different temperatures. Tables B.1 and B.2 in Appendix B display the results. An average grain size of 0.62 µm, 0.59 µm, 0.56 µm and 0.55 µm was found for films with a thickness of 17.75 µm, 31.25 µm, 39.5 µm and 47.5 µm respectively. An average grain size of 0.45 µm, 0.61 µm, 0.84 µm and 1.89 µm was found for films sintered at 1150°C, 1200°C, 1250°C and 1300°C respectively. Additional measurements on separate samples yielded similar results and proved that the trends were not arbitrary.

The SEM images used for the grain size measurements are seen in Figures 4.13 and 4.14. Although complete densification did not occur in most situations the films were adequately sintered and scratch tests confirmed that BaTiO$_3$ was not present in powder form. Sintering at higher temperatures to yield better densification was avoided to prevent the Ni substrate from melting. Thermal consolidation of the films occurred when the thermodynamic driving force minimized the Gibb’s free energy of the system and atoms traveled to lower energy positions to decrease the total free energy. The interfacial area of the particles decreased during sintering due to material transport and neck formation occurred which caused the particles to move closer to each other. At this point the particles were referred to as grains. As sintering progressed impurities such as BaCO$_3$ moved towards the grain boundaries and affected the grain growth behavior. Figures 4.15 and 4.16 display the average grain size as a function of film thickness and sintering temperature. Significant variation in the average grain size was not observed for films with different thicknesses. Only a 11.29% decrease was seen over a range of 17.75 µm to 47.5 µm. Sintering temperature had a more pronounced effect on the average grain size where a 320% increase was seen over a range of 1150°C to 1300°C with a sharp increase above 1250°C.
Figure 4.13: SEM images of BaTiO$_3$ films at a magnification of 15,000× with a thickness of

(a) 17.75 µm (b) 31.25 µm (c) 39.5 µm (d) 47.5 µm.
Figure 4.14: SEM images of BaTiO$_3$ films at a magnification of 15,000× sintered at
(a) 1150°C (b) 1200°C (c) 1250°C (d) 1300°C.
Figure 4.15: Average grain size as a function of film thickness.

Figure 4.16: Average grain size as a function of sintering temperature.
4.5 Percent Area of Pores at Different Thicknesses and Sintering Temperatures

The percent area fraction of pores of the films with varying thicknesses and sintering temperatures was determined in *ImageJ* by calculating the total surface area of the images and pores in pixels and using Equation 3.7. Table 4.5 displays the results and Figures 4.17 and 4.18 show the bare outlines of the pores. As with the grain size measurements, additional measurements on separate samples yielded similar results and proved that the trends were not arbitrary and the porosity was uniform throughout the sample. A bimodal pore size distribution in Figures 4.17 and 4.18 suggested that the powder was strongly agglomerated after deposition. This agglomeration was the main reason behind the high porosity of the films and was a consequence of using a high deposition voltage (20 V). Bubble formation at the electrodes due to the electrolysis of water did not contribute to the porosity. The pores were considered open pores in all cases except at a sintering temperature of 1300°C where they were considered closed. It was in these pores where trapped CO$_2$ may have reacted with Ba$^{2+}$ to form BaCO$_3$. The percent area of pores only increased from 10% to 12.5% over a thickness range of 17.75 µm to 47.5 µm as seen in Figure 4.19 and decreased significantly from 12.8% to 1.2% over a sintering temperature range of 1150°C to 1300°C with a sharp decrease below 1250°C as seen in Figure 4.20.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Preparation</th>
<th>Total surface area (pixels)</th>
<th>Surface area of pores (pixels)</th>
<th>Percent area of pores (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>17.75 µm thickness</td>
<td>784384</td>
<td>78320</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>31.25 µm thickness</td>
<td>784384</td>
<td>89413</td>
<td>11.4</td>
</tr>
<tr>
<td>3</td>
<td>39.5 µm thickness</td>
<td>784384</td>
<td>98243</td>
<td>12.5</td>
</tr>
<tr>
<td>4</td>
<td>47.5 µm thickness</td>
<td>786432</td>
<td>98530</td>
<td>12.5</td>
</tr>
<tr>
<td>1’</td>
<td>1150°C sintering</td>
<td>786432</td>
<td>101041</td>
<td>12.8</td>
</tr>
<tr>
<td>2’</td>
<td>1200°C sintering</td>
<td>783360</td>
<td>86208</td>
<td>11</td>
</tr>
<tr>
<td>3’</td>
<td>1250°C sintering</td>
<td>786432</td>
<td>75858</td>
<td>9.6</td>
</tr>
<tr>
<td>4’</td>
<td>1300°C sintering</td>
<td>786432</td>
<td>9620</td>
<td>1.2</td>
</tr>
</tbody>
</table>
Figure 4.17: Pore outlines of BaTiO$_3$ films at a magnification of 15,000× with a thickness of

(a) 17.75 µm (b) 31.25 µm (c) 39.5 µm (d) 47.5 µm.
Figure 4.18: Pore outlines of BaTiO$_3$ films at a magnification of 15,000× sintered at
(a) 1150°C (b) 1200°C (c) 1250°C (d) 1300°C.
Figure 4.19: Percent area of pores as a function of film thickness.

Figure 4.20: Percent area of pores as a function of sintering temperature.
4.6 Dielectric Measurements at Different Thicknesses and Sintering Temperatures

The room temperature dielectric constant and dissipation factor of the samples with varying thicknesses and sintering temperatures were determined and compared at a frequency of 1 Hz. The dielectric constant increased by 132.07% from 2900 to 6730 as the thickness increased from 17.75 µm to 47.5 µm. This relationship can be seen in Figure 4.21. The dissipation factor decreased by 77.78% from 0.27 to 0.06 with increasing thickness as seen in Figure 4.22.

Only a slight variation in grain size and porosity occurred over this thickness range. Therefore, both of their effects did not provide any explanation on why the dielectric constant increased or the dissipation factor decreased. In fact, the slight decrease in grain size was expected to lower the dielectric constant and the increase in porosity was expected to increase the dissipation factor. It was speculated that the presence of a low dielectric constant interfacial layer affected the dielectric behavior of the film. The formation of Ni-Ba-Ti alloy interfacial layers were reported for multilayer capacitors of BaTiO$_3$ on Ni substrates [81]. In this case, the presence of the interfacial layer was made possible due to residual carbon creating a local heavily reducing atmosphere during sintering which reduced BaTiO$_3$ to Ba and Ti. The alloy contained higher amounts of Ba than Ti, which caused the BaTiO$_3$ dielectric layer near the interface to be rich in Ti. The lower dielectric constant of this layer most probably caused the dielectric constant to increase with thickness because as the thickness increased this layer had less of an effect on the higher dielectric constant BaTiO$_3$ material. The dissipation factor increased with decreasing film thickness due to the presence of a higher dielectric leakage current.
Figure 4.21: Dielectric constant as a function of frequency at various thicknesses.

Figure 4.22: Dissipation factor as a function of frequency at various thicknesses.
The dielectric constant increased by 273.53% from 1700 to 6350 as the sintering temperature increased from 1150°C to 1300°C. This relationship can be seen in Figure 4.23. The dissipation factor decreased by 82.61% from 0.23 to 0.04 with an increase in sintering temperature as seen in Figure 4.24. A large portion of the decrease occurred above 1250°C and specifically at 1300°C.

The behavior of the dielectric constant and dissipation factor was related to the variation in grain size and porosity. Initially, the domain-wall energy development due to the formation of multiple domains was too costly and grain clamping did not occur at small grain sizes so the strain in the material was very high and suppressed the tetragonal lattice distortion leading to lower dielectric constants. As the grain size increased there was an increase in multidomain structures (twinning) and hence unit cell tetragonality. The presence of multidomain structures reduced the suppressive strains in the lattice and drove an increase in the dielectric constant by increasing tetragonality. The dissipation factor also decreased with an increase in grain size therefore sintering BaTiO₃ at temperatures above 1300°C seemed desirable. A decrease in porosity at higher sintering temperatures lead to an increase in dielectric constant and a decrease in dissipation factor. The significant decrease in the dissipation factor at a sintering temperature of 1300°C was attributed to the formation of closed pores. The presence of BaCO₃ at temperatures of 1250°C and 1300°C did not have a noticeable impact on decreasing the dielectric constant because no exaggerated grain growth occurred. It may have contributed in increasing the dissipation factor since the dissipation factor is defined by its grain boundary properties. However, this increase was insignificant compared to the effect of porosity.
Figure 4.23: Dielectric constant as a function of frequency at various sintering temperatures.

Figure 4.24: Dissipation factor as a function of frequency at various sintering temperatures.
4.7 Surface Morphology of Substrate at Various Etching Times

In order to understand the effect of ultrasonic etching on the surface morphology of nickel two samples were etched ultrasonically, one etched non-ultrasonically and one was left unetched for comparison purposes. The surface roughness and pitting increased with etching time and ultrasonic agitation as seen in Figure 4.25. Ultrasonic etching enhanced the mass transfer and influenced the boundary layer between the etchant and nickel foil by reducing the concentration polarization and lead to an increased etching efficiency.

Figure 4.25: SEM images of nickel substrate at a magnification of 50× with (a) no etching (b) etching for 60 sec (c) ultrasonic etching for 60 sec (d) ultrasonic etching for 120 sec.
4.8 Capacitance at Various Etching Times

The capacitance of the samples discussed in Chapter 4.7 was directly determined using the impedance analyzer after depositing a 17.75 µm thick layer and sintering at 1200°C. The results are displayed in Figure 4.26. Etching a substrate for 60 seconds increased its capacitance by 27.47% from $2.33 \times 10^{-8}$ F to $2.97 \times 10^{-8}$ F at a frequency of 1 Hz. Using ultrasonic agitation for the same amount of time further increased the capacitance by 8.75% from $2.97 \times 10^{-8}$ F to $3.23 \times 10^{-8}$ F. The highest capacitance was achieved by doubling the ultrasonic agitation time to 120 seconds. An 11.46% increase was observed from $3.23 \times 10^{-8}$ F to $3.6 \times 10^{-8}$ F in this case proving that an increase in surface roughness and pitting had a positive influence on the capacitance. Despite this positive effect, increasing the surface area of the electrode probably increased the diffusion of Ni into BaTiO$_3$ escalating the likelihood of NiO formation.

Figure 4.26: Capacitance as a function of frequency at various etching times.
Chapter 5

Conclusions

The aim of this study was to develop high capacitance films using rapid electrophoretic deposition of pure BaTiO$_3$ on ultrasonically etched nickel electrodes. This was achieved by maximizing the dielectric constant, which was considered to be a material factor, and the interfacial surface area, which was considered to be a geometric factor.

The tetragonality of hydrothermal BaTiO$_3$ powder was confirmed using X-ray diffraction therefore the powder proved to be a ferroelectric and capable of forming 90° and 180° domain walls through spontaneous polarization. A mean BaTiO$_3$ particle size of 0.943 µm was found using laser scattering and a value of 0.209 µm was found using a SEM. The laser scattering method yielded a result that was significantly greater than the manufacturer’s specification of 0.2 µm. This proved that ultrasonic agitation of the particles prior to laser scattering was not sufficient to deagglomerate them. An important observation made by the SEM analysis was the large variation in particle size ranging from ~0.5 µm to ~0.1 µm.

The zeta potential measurement of an aqueous-organic suspension (ethanol, acetone and water) containing BaTiO$_3$ was taken to better understand the stability of the solution during electrophoretic deposition and prevent flocculation and coagulation. A maximum value of ~55 mV was observed at pH levels below 6. The pH of the solution used for preparing the samples was 6.8. This value corresponded to a zeta potential of 50 mV and was considered appropriate therefore further acidification of the solution was not necessary. The isoelectric point was determined as 10.8 and was avoided. Using an aqueous-organic solution provided a balance between low environmental impact and high deposition quality.
The presence of BaCO$_3$ impurities was proven at sintering temperatures of 1250°C and 1300°C using X-ray diffraction. The formation of BaCO$_3$ was possible during the hydrothermal synthesis procedure and electrophoretic deposition due to atmospheric absorption of CO$_2$. This might have been prevented by O$_2$ purging. During the drying and sintering steps CO$_2$ may have also been trapped inside closed pores in the films and reacted with Ba$^{2+}$ adding to the BaCO$_3$ content. TiO$_2$ was not observed, proving that the solution pH of 6.8 was not acidic enough to allow its formation and the stoichiometry reported by the manufacturer was accurate. NiO was also not present proving that the solubility limit of NiO in BaTiO$_3$ was not reached and the reducing atmosphere of nitrogen + 5% hydrogen was sufficient to prevent contamination.

The behavior of the electrophoretic deposition rate was studied by plotting the weight of green films at different deposition times. The rate decreased when a constant voltage of 20 V was applied indicating that the electric field’s influence decreased as the thickness of the deposited BaTiO$_3$ film increased. The behavior of the thickness was similar to that of the weight. Rapid deposition times of 2 to 8 seconds yielded uniform green films and offered a potential for cost reduction compared to longer deposition times implemented in industry.

A significant variation in the average grain size was not observed for films with different thicknesses. The grain size changed from 0.62 µm to 0.55 µm over a range of 17.75 µm to 47.5 µm. Sintering temperature had a more pronounced effect on the average grain size where it varied from 0.45 µm to 1.89 µm over a range of 1150°C to 1300°C with a sharp increase above 1250°C.

A bimodal pore size distribution in the samples suggested that the powder was strongly agglomerated after deposition. This agglomeration was the main reason behind the high porosity of the films and was a consequence of using a high deposition voltage. Bubble formation at the electrodes due to the electrolysis of water did not contribute to the porosity. The percent area of
pores only increased from 10% to 12.5% over a thickness range of 17.75 µm to 47.5 µm and decreased significantly from 12.8% to 1.2% over a sintering temperature range of 1150°C to 1300°C with a sharp decrease below 1250°C.

The dielectric constant increased from 2900 to 6730 as the thickness increased from 17.75 µm to 47.5 µm. The dissipation factor decreased from 0.27 to 0.06 with increasing thickness. The minor change in grain size and porosity did not have a significant effect on the dielectric constant or dissipation factor. A low dielectric constant interfacial layer most probably caused the dielectric constant to increase with thickness because as the thickness increased this layer had less of an effect on the higher dielectric constant BaTiO₃ material. The dissipation factor increased with decreasing film thickness due to the presence of a higher dielectric leakage current. The dielectric constant increased from 1700 to 6350 and the dissipation factor decreased from 0.23 to 0.04 as the sintering temperature increased from 1150°C to 1300°C. The increase in dielectric constant was mainly attributed to an increase in tetragonality with grain size. The decrease in dissipation factor was mainly attributed to the decrease in porosity and the formation of closed pores. Although the presence of BaCO₃ may have contributed to the electrical properties its effect was insignificant compared to the grain size and porosity.

The surface roughness and pitting of the nickel foil increased with etching time and ultrasonic agitation. Ultrasonic etching enhanced the mass transfer and influenced the boundary layer between the etchant and foil by reducing the concentration polarization and lead to an increased etching efficiency. Etching a substrate for 60 seconds increased its capacitance by 27.47% at a frequency of 1 Hz. Using ultrasonic agitation for the same amount of time further increased the capacitance by 8.75%. The highest capacitance was achieved by doubling the ultrasonic agitation time to 120 seconds where an additional 11.46% increase was observed.
Chapter 6

Future Work

Due to the affinity of Ba for CO\textsubscript{2} the formation of BaCO\textsubscript{3} was possible during the hydrothermal synthesis procedure and electrophoretic deposition caused by atmospheric absorption of CO\textsubscript{2}. It is suggested that O\textsubscript{2} purging be used to prevent BaCO\textsubscript{3} contamination in future studies. High temperature calcination of the commercial powder prior to deposition may also reduce the amount of BaCO\textsubscript{3} formation.

Although the percent area of pores decreased from 12.8% to 1.2% over a sintering temperature range of 1150°C to 1300°C it is recommend that a slightly higher temperature be used to increase the densification of the films and further reduce porosity. The melting point of the Ni substrate needs to be considered.

Ultrasonic etching times greater than 120 seconds can be used for the 125 \textmu m Ni substrate. Magnetic stirring can also be implemented with ultrasonic agitation to further enhance the etching efficiency and lead to higher capacitances.
References


Appendix A – Laser Scattering Particle Size Analysis Output

Figure A.1: Particle size distribution of ultrasonically stirred BaTiO₃ in deionized water using an LA-910 Horiba Laser Scattering Particle Size Analyzer (first half of table).
Figure A.2: Particle size distribution of ultrasonically stirred BaTiO$_3$ in deionized water using an LA-910 Horiba Laser Scattering Particle Size Analyzer (second half of table).
## Appendix B – Grain Size Measurements

Table B.1 – Average grain size determination of samples with different thicknesses.

### 17.75 µm

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Average grain size (µm): 0.62

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Average grain size (µm): 0.59

### 39.5 µm

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Table B.2 – Average grain size determination of samples with different sintering temperatures.

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