EFFECTS OF MICROSTRUCTURAL DEFECTS
ON THE PERFORMANCE OF BASE-METAL
MULTILAYER CERAMIC CAPACITORS

A Dissertation in
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by
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ABSTRACT

Multilayer ceramic capacitors (MLCCs), owing to their processing conditions, can exhibit microstructure defects such as electrode porosity and roughness. The effect of such extrinsic defects on the electrical performance of these devices needs to be understood in order to achieve successful miniaturization into the submicron dielectric layer thickness regime.

Specifically, the presence of non-planar and discontinuous electrodes can lead to local field enhancements while the relative morphologies of two adjacent electrodes determine variations in the local dielectric thickness. To study the effects of electrode morphologies, an analytical approach is taken to calculate the electric field enhancement and leakage current with respect to an ideal parallel-plate capacitor. Idealized electrode defects are used to simulate the electric field distribution. It is shown that the electrode roughness causes both the electric field and the leakage current to increase with respect to that of the ideal flat parallel-plate capacitor. Moreover, finite element methods are used to predict electric field enhancements by as high as 100% within capacitor structures containing rough interfaces and porosity.

To understand the influence of microstructural defects on field distributions and leakage current, the real three-dimensional microstructure of local regions in MLCCs are reconstructed using a serial-sectioning technique in the focused ion beam. These microstructures are then converted into a finite element model in order to simulate the perturbations in electric field due to the presence of electrode defects. The electric field is
three times the average value, and this leads to increase in current density of these devices. It is also shown that increasing sintering rates of MLCCs leads to improved electrode morphology with smoother more continuous electrodes, which in turn leads to a decrease in electric field enhancement and calculated leakage current density. To simulate scaling effects, the dielectric layer thickness is reduced from 2.0µm to 0.5µm in the three-dimensional microstructure keeping the same electrode morphology. It is seen that the effect of microstructure defects is more pronounced as one approaches thinner layers, leading to higher local electric field concentrations and a concomitant drop in insulation resistance. It is also seen that the electric field values are as high as 3.8 times the average field in termination regions due the disintegrated structure of the electrodes.

In order to assess the effect of microstructure on MLCC performance, two sets of multilayer capacitors subjected to two vastly different sintering rates of 150°C/hr and 3000°C/hr are compared for their electrical properties. Capacitors with higher electrode continuity exhibit proportionally higher capacitance, provided the grain size distributions are similar. From the leakage current measurements, it is found that the Schottky barrier at the electrode-dielectric interface controls the conduction mechanism. This barrier height is calculated to be 1.06 eV for slow-fired MLCCs and was 1.15 for fast-fired MLCCs. This shows that high concentration of electrode defects cause field perturbations and subsequent drop in the net Schottky barrier height. These results are further supported by frequency-dependent impedance measurements. With temperature dependence behavior of current-voltage trends we note that below temperatures of 135°C, the conduction is controlled by interfacial effects, whereas at higher temperatures it is
consistent with bulk-controlled space charge limited current for the samples that are highly reoxidized.

The final part of this work studies the various aspects of the initial stages of degradation of MLCCs. MLCCs subjected to unipolar and bipolar degradation are studied for changes in microstructure and electrical properties. With bipolar degradation studies new insights into degradation are gained. First, the ionic accumulation with oxygen vacancies at cathodes is only partially reversible. This has implications on the controlling interface with electronic conduction. Also, it is shown that oxygen vacancy accumulation near the cathodes leads to a drop in insulation resistance. The capacitance also increases with progressive steps of degradation due to the effective thinning of dielectric layer. The reduction in interfacial resistance is also confirmed by impedance analysis. Finally, it is observed that on degradation, the dominant leakage current mechanism changes from being controlled by cathodic injection of electrons to being controlled by their anodic extraction. Some of the key discoveries and conclusions established under this dissertation are:

1. Local electric fields are strongly perturbed through microstructure defects at the electrode interface of MLCCs.
2. Enhanced leakage currents result from the local field, and increasingly gain importance in the miniaturization to submicron MLCCs.
3. Methodologies that incorporate focused ion beam milling and imaging can provide excellent data on the morphological distribution within multilayer structures at the mesoscale.
4. Fast firing processes limit the defect size and densities at the electrode interfaces and offer enhanced MLCC performance for thin-layer devices.

5. High temperature conductivity above 135°C in reoxidized samples is bulk controlled, and this has implications on interpreting the highly accelerated lifetime tests.

6. Local non-stoichiometry in regard to base metal MLCCs exist even after reoxidation treatments and provide local field enhancement in addition to the morphological defects.

7. Electromigration of oxygen vacancy defects are only partially reversible and permanent non-stoichiometric regions can exist at the interfaces.

8. Bipolar degradation schemes with partial degradation result in a variety of microstructural, stoichiometric, and electrical changes.

9. A self-consistent explanation of these effects gives compelling evidences of interface controlled conduction in n-type oxides, with rate-limiting conduction often being controlled at the dielectric-electrode interfaces through a field-assisted thermionic emission process, and field enhanced microstructural and stoichiometric features overriding in many cases the electron injection at the cathodic electrode.
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Chapter 1

INTRODUCTION

1.1 Motivation

Multi-layer ceramic capacitors (MLCCs) consist of numerous, often hundreds of, parallel-plate capacitors connected to maximize capacitive volumetric efficiency. Recent trends in MLCC manufacturing revolve around reducing the dielectric thickness of these devices to submicron levels in order to achieve higher capacitance. State-of-the-art MLCCs having dielectric layer thickness as low as 0.5 µm have been manufactured using the tape casting technique.

However, interfacial defects, non-stoichiometry, and other physical imperfections become extremely important to control at this length scale, as there is little room for error in the manufacturing process. Moreover, this thickness reduction comes with a caveat: for a given rated voltage, the electric field across a single layer increases as the layer thickness decreases, thus adversely impacting the lifetime of an MLCC in the circuit. Also, the insulation resistance of such devices does not scale linearly with active layer thickness, often decreasing rapidly as they tend to thinner layers, thus leading to higher values of leakage current and reduced operating voltage.

Over the past decade, the average dielectric layer thickness has decreased and the applied electric field has increased leading to concerns regarding the reliability of
MLCCs (Figure 1.1). Interestingly, in order to tackle this problem, MLCC manufacturers tend to reduce the BaTiO$_3$ grain size in order to pack more grains across the thickness of the dielectric layer and thus, maintain the grain boundary resistance. However, due to size effects, smaller grains lead to lower permittivity and thus lower capacitance.$^{1-3}$

![Graph: Dielectric Thickness vs Electric Field](image)

**Figure 1.1**: Trend of dielectric layer thickness and electric field.$^4$

Furthermore, in thin-layer dielectrics the effects of microstructural heterogeneities will be much more significant, especially in terms of local electric field enhancements at electrode discontinuities and roughness, and eventually device performance. As the dielectric layer thickness is reduced, the majority of insulation resistance is contributed by the metal-dielectric interface. Hence, controlling the morphology of electrodes is critical for sustained performance of thin-layer MLCCs. To help solve this problem, a
better understanding of the three-dimensional microstructure in real multilayer devices is required. Such information would enable in accurate estimation of electric fields in these devices using finite element modeling, and thus identify the weak-spots where failure is most likely to happen. It would also be instrumental in predicting the performance of MLCCs as the dielectric layer thickness is reduced, keeping the electrode morphology the same. Previously, faster sintering rates have been found to improve the electrode morphology of MLCCs and their overall performance.\textsuperscript{5, 6} The three-dimensional microstructure analysis would be helpful in explaining this causal relationship between electrode morphology and device performance. Figure 1.2 sums up the factors that are believed to be critical for improved performance of MLCCs.

![Figure 1.2: A schematic illustrating the impact of processing on microstructure and device performance.](image-url)
A significant amount of effort has also gone into understanding the degradation mechanisms of perovskite dielectrics.\textsuperscript{7-9} It is generally believed that the degradation in the resistance of MLCCs is initiated by the time-dependent electromigration of oxygen vacancies that are produced during co-firing of MLCCs in reducing conditions.\textsuperscript{10-13} The kinetics of this degradation process depend on several processing variables such as dielectric and electrode chemistry, layer thickness and lay-down, processing temperatures and pO\textsubscript{2}, sintering rates, all of which affect the microstructure and distribution of dopants and point defects within the material.\textsuperscript{14-17} However, what needs to be understood is whether this degradation is a reversible process when there is an electromigration of the positively charged oxygen vacancies to the blocking cathode. This can be achieved by allowing a partial degradation of MLCCs at a single bias, reversing the bias in some cases, and allowing a partial degradation to occur in the opposite direction, as illustrated in figure 1.3.

![Diagram showing the degradation mechanisms of MLCCs](image)

Figure 1.3: Oxygen vacancies in the dielectric tend to pileup at the cathode during degradation. The schematic poses questions about the reversibility of this pileup in the event of reversal of electrode polarities.
What also needs to be understood are the changes taking place in the device characteristics (capacitance, impedance, and leakage current) of MLCCs during the course of the degradation and the mechanism responsible for those changes. The analysis of the aforementioned properties in partially degraded MLCCs would provide some valuable insight into the degradation mechanism in these devices.

1.2 Objectives and Dissertation Organization

The objective of this work is to identify and evaluate various defects arising out of MLCC processing and quantify their impact on device performance and reliability. As the dielectric and electrode layer thicknesses are scaled down and approach the same length scale as the dielectric grain size, microstructural imperfections become increasingly influential on the device electrical performance. Specifically, local electric field enhancements due to these electrode defects tend to increase the leakage current density and reduce the insulation resistance of the MLCCs. Also, the degradation of MLCCs is accompanied by micro-chemical oxygen stoichiometry changes.

The first part of the dissertation will concentrate on identifying the various electrode defects in MLCCs. The effects of these defects on electric field distribution will be analyzed using finite element modeling of idealized electrode defects such as roughness and porosity. Additionally, an analytical approach will be used to represent electrode roughness and calculate electric field and leakage current.

The second part of the dissertation revolves around quantifying the three-dimensional microstructure aspects of real MLCCs. A reconstruction will be done using
images taken from serial sectioning using the focused ion beam. This 3D microstructure will be used to calculate the effect of electrode defects on electric field and leakage current. The effect of scaling down the dielectric layer thickness will also be discussed using the 3D microstructure images. This will guide future manufacturing of MLCCs.

The third part of the dissertation will discuss the effect of faster sintering rates of green MLCC chips on their microstructure. Slow-fired and fast-fired MLCCs will be compared for their microstructure and subsequent electrical properties such as leakage current, capacitance, and impedance. This will advocate advantages of fast firing with regard to future MLCC production.

The final part of the dissertation is focused on the degradation phenomena of MLCCs. Partially degraded MLCCs are studied for their electrical properties and changes in microchemistry, especially oxygen stoichiometry, using TEM EELS analysis. Specifically, the electromigration of oxygen vacancies and the reversibility of this phenomenon have been studied by comparing MLCCs that have been degraded in both forward and reverse bias direction. The degradation mechanisms have also been analyzed using these studies. New insights are gained when comparing data obtained in this work with recent Kelvin probe data from the Murata group.

Finally, based on these studies some conclusions have been drawn. Also, techniques that better characterize the microstructure of real multilayer ceramic devices have been developed. Some of the possible avenues for further research have also been discussed.

The appendix section describes in detail the method of Schottky barrier calculation using the current-voltage data collected from MLCCs.
1.3 References


2.1 The Physics of Capacitors

2.1.1 Introduction to Capacitors

A capacitor is a device that stores electrical charge. Capacitance $C$ is a measure of the ability of two conductors in close proximity to hold an electrical charge $q$ under the influence of an external electric potential difference $V$ across them and is defined as:

$$ C = \frac{q}{V} \quad (2.1) $$

where $C$ is in Farads, $q$ is in Coulombs, and $V$ is in Volts. The capacitance of a vacuum capacitor is only dependent on its geometry. For example, the capacitance of a parallel plate vacuum capacitor $C_0$ is given by:

$$ C_0 = \frac{\varepsilon_0 a}{d} \quad (2.2) $$

where $\varepsilon_0$ is the permittivity of free space and its value is $8.854 \times 10^{-12}$ F-m$^{-1}$, $a$ is the area of the two plates, and $d$ is the separation between them. However, if a dielectric material is placed between the electrode plates, the capacitance $C$ is increased, and is given by:

$$ C = \frac{\varepsilon a}{d} = \frac{\varepsilon \varepsilon_0 a}{d} \quad (2.3) $$

Chapter 2

BACKGROUND STUDY

2.1 The Physics of Capacitors

2.1.1 Introduction to Capacitors

A capacitor is a device that stores electrical charge. Capacitance $C$ is a measure of the ability of two conductors in close proximity to hold an electrical charge $q$ under the influence of an external electric potential difference $V$ across them and is defined as:

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$$ C = \frac{\varepsilon a}{d} = \frac{\varepsilon \varepsilon_0 a}{d} \quad (2.3) $$
where $\varepsilon$ is the dielectric permittivity, and $\varepsilon_r$ is the relative permittivity of the material placed between the plates of the capacitor. Thus, higher the relative permittivity, the higher the capacitance, and thus the more charge that can be stored for a given voltage. Capacitors are used in several applications including blocking, coupling and decoupling, a.c.-d.c. separation, filtering and energy storage. The electrostatics of a parallel plate capacitor with applied bias $V$ is illustrated in figure 2.1.

![Figure 2.1: The electrostatics of a parallel plate capacitor. Here $t$ is the thickness of the two conducting plates, and $d$ is the separation between them. The variation of net charge density $\rho$, electric field $E$ and potential difference $V$ is shown.](image)

Poisson’s equation for the potential distribution $\phi$ in the presence of a free charge distribution $\rho_f$ is given by:

$$\nabla^2 \phi = -\frac{\rho_f}{\varepsilon} \quad (2.4)$$

where $\varepsilon$ is the permittivity of the medium between the two plates.
If the free charge density between the two plates is zero, equation (2.4) reduces to a Laplace form given by:

\[ \nabla^2 \phi = 0 \tag{2.5} \]

which can be solved for the one-dimensional problem in figure 2.1:

\[ \frac{\partial^2 \phi}{\partial x^2} = 0 \tag{2.6} \]

Here, the boundary conditions are given by \( \phi(-d/2)=0 \), and \( \phi(d/2)=V \). Thus:

\[ \phi(x) = \frac{V}{d} x + \frac{V}{2} \tag{2.7} \]

Also, the negative gradient of electric potential gives the electric field:

\[ E = -\nabla \phi \tag{2.8} \]

Thus, differentiating equation (2.7) with respect to \( x \) yields:

\[ E(x) = -\frac{V}{d} = \text{Constant} \tag{2.9} \]

This is also illustrated in figure 2.1, where the field is constant between the plates and equals \( V/d \) in the negative \( x \) direction. Also, the potential difference at any point \( x \) can be given as:

\[ \phi(x) - \phi(0) = \frac{V}{d} x + \frac{V}{2} \tag{2.10} \]

Thus, for an ideal homogeneous parallel plate capacitor, the potential difference increases linearly from the negative electrode to the positive electrode, and the electric field is a constant and is equal to \( V/d \). It should be noted that in the absence of free space charge between the plates, the field is independent of the permittivity of the medium between them. However, the capacitance and charge stored increase with increased permittivity.
2.1.2 Dielectric Theory

Various materials are used as capacitive elements in electronic applications. Important properties in this context include dielectric permittivity, dissipation factor and dielectric strength. Dielectric response results from the short-range motion of charge carriers under the influence of applied electric field. This motion leads to storage of charge and thus, electrical energy. Thus, the dielectric acquires a dipole moment and becomes “polarized”.

Theory of Polarization

There are four primary mechanisms of polarization in ceramics and glasses. Each mechanism involves a short-range motion of charges and contributes to the total polarization of the material.

1. Atomic Polarization

This polarization is attributed to the shift of the valence electron cloud of the atoms within the material with respect to the nucleus, typically occurring at a very high frequency (~$10^{15}$ Hz) due to the smaller mass of participating charges. An absorption peak in the optical range characterizes this mechanism. Hence, the refractive index $n$ of the dielectric is related to its relative permittivity at optical frequency as follows:

\[ n^2 = \varepsilon_r \] (2.11)
2. Ionic Polarization

The ionic polarization is attributed to the displacement of positive and negative ions in a material with respect to each other, typically occurring at frequencies in the infrared (IR) range \(10^{12} - 10^{13}\) Hz. An absorption peak in the IR range also characterizes this mechanism.
3. Dipolar Polarization

Dipolar effects contribute to polarization in the sub IR range. It is broadly divided into two categories. In the first category, which occurs at high frequencies \((10^9 - 10^{10})\) Hz, molecules of liquid or polymers containing a permanent dipole moment can rotate, giving rise to a net dipole orientation in the direction of applied field. This mechanism is often referred to as orientation polarization. The second category of dipolar polarization involves reorientation of individual dipoles within the ionic structure of an insulator between two or more equilibrium positions. This typically occurs in low frequency range \((10^3 - 10^6)\) Hz. In ferroelectric materials, polarization occurs through the motion of domain walls so that the domain in the direction of the applied field grows in size. As opposed to atomic and ionic polarizations that are resonance processes and temperature independent, the dipolar polarization is a relaxation process and is strongly temperature dependent.

4. Space Charge Polarization

This mechanism occurs when a physical barrier such as a grain boundary or a phase boundary impedes mobile charge carriers. The charge pile-up at the barriers gives rise to a space charge. Similar to the dipolar polarization, space charge polarization is also a relaxation process and is temperature dependent.

In the presence of these mechanisms the net polarization vector \(P\) (units of \(\text{C/m}^2\)) can be given by:

\[
P = P_{\text{atomic}} + P_{\text{ionic}} + P_{\text{dipolar}} + P_{\text{space-charge}} \tag{2.12}
\]
If a dielectric material is present, the dielectric displacement vector $D$ (units of C/m$^2$) is given by:

$$D = \varepsilon_0 \varepsilon_r \vec{E}$$  \hspace{1cm} (2.13)

But the displacement is also the sum of electric field displacement in the vacuum and the net polarization of the material:

$$\vec{D} = \varepsilon_0 \vec{E} + \vec{P}$$  \hspace{1cm} (2.14)

Thus, rearranging equations (2.13) and (2.14), the polarization vector can be given by:

$$\vec{P} = \varepsilon_0 (\varepsilon_r - 1) \vec{E} = \chi \varepsilon_0 \vec{E}$$  \hspace{1cm} (2.15)

where $\chi$ is the linear dielectric susceptibility. Under the influence of an a.c. field, the polarization oscillates with the field and hence, the complex permittivity $\varepsilon^*$ is expressed as follows:

$$\varepsilon^* = \varepsilon' - j \varepsilon''$$  \hspace{1cm} (2.16)

where $\varepsilon'$ is the dielectric permittivity which denotes the charge storage, $\varepsilon''$ is the dielectric loss factor, and $j = \sqrt{-1}$. Figure 2.3 shows the variation of the $\varepsilon'$ and $\varepsilon''$ with frequency and the various polarization mechanisms contributing to it. The loss tangent ($tan \ \delta$), also known as dissipation factor, is the ratio of the imaginary and real part of permittivity and is illustrated in figure 2.4.
Figure 2.3: Variation of $\varepsilon'$ and $\varepsilon''$ with frequency. The figure also illustrates the contributions from various polarization mechanisms to the permittivity.\textsuperscript{1}

Figure 2.4: Permittivity in the complex plane.
2.2 Multilayer Ceramic Capacitors

Multilayer ceramic capacitors consist of numerous dielectric layers sandwiched between internal interdigitated electrodes in order to achieve very high volumetric capacitance. The electrodes are then terminated at the two ends with external electrodes to give rise to several plate capacitors connected in parallel. Thus, if there are \( n \) electrode layers with dielectric layers of relative permittivity \( \varepsilon_r \) sandwiched between them, then the total capacitance of the MLCC is expressed as:

\[
C_{\text{tot}} = (n - 1) \frac{\varepsilon_0 \varepsilon_r a}{d} \quad (2.17)
\]

where \( a \) is the area of the two electrodes and \( d \) is the separation distance between them.

![Figure 2.5: Schematic of an MLCC and its equivalent circuit.](image)

The schematic of an MLCC and the equivalent circuit representing it are shown in figure 2.5. Over the past decade, a lot of effort has gone in achieving higher volumetric capacitance in MLCCs by reducing the dielectric layer thickness and thus accommodating more number of layers in the MLCCs.\(^2\), \(^3\)
Typically, barium titanate (BaTiO₃) is the material of choice for the dielectric layer in MLCCs. The internal electrodes are made up of either precious metal (Pd, Ag, or Pd-Ag alloy) or base metal (Ni), which is fast replacing precious metal electrodes due to cost considerations. The processing of MLCCs broadly involves the following steps:

1. Tape casting of slurry made out of fine-ceramic powder into sheets of given thickness.
2. Screen-printing of electrode ink made out of fine metal powder on the tape-cast ceramic sheets.
3. Stacking of those sheets and cutting them into the given case-size of capacitors
4. Sintering the green MLCC chips
5. Applying termination copper paste and sintering

The details of the processing conditions of MLCCs are discussed later in this chapter.

Table 2.1: EIA specifications for various classes of MLCCs

<table>
<thead>
<tr>
<th>EIA code</th>
<th>Temperature Range (°C)</th>
<th>EIA code</th>
<th>Capacitance Change (based on 25° C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>X5</td>
<td>-55 to +85</td>
<td>D</td>
<td>±3.3%</td>
</tr>
<tr>
<td>X7</td>
<td>-55 to +125</td>
<td>E</td>
<td>±4.7%</td>
</tr>
<tr>
<td>X8</td>
<td>-55 to +150</td>
<td>F</td>
<td>±7.5%</td>
</tr>
<tr>
<td>Y5</td>
<td>-30 to +85</td>
<td>P</td>
<td>±10%</td>
</tr>
<tr>
<td>Z5</td>
<td>+10 to +85</td>
<td>R</td>
<td>±15%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>S</td>
<td>±22%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>T</td>
<td>+22 to -33</td>
</tr>
<tr>
<td></td>
<td></td>
<td>U</td>
<td>+22 to -56</td>
</tr>
<tr>
<td></td>
<td></td>
<td>V</td>
<td>+22 to -82</td>
</tr>
</tbody>
</table>
Based on their operating temperature range and the corresponding change in capacitance, MLCCs can be classified into several categories defined by the Electronics Industries Alliance (EIA) (shown in Table 2.1). Thus, for an X5R based capacitor, the capacitance value at 25°C changes by no more than ±15% in the temperature range of -55 to +85 °C. Presently, state of the art MLCCs have case-sizes as small as 0.01” × 0.005”, with dielectric layers of thickness less than 0.5 µm.4

2.2.1 Barium Titanate-based Dielectrics

Barium titanate (BaTiO₃) is one of the most widely used ceramic dielectric for MLCC applications. It has a perovskite crystal structure (figure 2.6), which is based on the mineral perovskite (CaTiO₃). In a typical cubic perovskite unit cell, 8 Ba²⁺ ions sit at the corners, 6 O²⁻ ions are at the face-centers, and the lone Ti⁴⁺ ion is situated at the body center. Thus, the Ti ion occupies the center of the oxygen octahedral interstice.

![Figure 2.6: Perovskite unit cell of BaTiO₃. The dotted lines highlight the oxygen octahedral interstice containing the Ti⁴⁺ ion.](image-url)
The crystal structure of BaTiO$_3$ varies with temperature as shown in figure 2.7. It is cubic above the Curie temperature (~120°C). Below the Curie temperature, the unit cell is distorted to a tetragonal phase with Ti$^{4+}$ ion being slightly off-centered along the c-axis. Similarly, the unit cell is orthorhombic below 5°C with the Ti$^{4+}$ ion being off-centered along the <110> direction, and rhombohedral below -90°C with the Ti$^{4+}$ being slightly shifted along the body-diagonal (<111> direction). These distortions give rise to a net dipole moment in the unit cell. This dipole is reorientable between equivalent directions and gives rise to ferroelectricity.

Barium titanate is used in MLCCs because it exhibits very high permittivity, which is attributed to contributions from large dipolar polarizability and domain wall motions. Figure 2.8 shows the variation of the relative permittivity of BaTiO$_3$ with temperature measured along the $a$ and $c$ directions. The abrupt changes in the relative permittivity correspond to the phase transitions.
The paraelectric to ferroelectric phase transition in BaTiO$_3$ occurs at the Curie temperature ($T_C \sim 120\, ^\circ C$). It has been observed that just above this temperature, the Curie-Weiss law gives the variation of susceptibility with temperature as follows:  

$$\chi = \frac{C}{T - T_C}$$  

(2.18)

where $C$ is the Curie constant and is about $1.5 \times 10^5 \, K$ for pure BaTiO$_3$. However, in order to meet industry standards, the capacitance of MLCC needs to be fairly uniform in a given operating range. This is achieved by several different ways:

1. Previous works have shown that reducing the grain size of BaTiO$_3$ suppresses the dielectric permittivity and thus, the temperature variation. Thus, finer grain size would lead to more uniform capacitance as a function of temperature.
2. Altering the grain microstructure to a core-shell structure is also instrumental in achieving uniform dielectric constant. A core-shell structure (figure 2.9) of a grain consists of a pure BaTiO$_3$ core surrounded by a shell doped with several additives such as Mn, Mg, Y, and rare-earth dopants such as Dy, Ho, and Er. This gives rise to diffuse phase transition leading to a uniform capacitance over a temperature range.

3. The development of (Ba$_x$Ca$_{1-x}$)(Ti$_y$Zr$_{1-y}$)O$_3$ solid solution based dielectrics have enabled manufacturers to achieve very high capacitance even at room temperature. These materials are used in the fabrication of Y5V or Z5U type MLCCs.

Figure 2.9: A TEM image of a core-shell grain in X7R-MLCC.
2.2.2 Processing of Barium Titanate for MLCCs

As discussed earlier, the MLCCs are fabricated through a powder-processing route in which tape-cast dielectric layers with screen-printed Ni internal electrodes are stacked together to form multilayer structures. The slurry used for tape casting consists of the dielectric powder of the requisite formulation and microstructure, and an organic binder. The tape cast and stacked multilayer structures are then subjected to a binder removal process consisting of a temperature hold at around 600°C for 8h in a reducing atmosphere with a pO$_2$ range of 10$^{-8}$ -10$^{-10}$ atm in order to burn out the organic binder. This is followed by a sintering step at around 1300°C for complete densification of the MLCCs. Increasing costs of Pd have led to a widespread use of base metals such as Ni as the electrode material for MLCCs.$^3$ However, unlike precious metals such as Pd and Ag, which are stable under oxidizing conditions during the sintering of green MLCCs, Ni tends to oxidize under such an atmosphere at ~1300°C as shown in figure 2.10. Hence, the BME MLCCs are subjected to sintering under reducing conditions in a pO$_2$ range of 10$^{-12}$ -10$^{-10}$ atm.

But sintering the BaTiO$_3$ under reducing conditions affects the reliability and degradation resistance of the MLCCs adversely.$^{23, 24}$ This can be explained by the following defect reaction using Kroger-Vink notation:$^{25}$

$$ O^x_o \rightarrow \frac{1}{2} O_2 + V_o + 2e^- $$  (2.19)

According to this reaction, under a reducing atmosphere, oxygen from the lattice escapes, leaving behind a positively charged oxygen vacancy and two electrons for charge compensation, which reduces the resistivity of the dielectric. In order to improve the
insulation resistance of the MLCC, a reoxidation annealing step at ~800-900 °C in a pO₂ of ~10⁻⁸ atm is employed for 8 h. Yang et al. have demonstrated the improvement of insulation resistance of X7R MLCCs with the reoxidation process.²⁶ Another way to improve the insulation resistance is the use of amphoteric dopants to suppress the formation of oxygen vacancies.²⁷-³² However, despite these treatments the oxygen vacancy concentrations are considerable, and so the BaTiO₃ acts as an n-type dielectric.

Figure 2.10: Stability of base metals against oxidation as a function of temperature and oxygen partial pressure. In order to avoid oxidation, the sintering conditions have to stay below the curves for corresponding electrode metals.²²
Rapid miniaturization of MLCCs over the past decade has placed the onus on the capacitor industry to reduce the dielectric layer thickness in order to maintain capacitance, as is given by equation (2.17). However, this comes at a cost. Previous works by Vollman et al. have shown the importance of grain boundaries in maintaining the insulation resistance of BaTiO₃ and SrTiO₃. This was due to the formation of a double Schottky barrier (figure 2.11) at the grain boundaries because of a space-charge layer resulting from a higher concentration of dopants. Hence, reducing the dielectric layer thickness without changing grain size would imply a lesser number of grain boundaries and thus, reduced grain boundary resistance to degradation. Thus, fine-grained ceramics need to be used for the dielectric layer in order to have more grain boundaries across the thickness.

Figure 2.11: A schematic of a double Schottky barrier at the grain boundary due to a concentration gradient of dopant, which form a space charge layer.
Moreover, with reduced dielectric layer thickness, the majority of the insulation resistance is provided by the metal dielectric interface. Hence, controlling the quality and stability of this interface, especially at thinner layers, becomes very critical.

### 2.2.3 Time-dependent Degradation Mechanism in MLCCs

The loss of insulation resistance in MLCCs is generally referred to as degradation. Such a phenomenon is generally time-dependent and is accompanied by a steady increase in the leakage current after a certain period of usage. When this leakage current increases beyond a certain point, the MLCC can no longer be operated at its rated voltage. It has been long understood from the work of Buessem et al. and Waser et al. that degradation in resistance is initiated by the oxygen vacancy migration toward the cathode over time.\textsuperscript{37-40} A significant amount of effort by Chazono et al. and others has gone into understanding the effect of processing on degradation behavior of Ni-based MLCCs.\textsuperscript{41-46} The grain boundaries, with adequate doping, can act as electrical barriers against oxygen vacancies.\textsuperscript{41, 47-49} Schottky barriers at the electrode interfaces also help in preventing electron injection into the dielectric. Impedance analysis by Yang et al. has shown clear evidence of degradation-induced drops in resistance contributions from the electrode interface, grain boundaries and grains (figure 2.12).\textsuperscript{49} However, of all these components, the most significant drop in resistance is observed at the electrode interface.
Figure 2.12: Change in insulation resistance as a function of temperature for as-produced and degraded MLCCs. It must be noted that resistance of electrode interface ($R_E$) is always greater than resistance of grain boundaries ($R_{GB}$), which in turn is greater than the resistance of grains ($R_G$). \(^{49}\)

Figure 2.13: High-resolution TEM images of the (111) planes showing long range ordered structures (indicated by white arrows) in BaTiO$_3$ grains near the cathode of degraded MLCCs. \(^{50}\)
In addition TEM studies near the electrode interface by Yang et al. have revealed significant changes in microstructure and even crystal structure. Figure 2.13, for example, shows the presence of a defect phase near the cathode of a degraded MLCC. The insert shows electron diffraction pattern with the basic reflections of the perovskite phase along with the superlattice reflection associated with the ordered vacancies. Electron-energy loss spectroscopy (EELS) analysis also revealed large departures in oxygen stoichiometry in the regions around the cathode leading to a stoichiometry of BaTiO$_{2.7}$, and a mixture of Ti$^{4+}$ and Ti$^{3+}$ in these regions. In fact, impedance studies by Liu et al. have revealed small polaron hopping conduction between Ti$^{4+}$ and Ti$^{3+}$ in the final stages of degradation.

2.3 Conduction Mechanisms in Metal-Insulator Systems

As mentioned earlier, with reducing dielectric layer thickness, the stability of the electrode-dielectric interface plays an increasingly important role in governing the reliability of MLCCs. An important aspect in this regard is to maintain a low leakage current density. It is known that conduction mechanisms in dielectric materials are generally non-ohmic. Several different mechanisms can control the leakage current in metal-insulator-metal systems. Metal-insulator contacts can be Ohmic or rectifying depending on the relative values of their work functions and the type of the majority charge carrier. Thus, if the work-function of metal ($\Phi_M$) is greater than the work-function of a n-type semiconductor or insulator ($\Phi_{S/C}$), then at thermal equilibrium, due to the lining up of their Fermi energy levels, a potential barrier ($\Phi_B$) is formed for any electron
injection from metal into the semiconductor/insulator. It also gives rise to a built-in potential barrier ($V_{bi}$) for electron transport from semiconductor/insulator into the metal. Such a contact is rectifying in nature and is known as Schottky contact. On the other hand, if $\Phi_M < \Phi_{S/C}$, it gives rise to an Ohmic contact. These two scenarios are shown in figure 2.14.

![Schottky Contact](image1.png) ![Ohmic Contact](image2.png)

Figure 2.14: Formation of Schottky and Ohmic contact at the metal-insulator (n-type) interface at thermal equilibrium.

### 2.3.1 Schottky Emission across Electrode-Dielectric Interface

The formation of a Schottky-barrier at the metal-insulator interface can lead to a scenario where the electron would have to be transported across the interface through thermionic excitation over the energy barrier. If the conduction takes place by thermionic emission of electrons from the metal into the conduction band of the semiconductor, it is known as the “reverse-bias” Schottky conduction. However, if the
conduction occurs through thermionic emission of electron from the conduction band of the semiconductor into the metal, it is known as the “forward-bias” Schottky conduction. Both these mechanisms are illustrated in figure 2.15.

![Figure 2.15: Reverse-bias and Forward bias Schottky emission across a metal-semiconductor/insulator (n-type) interface.](image)

Taking the image potential into account, the reverse-bias Schottky controlled current density \( J_{SC} \) is given as:

\[
J_{SC} = A^* T^2 \exp \left( \frac{\alpha E^{1/2} - \Phi_M - \Phi_{S/C}}{k_B T} \right) 
\]  
(2.20)

where \( A^* \) is the Richardson constant for the semiconductor, \( T \) is the absolute temperature, \( \alpha \) is a constant which depends on the relative permittivity, \( E \) is the electric field. The current density due to forward-bias electron emission from semiconductor into metal is given by:

\[
J = J_0 \exp \left( \frac{qV}{nk_B T} \right) 
\]  
(2.21)
where \( V \) is the applied voltage, \( q \) is the electron charge, and \( n \) is the “ideality factor”
\[
\frac{1}{n} = 1 - \frac{\partial \phi}{\partial V} \quad \text{given by:}
\]
(2.22)

Here \( (\partial \phi/\partial V) \) is the change of energy barrier with respect to applied bias \( V \). \( J_0 \) is the saturation current density and is given by:
\[
J_0 = A' T^2 \exp \left( \frac{-\phi_B}{k_B T} \right) \quad (2.23)
\]

Several studies on metal-dielectric systems have reported the occurrence of Schottky conduction mechanism.\(^{26, 41, 56}\) Typically in BME MLCCs, the oxygen vacancy concentration in BaTiO\(_3\) causes it to behave like a n-type dielectric.

### 2.3.2 Poole-Frenkel Conduction

The Poole-Frenkel mechanism is dominant when the leakage current is governed by a large number of charged traps in the bulk.\(^{57}\) Although Poole-Frenkel conduction has not been observed in base-metal electrode BaTiO\(_3\) multilayer capacitors, it is quite common in other dielectric materials.\(^{58-61}\) The Poole-Frenkel current is given as:
\[
J_{PF} = \mu E \exp \left( \frac{-\phi_B}{2k_B T} \right) \exp \left( \frac{2\beta_s E^{1/2}}{k_B T} \right) \quad (2.24)
\]

where \( \beta_s = (e^3/4\pi\epsilon)^{1/2} \) and \( \mu \) is the electronic conductivity.
2.3.3 Fowler-Nordheim Tunneling

On application of a very high electric field or if doping/defect levels near the metal dielectric interface are very high, it can lead to severe band banding, which in turn makes the depletion region very thin. This makes it possible for electrons to tunnel quantum mechanically through the Schottky barrier without any thermionic excitation over it. This phenomenon was first reported by Fowler and Nordheim and is illustrated in figure 2.16. This kind of conduction has previously been observed in (Ba$_x$Sr$_{1-x}$TiO$_3$) films and BaTiO$_3$ MLCCs.

![Figure 2.16: Schematic of electron tunneling through a Schottky barrier due to band-bending under an applied bias of V.](image)

The Fowler-Nordheim tunneling current density is given by:

$$J_{FN} = K_1 \frac{E}{\phi_b} \exp \left( -K_2 \frac{\phi_b^{3/2}}{E} \right)$$ (2.25)

where $K_1$ and $K_2$ are constants related to the electron effective mass.
2.4 Importance of Electrode-Dielectric Interface Morphology

For various thin-film devices, such as capacitors and actuators, thinner dielectric layers with lower electrical leakage current are necessary for advanced performance.\textsuperscript{2,3,65} The device properties, however, can be severely limited by the morphology of the metal-insulator interface. The presence of rough interfaces and electrode discontinuities has been found to be detrimental to the miniaturization of such devices in many ways.\textsuperscript{66-71} Perturbations in the local electric field could either result from local roughness of the interface or from the change in the interelectrode spacing, and thus dielectric layer thickness. Previous works have revealed roughness at metal-insulator interface as sites of electric field enhancement.\textsuperscript{69,72,73} This increase in electric field gives rise to a higher leakage current.\textsuperscript{74-78} The interface roughness has also been found to influence the conductivity of metallic and semiconducting films.\textsuperscript{79-84}

Notably, the magnitude of the increase in leakage current also depends on the relevant conduction mechanism. For example, the Schottky and Poole-Frenkel mechanisms have an exponential dependence on electric field, and hence are extremely sensitive to perturbations in electric field. Kim et al. studied the effect of Al-Ta$_2$O$_5$ interface roughness on leakage current.\textsuperscript{85} It was reported that the transition from Schottky to Poole-Frenkel dominated conduction occurred at a lower applied field for a rougher interface. Thus, not only does roughness perturb the electric field in the Ta$_2$O$_5$ film, it can also change its dominant electrical transport mechanism for a given applied voltage. Recently, Levi et al. reported an enhancement in electric field in BaTiO$_3$ thin films due to the presence of grain boundary grooving on Ni substrates.\textsuperscript{86} This field enhancement in
turn led to a larger leakage current controlled by the forward-bias Schottky conduction at
the anode as opposed to the reverse-bias Schottky mechanism which was observed away
from the grain boundary (figure 2.17).

Figure 2.17: Schematic representation of conduction mechanism with and without grain
boundaries for a BaTiO\textsubscript{3} film on a Ni substrate.\textsuperscript{86}
In the case of multi-layer ceramic capacitors (MLCCs), two microstructural effects become important as the layer thicknesses are decreased. First, electrode discontinuities, which lower the total capacitance through reduced electrode surface area, become more difficult to prevent as the layer thicknesses are decreased.\(^7\) Secondly, the scale of the electrode roughness becomes a more significant fraction of the total dielectric thickness. Concomitant decreases in insulation resistance have been observed with decreasing dielectric layer thickness.\(^8\) As shown by Nakano et al., the presence of electrode defects has a significant effect in terms of reducing the insulation resistance of MLCCs.\(^8\) Polotai et al. demonstrated a considerable improvement in the electrical properties of MLCCs by improving the continuity of their electrodes through unique sintering conditions.\(^7\)

**2.5 Three-dimensional Image-based Finite Element Modeling of Electric Field**

Three-dimensional characterization can be extremely beneficial to assess the effects of microstructure on various properties such as Young’s Modulus, tensile strength, grain-size and connectivity etc.\(^8\) In recent years, serial sectioning has become a well-established technique to reconstruct 3D microstructures from a series of 2D images.\(^9\) The advent of the focused ion beam with dual electron beam capabilities has made it possible to automate the entire process of simultaneous serial sectioning and imaging.\(^9\) Various computer-aided techniques can be utilized to convert these 2D serial section images into a 3D microstructure.
The finite element method (FEM) is a numerical technique for finding solutions of partial differential equations and integral equations. The method involves breaking a system into a finite number of simple discrete elements, which are then reconnected at nodes to form a mesh. A given engineering problem pertaining to this system can then solved for a set of boundary conditions through FEM. P.P. Silvester pioneered the application of FEM in electromagnetism. Several researchers such as Gaillard et al., Fleig et al., and Deken et al. have used this method to solve electrostatic problems in capacitive systems. Specifically, it has been instrumental in showing that the roughness at the interface in various metal-insulator-metal structures were responsible for local electric field enhancement which in turn led to a higher leakage current.

With advances in computational power, image-based finite element modeling has evolved considerably over the last decade, so that it is now possible to incorporate precise 3D features from a reconstructed microstructure into a model, on which various simulations can be carried out to give precise results. Earlier work by Chawla et al. and Lewis et al. were able to use some of these techniques to predict mechanical behavior of various materials. Similar calculations in electrostatics can take into account the superposition effects from all the morphological defects present in a given volume while calculating electric field distribution. They can also reveal the areas with high local electric field in various electrical devices, which could be instrumental in failure analysis.
2.6 References


Chapter 3

EXPERIMENTAL PROCEDURE

3.1 Fabrication of Multilayer Ceramic Capacitors

The MLCCs used in the present study were commercially manufactured using the tape-casting technique. The dielectric was a BaTiO$_3$-based X7R material formulated with chemical additives such as Y$_2$O$_3$ (0.5–1.0 at.%), MgO (~0.5 at. %), Li$_2$O-B$_2$O$_3$-SiO$_2$ (1.0–1.5 at. %) and MnO (~0.1 at. %). The powder was mixed with organic binder such as polyvinyl butaryl (PVB) and a plasticizer, made into a slip and tape-cast into continuous strip of given thickness. The tape was cut into sheets on which the electrode ink was patterned. The sheets were then stacked, consolidated, and diced as illustrated in figure 3.1. This technique exposed the electrodes of successive layers at the two end-faces.

![Figure 3.1: Stacking arrangement and cutting of tape-cast sheets with electrodes printed to form MLCCs. The stack is diced along lines AA’ and BB’ to expose the electrodes at the opposite faces.](image)

2
The tape-cast capacitors were subjected to a typical binder removal process, consisting of a temperature hold between 400°C-600°C under a pO$_2$ of $\sim 10^{-8}$ to $10^{-10}$ atm in order to burn out the organic binder. In order to prevent oxidation of the Ni electrodes, the green MLCC chips were co-fired at $\sim 1300°C$ at a pO$_2$ of $\sim 10^{-10}$ atm. The co-fired MLCCs were then reoxidized at 800°C at a pO$_2$ of $\sim 10^{-8}$ atm. The sintered chips were terminated on the ends with copper electrodes and fired under reducing conditions. The entire schematic of MLCC processing is shown in figure 3.2.

Two different sources of MLCCs with Ni internal electrodes and X7R specifications were used in this study. Most of the microstructure and degradation studies were carried out on non-commercial MLCCs with Ni electrodes and X7R specifications manufactured by KEMET Corporation. The average dielectric layer thickness for those parts was 2.2 µm. The capacitors were of 0805 case-size, which is $0.08'' \times 0.05''$, the number of layers was 475, and the rated voltage was 10V. These structures were sintered at PSU in the atmosphere-controlled facilities in the Center for Dielectric Studies. Some of these MLCCs were also sintered at different rates ranging from 200°C/hr to 3000°C/hr in a custom-built furnace with atmosphere control and rate control capabilities to study their microstructure.

The other set of MLCCs prepared by Mr. Kazumi Kaneda (Taiyo Yuden) comprised of experimental prototyped capacitors with only 10 dielectric layers, each with an average thickness of 3.5 µm. Two different batches of MLCCs were sintered at heating rates of 150°C/hr and 3000°C/hr in the same custom-built furnace. Based on prior work, the difference in heating ramp rates were expected to lead to markedly different
electrode morphologies.¹ These MLCCs were used to study the effect of sintering rates on electrical properties. Also, some of the MLCCs were not given a typical “reoxidation” treatment in order to eliminate the effect of incomplete non-ideal reoxidation reactions in MLCCs.

Figure 3.2: Schematic of MLCC processing.³
3.2 Rate-controlled Sintering of MLCCs

In order to study the influence of sintering rate on microstructure of MLCCs, these devices were sintered in a furnace with rate-control capabilities. The MLCCs were subjected to this sintering step after the binder burnout process. The system is equipped with a programmable temperature controller, which enables the user to program the complete sintering profiles including starting temperatures, heating rates, holding temperatures and times, and cooling rates. The system is also equipped with a gas control apparatus that uses a H₂O-N₂-H₂ gas mixture to control the sintering atmosphere and the pO₂. An in-built pO₂ sensor tracks the oxygen partial pressure. The schematic of the system is shown in figure 3.3 and Table 3.1 lists the parameters that were used during the sintering processes.

Figure 3.3: Schematic of furnace with rate-controlled heating capabilities.
Table 3.1: Various parameters for the rate-controlled sintering step

<table>
<thead>
<tr>
<th>Control Parameter</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Starting temperature</td>
<td>300°C</td>
</tr>
<tr>
<td>Heating rate</td>
<td>150°C/hr – 3000°C/hr</td>
</tr>
<tr>
<td>Holding temperature</td>
<td>1280°C – 1300°C</td>
</tr>
<tr>
<td>Holding time</td>
<td>0 – 2 hr</td>
</tr>
<tr>
<td>Sintering atmosphere pO₂</td>
<td>$10^{-9} – 10^{-12}$ atm</td>
</tr>
<tr>
<td>Cooling rate</td>
<td>3000°C/hr</td>
</tr>
</tbody>
</table>

3.3 Electric Field Calculations using Finite Element Modeling

3.3.1 Idealized Microstructure

The effect of electrode defects on electric field distributions was investigated using the finite element method. The average dielectric layer thickness of the model was 10 µm. The software package ANSYS was used to solve for electric field and potential distributions in the dielectric layer. The element type chosen for the analysis was SOLID231 and the average mesh size of the model was 2.5 µm with some local refinements around defect features. The Laplace equation $\phi$ for electrical potential, denoted in equation 3.1, was solved, with the potential at each electrode as the boundary condition.

$$\nabla^2 \phi = 0 \quad (3.1)$$

The potential is subsequently differentiated with respect to position to give electric field.
Figure 3.4: (a) A model parallel plate capacitor whose electrodes are subjected to potential difference of 1V. The (b) Potential profile (all values are in V), and (c) Electric field profile (all values are in V/m) are evaluated.

Figure 3.4 shows an example of such a simulation for an ideal parallel plate capacitor, whose two electrodes are 10 µm apart, and are subjected to a potential difference of 1V. As expected, across the gap between the electrodes, the potential drops linearly and the electric field is constant.

3.3.2 Three-dimensional Microstructure

For quantitative microstructural analysis, MLCC cross-sections were mechanically polished and ion-beam milled using a dual-beam focused ion
beam/scanning electron microscope (FIB/SEM) (Quanta 200; FEI Company, Eindhoven, The Netherlands) with a 30kV 5nA Ga\(^+\) beam. Serial-section milling and electron-induced secondary electron imaging of the MLCC were performed using the Auto Slice & View\textsuperscript{TM} application in the FIB. Figure 3.5 shows a schematic of the serial sectioning and imaging process. Based on the typical size of the electrode defects, the serial section images were captured at an interval of 250 nm. This was adequate in order to capture the finer features of the microstructure such as electrode roughness and porosity. All the images were captured in the “tilt-correction” mode in the FIB since the electron beam is not normal to the milled cross-section. Subsequently, all the images were aligned before further image processing.

Figure 3.5: Schematic of the serial-sectioning technique using focused ion beam milling.
All the 3D reconstructions and mesh generation were done using the software Avizo. Typically 20-30 serial-section images from the MLCC were taken and combined to form a 3D volume. A typical 3D volume is divided into voxels, where a voxel is a 3D equivalent of a pixel of the 2D image. In the present work, the scale of the voxel was as follows:

$$1 \text{ voxel} = 1 \times 1 \times 6.25 \text{ cubic pixels} = 0.05 \times 0.05 \times 0.25 \mu m^3$$

The original volume is cropped down to a smaller volume consisting of two electrodes for further finite element analysis. This volume can be treated as a parallel-plate capacitor with rough and discontinuous electrodes. Each of the slice-images was segmented into three different phases, electrode, dielectric and porosity, based on the grayscale values. Subsequently, the images were converted into a volume, on which an “adaptive” mesh with size range 2-8 pixels was generated in order to capture the intricate details in the volume. The mesh was subjected to surface simplification and various tests to determine and improve its quality. It was adapted to the local microstructure, thus refining around microscopic features and the electrode-dielectric interface. Typically a meshed model had a total of over 150,000 tetrahedron elements and over 200,000 nodes. The entire meshed volume was exported to COMSOL (figure 3.6), the finite element solver, and solved for potential and electric field distribution for various applied voltage drops across the electrodes using the Poisson’s equation for electric potential, $\phi$, given in equation 3.2:

$$\nabla^2 \phi = -\frac{\rho_f}{\varepsilon}$$  \hspace{1cm} (3.2)

$\rho_f$ is the free charge density, assumed to be zero, and $\varepsilon$ is the permittivity of the dielectric.
Figure 3.6: A typical meshed volume extracted from a three-dimensional microstructure of MLCC.

In order to study the effect of reducing the dielectric layer thickness, the thickness of the dielectric in the serial images were cropped from 40 pixels to 10 pixels in steps of 10, down to a final thickness of 0.5 µm, while keeping the electrode morphology exactly the same. The electric field distribution was calculated for each of these cases. Results are discussed in further detail in chapter 5.

3.4 Partial Degradation of MLCCs

Prototyped MLCCs were subjected to degradation process in a temperature range of 220°C - 230°C at 30V DC bias using a pA meter/DC voltage source HP-4140B (Hewlett Packard). The leakage current reached a steady state value and then gradually increased, signifying the onset of degradation process. However, the MLCCs were not allowed to fail completely, and the DC bias was removed after only a 50-150% increase in leakage current over the steady state value. This is referred to as step-1 of the
degradation process. In some cases, the bias was reversed to -30V, and the MLCCs were allowed to degrade till a 50% - 150% increase in leakage over the steady state value. This is referred to as step-2 of the degradation process. Figure 3.7 shows the typical leakage current as a function of time during step-1 and step-2. The partially degraded MLCCs were studied for their electrical behavior such as current-voltage characteristics, capacitance and impedance. Microscopic analysis was also done in order to ascertain the changes in the material properties during the course of degradation.

![Figure 3.7: Change of leakage current over time for step-1 followed by step-2. Notably, the magnitude of the steady state leakage current is much higher in the second step of degradation. Also, the second step of degradation is much faster than the first step.](image-url)
3.5 Electrical Characterization

3.5.1 Current-Voltage (I-V) Measurements

The conduction mechanisms in MLCCs were studied using current-voltage characteristics. These measurements were made using a pA meter/DC voltage source HP-4140B (Hewlett Packard) and a DC bias from 1V to 20V in the temperature range of 50°C to 170°C. The steady state leakage current was measured after keeping the sample at a constant bias for more than four minutes, and permitting relaxation of the depolarization current. Typical sample size was 2mm × 1.2mm × 1.2mm. Figure 3.8 shows the experimental setup for a current-voltage measurement. Figure 3.9 shows a typical I-V data for an X7R MLCC measured between 90°C and 135°C.

![Experimental setup for a current-voltage measurement of an MLCC.](image)

Figure 3.8: Experimental setup for a current-voltage measurement of an MLCC.
3.5.2 Capacitance and Impedance Measurements

Figure 3.9: Current vs. Voltage of an X7R MLCC at various temperatures under forward and reverse bias.

Figure 3.10: Experimental setup for TCC measurements of a MLCC.
The temperature dependence of capacitance (TCC) was measured in the temperature range of -60°C to 150°C using an HP4284A LCR meter (Hewlett-Packard, Santa-Clara, CA) operated in a frequency range of 100 Hz to 10 kHz without any DC bias. Figures 3.10 and 3.11 show the setup and an example of TCC data for an X7R MLCC respectively.

![Graph of Temperature Capacitance Characteristics (TCC) for an X7R MLCC.](image)

Figure 3.11: Temperature Capacitance Characteristics (TCC) for an X7R MLCC.

The impedance of the MLCCs was measured over the frequency range of 0.1 Hz to $10^6$ Hz at a $V_{\text{rms}}$ of 40 mV using a Solartron SI1287 electrochemical interface and 1255B frequency response analyzer (FRA). The electrochemical impedance software Z-plot™ and Z-view™ were used for analysis and fitting of the impedance data. For as-reduced MLCCs, the impedance measurements were carried out in the temperature range of 240°C to 270°C.
However, for prototyped MLCCs that had been subjected to reoxidation, the impedance measurements had to be carried out at much higher temperature range of 375°C to 450°C in order to lower their impedance to values that could be measured by the system. In order to avoid oxidation of the copper terminations at those temperatures, these measurements were carried out in a N₂ atmosphere. The setup of the impedance measurement system is shown in figure 3.12. The imaginary part of the impedance is plotted with respect to the real part of the impedance with frequency being swept from 10⁶ Hz to 0.1 Hz. Such plots are known as impedance spectra. Figure 3.13 shows a typical impedance spectrum for an X7R MLCC.
Figure 3.13: Impedance spectra for X7R MLCCs from 375°C to 450°C over a frequency range of 0.1 Hz to $10^6$ Hz.

3.6 Scanning Electron Microscopy

The samples for scanning electron microscopy (SEM) imaging of MLCC were prepared by mechanical polishing of MLCC cross-section exposing all the electrodes. The polishing media used were 0.5 µm alumina, followed by 0.02 µm colloidal silica. SEM imaging was performed using a Hitachi S-3000N SEM (Tokyo, Japan) operated at an accelerating voltage of 20kV in a secondary electron imaging mode. Voltage contrast SEM (VC-SEM) was also performed using the same instrument operated at a voltage of 2.5kV and a DC bias of 5 V across the MLCC electrodes. Figure 3.14 shows a special homemade sample holder used for voltage-contrast SEM.
3.7 Transmission Electron Microscopy

3.7.1 Sample Preparation

Two different methods were used to prepare samples for transmission electron microscopy (TEM): (a) the traditional procedure involving polishing and ion milling, and (b) FIB in-situ sample preparation by the total release method.\textsuperscript{5,6}

The traditional method involved cross-section polishing of MLCCs on silicon carbide paper followed by lapping with a diamond solution. Then the polished surface
was glued to the holder and its opposite face was similarly polished till the sample was about 30 µm thick. Then the samples were removed from the holder by immersing in acetone and mounted on to a 3 mm copper grid using an epoxy-based adhesive. The samples attached to the grid were subjected to ion milling using an EA Fishione Model 3000 ion mill operated at 5 kV and 5 mA with an inclination angle of 10-15° for four hours till becoming electron transparent around the milled holes. A final milling for 10 minutes at 3 kV and 3 mA at an angle of 10° was used to remove any ion-beam-induced amorphous layer. Plasma cleaning was also carried out for 10 minutes to remove any remaining surface contaminants.

The FIB *in-situ* method was used to lift off specific regions extracted within the MLCC for TEM analysis. Once this region was identified from the bulk, it was milled out in the FIB and attached to a micromanipulator (Autoprobe 200, Omniprobe Inc., Dallas, TX) using Pt deposition. Then this micromanipulator was translated onto a TEM sample holder (a copper grid) and attached to it. The sample on the grid was further thinned down in the FIB with decreasing ion currents to reduce the ion beam damage. The final ion current used was 30 pA. The sample was then plasma cleaned for 10 minutes to remove any amorphous layer or surface contaminants.

### 3.7.2 TEM analysis

The microstructure and microchemistry were studied using a JEOL-2010 field emission TEM (JEOL, Tokyo, Japan) with an operating voltage of 200 kV. The grain size of the dielectric was measured in the bright-field TEM mode using the transmitted
electron beam. The high-resolution TEM (HRTEM) images were recorded with a Gatan slow-scan CCD camera. Electron energy-loss spectroscopy (EELS) was performed using a Gatan Enfina parallel electron energy-loss spectrometer attached to the JEOL 2010 microscope. The energy resolution measured from the zero-loss peak full width at half maximum (FWHM) was 1.3 eV. EELS were recorded in TEM-diffraction mode with a collection angle of 14 mrad and convergence angle of 3 mrad. In this thesis, earlier methods outlined by Yang et al. were used to quantify the spatial oxygen stoichiometry of BaTiO$_3$.\textsuperscript{7}
3.8 References


Chapter 4

THE EFFECT OF ELECTRODE ROUGHNESS AND POROSITY ON CAPACITANCE, ELECTRIC FIELD ENHANCEMENT AND LEAKAGE CURRENT: IDEALIZED MORPHOLOGY*

4.1 Introduction

In the case of multi-layer ceramic capacitors (MLCCs), there has been a continuous scaling down of both the dielectric and electrode layer thickness to increase volumetric efficiency (capacitance per volume). 1 Two microstructural defects assume importance as the layer thicknesses are decreased. First, there is electrode porosity, which lowers the total capacitance through reduced electrode surface area; this becomes more difficult to prevent as the layer thicknesses are decreased.2 Secondly, there is electrode roughness, whose scale becomes a more significant fraction of the total dielectric thickness with downsizing. It has been shown in the past that insulation resistance decreases with decreasing dielectric layer thickness, with electrode defects playing a significant role in this reduction.3,4 Polotai et al. also showed that the electrical properties of MLCCs improved considerably by improving the continuity of their electrodes through fast and complex sintering profiles.5

This chapter quantitatively investigates the effect of idealized electrode defects on the electric field and leakage current in MLCCs. Two different effects arising from electrode roughness are studied. First, the non-uniformity of the dielectric layer thickness due to electrode roughness is studied analytically. The resulting electric field and leakage current are calculated with idealized morphologies. Secondly, the local effects of electrode roughness on electric field distribution are also studied using finite element modeling. A finite element analysis is also used to model and study the effect of electrode porosity on electric field distribution and leakage current inside the dielectric layer.

4.2 Defects in MLCCs

The SEM micrograph in figure 4.1 shows the different kinds of microstructure defects that are present in the MLCC electrodes. These electrodes have pores and also are uneven or rough. There are two possible extremes in which these uneven electrodes can be aligned with respect to each other - the troughs and crests of the two electrodes are either in phase with each other (Type I) or are out of phase (Type II) as shown in the figure. Figure 4.2 shows a cross-section of a MLCC in the VC-SEM mode. In this mode, the negatively biased electrode appears bright and the positively biased electrode appears dark. However, some regions around pores in the positive electrodes appear bright, indicating that electrode defects cause non-uniformity in electric potential distribution, which leads to local electric field enhancement around these defects.
Figure 4.1: SEM micrograph of a MLCC cross-section showing the presence of various electrode defects such as roughness and pores.

Figure 4.2: SEM micrograph of a MLCC cross-section in a voltage contrast mode. The brighter electrodes are negatively biased and the darker electrodes are positively biased.
4.3 Analytical Study of the Effect of Non-uniform Dielectric Layer Thickness

The interface between the dielectric and metal electrodes in a multilayer ceramic capacitor displays numerous undulations, which can be characterized as type I or type II, as shown in figure 4.1. In order to model electrode roughness effects, the metal-dielectric interface is undulated with a particular amplitude and wavelength. Figures 4.3(a) and 4.3(b) show the type I and type II electrode alignments respectively. The surface of each electrode is approximated as a sinusoidal function given by:

\[ R(x) = A \sin\left(\frac{2\pi}{L} x \right) \]  

(4.1)

where, \( A \) is the amplitude of roughness and \( L \) is the wavelength. The mean dielectric layer thickness is \( d_0 \), and \( x \) is the direction along the length of the cross-section.

Figure 4.3: Interdigitated model capacitor: Two cases of relative alignment of uneven electrodes: (a) Type I, and (b) Type II. Here \( d_0 \) is the mean dielectric layer thickness, \( A \) is the amplitude of roughness and \( L \) is the wavelength.
4.3.1 Capacitance

The presence of unevenness in electrodes is expected to have an effect on the capacitance, which is a function of both the area of the electrodes and the distance between them. The relative position of unevenness in the opposite electrodes would affect the electrode area and the interelectrode distance. Therefore, the analytical treatment for type I and type II capacitors would be different.

A. Type-I capacitors

In type-I capacitors, the distance between the electrodes constantly changes as a function of position. Hence, in order to solve for capacitance analytically, each dielectric layer can be assumed to be comprised of smaller discrete capacitors connected in parallel. The distance between the electrodes at any position $x$ is given by:

$$d = d_0 + 2A \sin\left(\frac{2\pi}{L} x\right)$$  \hspace{1cm} (4.2)

It has been assumed that the unevenness of electrodes is unidirectional, i.e. $d$ is constant in the $z$ direction. Thus the area of an elemental capacitor equals the product of the capacitor depth $t$ and the elemental length $dx$ and the elemental capacitance is given by:

$$dC = \frac{\varepsilon t}{d_0 + 2A \sin\left(\frac{2\pi}{L} x\right)} dx$$ \hspace{1cm} (4.3)

If the number of undulations, each of length $L$ is $N$, the total length over which the capacitance has to be integrated is $NL$. So the net capacitance is given by:

$$C = \int_{0}^{NL} \frac{\varepsilon t}{d_0 + 2A \sin\left(\frac{2\pi}{L} x\right)} dx$$ \hspace{1cm} (4.4)
The net capacitance for an ideal parallel plate capacitor of length $NL$, depth $t$, and thickness $d_0$ is given by:

$$C^0 = \frac{\varepsilon t NL}{d_0} \quad (4.5)$$

The ratio of $C$ and $C^0$ can give us the normalized capacitance for type I capacitors:

$$\frac{C}{C^0} = \frac{d_0}{NL} \int_0^{NL} \frac{1}{d_0 + 2A \sin\left(\frac{2\pi}{L} x\right)} dx \quad (4.6)$$

Appropriate substitution for $\frac{2\pi}{L} x = \theta$ in equation (4.6) gives:

$$\frac{C}{C^0} = \frac{1}{2N\pi} \int_0^{NL} \frac{1}{1 + 2 \frac{A}{d_0} \sin\theta} d\theta \quad (4.7)$$

From equation (4.7) it can be seen that the normalized capacitance is only a function of the ratio $A/d_0$. From figure 4.4, it can be seen that a higher $A/d_0$ ratio in type I capacitors gives rise to a higher capacitance.

**B. Type-II capacitors**

In type-II capacitors the distance between the electrodes remains constant and equal to that of an ideal capacitor, $d_0$, but the net area between the electrodes is more than that of an ideal capacitor. Hence, calculating the net capacitance requires computing the length of the curve representing the uneven electrode surface:

$$C = \frac{\varepsilon t}{d_0} \int_0^{NL} \sqrt{1 + \frac{4\pi^2 A^2}{L^2} \cos^2\left(\frac{2\pi}{L} x\right)} dx \quad (4.8)$$
Figure 4.4: Normalized capacitance of type I capacitors as a function of amplitude of unevenness, $A$, for different values of dielectric layer thickness, $d_0$.

The above calculation assumes that there are $N$ undulations, each of length $L$.

Using equation (4.5) the normalized capacitance for type II capacitors is given as:

$$\frac{C}{C^0} = \frac{1}{NL} \int_0^{NL} \left[ 1 + \frac{4\pi^2 A^2}{L^2} \cos^2 \left( \frac{2\pi x}{L} \right) \right] dx$$  \hspace{1cm} (4.9)

Appropriate substitution for $\frac{2\pi x}{L} = \theta$ in equation (4.9) gives:

$$\frac{C}{C^0} = \frac{1}{2N\pi} \int_0^{2N\pi} \left[ 1 + \frac{4\pi^2 A^2}{L^2} \right] \cos^2 \theta d\theta$$  \hspace{1cm} (4.10)
From equation (4.10) it can be seen that the normalized capacitance depends only on the ratio $A/L$, which is different from type I. From figure 4.5, it is seen that the normalized capacitance increases for higher values of $A/L$.

Figure 4.5: Normalized capacitance of type II capacitors as a function of amplitude of unevenness, A, for different values of wavelength of roughness, L.
4.3.2 Electric Field Distribution

Assuming that the dielectric material has uniform electrical properties and single crystal structure, the only determining factor for electric field would be the distance between the parallel plates and hence dielectric layer thickness. The dielectric layer thickness for type I capacitors as a function of position is given by:

\[ d = d_0 + 2A \sin \left( \frac{2\pi x}{L} \right) \]  \hspace{1cm} (4.11)

Hence, the electric field as a function of position for an applied potential \( V \) is:

\[ E = \frac{V}{d} = \frac{V}{d_0 + 2A \sin \left( \frac{2\pi x}{L} \right)} \]  \hspace{1cm} (4.12)

The electric field for a perfect parallel plate capacitor is constant and is given as:

\[ E^0 = \frac{V}{d_0} \]  \hspace{1cm} (4.13)

Thus, the normalized electric field for type I capacitors is:

\[ \frac{E}{E^0} = \frac{1}{1 + 2 \frac{A}{d_0} \sin \left( \frac{2\pi x}{L} \right)} \]  \hspace{1cm} (4.14)

Here it can be noted that the normalized electric field is a function only of the \( A/d_0 \) ratio. The normalized electric field can exceed unity for a range of values of the position \( x \), thus indicating local electric field enhancement.

For type II capacitors, the dielectric thickness is constant and hence the average electric field remains constant in this simple analytical treatment.
4.3.3 Leakage Current Density

It is known that the conduction mechanisms in dielectric materials are generally non-Ohmic. Various mechanisms like Schottky, Poole-Frenkel, Fowler-Nordheim tunneling, polaron hopping etc. can control the leakage current density.⁶⁻¹⁰ Also notable is the fact that all of these mechanisms have an exponential dependence on the electric field strength. Moreover, it has been shown in the previous section that as a result of uneven electrodes, the electric field varies inside the dielectric layer, which would cause a concomitant variation in the leakage current density. So, all in all the current-voltage behavior is complex and still not fully understood in ferroelectric oxides.

In the present study, the Schottky and the Poole-Frenkel mechanisms are modeled for type I and type II capacitors. For each of the mechanisms, the leakage current is calculated for a perfectly flat plate capacitor, and analogous to the previous section, a normalized leakage current has been defined.

The Schottky mechanism is important when a potential barrier is created at the electrode-dielectric interface. Taking image potential into account, the Schottky current density is given as:⁷

\[ J_{SC} = A^* T^2 \exp \left( \frac{\alpha E^2 \phi_{B}}{k_B T} \right) \]  \hspace{1cm} (4.15)

where \( A^* \) is the Richardson constant, \( \alpha \) is a constant which depends on the relative permittivity, \( E \) is the electric field, and \( \phi_{B} \) is the zero-bias Schottky barrier height.

The Poole-Frenkel mechanism is dominant when the leakage current is governed by a large number of charged traps in the bulk. Although Poole-Frenkel conduction has
not been observed in base-metal electrode BaTiO$_3$ multilayer capacitors, it is quite common in other dielectric materials and is affected by interface roughness.$^4, ^{11-13}$ The Poole-Frenkel current is given as:

$$J_{PF} = \mu E \exp\left(\frac{-\phi_B}{2k_BT}\right) \exp\left(\frac{2\beta_s E^{1/2}}{k_BT}\right)$$  \hspace{1cm} (4.16)

where $\beta_s = \left(e^3/4\pi\varepsilon\right)^{1/2}$ and $\mu$ is the electronic conductivity.

### A. Type I capacitors

The Schottky conduction given in equation (4.15), is expressed here in terms of the microstructure variables:

$$J_{SC}^0 = A^* T^2 \exp\left(\frac{\alpha}{k_BT} \sqrt{\frac{V}{d_0} - \frac{\phi_B}{k_BT}}\right)$$  \hspace{1cm} (4.17)

Taking into account the variation in electrode thickness as a function of position for type I capacitors, the equation (4.17) is modified to the following form:

$$J_{SC}(x) = A^* T^2 \exp\left(\frac{\alpha}{k_BT} \sqrt{\frac{V}{d_0 + 2A \sin\left(\frac{2\pi}{L}x\right)} - \frac{\phi_B}{k_BT}}\right)$$  \hspace{1cm} (4.18)

If the number of undulations of wavelength $L$ is $N$, the total length of the capacitor is $NL$. Assuming that $A^*$ is constant, for a given temperature the normalized Schottky leakage current density over the entire electrode area is given by:

$$\frac{\langle J_{SC} \rangle}{J_{SC}^0} = \frac{1}{NL} \int_0^{NL} \exp\left(\frac{\alpha}{k_BT} \sqrt{\frac{V}{d_0} - \frac{\phi_B}{k_BT}}\right) dx$$  \hspace{1cm} (4.19)

Substituting $\frac{2\pi}{L}x = \theta$ in equation (4.19) gives:
\[
\frac{\langle J_{SC} \rangle}{J_{SC}^0} = \frac{1}{2N\pi} \int_0^{2N\pi} \exp \left( \frac{\alpha}{k_B T} \left( \sqrt{\frac{V}{d_0 + 2A\sin \theta}} - \sqrt{\frac{V}{d_0}} \right) \right) d\theta
\]  
\tag{4.20}

From equation (4.20) it can be seen that the normalized Schottky leakage current is a function of both \(d_0\) and \(A\). Thus, for the same value of \(A/d_0\), its values would change for different values of \(A\) and \(d_0\).

The Poole-Frenkel mechanism also has an exponential dependence on the electric field. Hence, using equation (4.12), for type I capacitors, the leakage current density is given by:

\[
J_{PF} = \mu \left( \frac{V}{d_0 + 2A\sin \left( \frac{2\pi}{L} x \right)} \right) \exp \left( -\frac{\phi_B}{2k_B T} \right) \exp \left( \frac{2\beta_S}{k_B T} \left( \sqrt{\frac{V}{d_0 + 2A\sin \left( \frac{2\pi}{L} x \right)}} - \sqrt{\frac{V}{d_0}} \right) \right)
\]  
\tag{4.21}

For a perfect capacitor, the Poole-Frenkel current is given by:

\[
J_{PF}^0 = \mu \left( \frac{V}{d_0} \right) \exp \left( -\frac{\phi_B}{2k_B T} \right) \exp \left( \frac{2\beta_S}{k_B T} \left( \sqrt{\frac{V}{d_0}} \right) \right)
\]  
\tag{4.22}

Assuming \(\mu\) to be a constant for both the cases, the normalized Poole-Frenkel leakage current density over the entire area is given by:

\[
\frac{\langle J_{PF} \rangle}{J_{PF}^0} = \frac{d_0}{NL \left( d_0 + 2A\sin \left( \frac{2\pi}{L} x \right) \right)} \int_0^{NL} \exp \left( \frac{2\beta_S}{k_B T} \left( \sqrt{\frac{V}{d_0 + 2A\sin \left( \frac{2\pi}{L} x \right)}} - \sqrt{\frac{V}{d_0}} \right) \right) dx
\]  
\tag{4.23}

Substituting \(\frac{2\pi}{L} x = \theta\) in equation (4.23) gives:

\[
\frac{\langle J_{PF} \rangle}{J_{PF}^0} = \frac{d_0}{2N\pi} \int_0^{2N\pi} \exp \left( \frac{2\beta_S}{k_B T} \left( \sqrt{\frac{V}{d_0 + 2A\sin \theta}} - \sqrt{\frac{V}{d_0}} \right) \right) \left( d_0 + 2A\sin \theta \right) d\theta
\]  
\tag{4.24}
Figure 4.6: Normalized leakage current of type I capacitors for (a) Schottky conduction mechanism (b) Poole-Frenkel conduction mechanism, as a function of amplitude of unevenness, $A$, for different values of dielectric layer thickness, $d_0$. 
As in the case of Schottky mechanism, the Poole-Frenkel mechanism also depends on the values of both \( d_0 \) and \( A \), and not merely the ratio of the two. Figures 4.6(a) and 4.6(b) show the variation of Schottky and Poole-Frenkel leakage currents respectively with changing amplitude of unevenness for different values of dielectric thickness at \( T=300 \) K, and \( V=1 \) V. Based on previous work by Levi et al., the value of \( \alpha \) was found to be \( 2.55 \times 10^{-23} \) J-V\(^{-1/2}\)-m\(^{1/2}\).\(^{14}\) Also, assuming that the permittivity of BaTiO\(_3\) is 2000, \( \beta_S \) was calculated to be \( 1.36 \times 10^{-25} \) J-V\(^{-1/2}\)-m\(^{1/2}\). The Boltzmann constant, \( k_B \), used in the calculations is \( 1.38 \times 10^{-23} \) J-K\(^{-1}\). Thus, the leakage current density is expected to increase with decreasing layer thickness, which is consistent with previous reports of the lowering of insulation resistance for decreasing dielectric layer thickness.\(^3\),\(^4\)

**B. Type II capacitors**

The average electric field for type II capacitors is constant since the distance between the two electrodes remains the same. Thus, the leakage current density is constant with respect to position, irrespective of the governing conduction mechanism. The average leakage current density increases due to the increase in the effective electrode area. Hence, calculating the average leakage current requires computing the length of the curve representing the uneven electrode surface:

\[
\langle J \rangle = \frac{\int_{0}^{N_L} J_0 \, t \, dl}{\int_{0}^{N_L} t \, dx} = \frac{J_0}{N_L} \int_{0}^{N_L} \sqrt{1 + \frac{4 \pi^2 A^2}{L^2} \cos^2 \left( \frac{2 \pi}{L} \right) x} \, dx \quad (4.25)
\]
Here \( J_0 \) is the leakage current density for any given mechanism, \( tdl \) is the elemental area along the surface of a rough electrode, and \( tdx \) is the elemental area along the surface of a flat electrode. From equation (4.25) the normalized leakage current density is given by:

\[
\frac{\langle J \rangle}{J_0} = \frac{1}{NL} \int_0^{NL} \sqrt{1 + \frac{4\pi^2 A^2}{L^2} \cos^2 \left( \frac{2\pi}{L} x \right)} \, dx 
\]

(4.26)

Substituting \( \frac{2\pi}{L} x = \theta \) in equation (4.26) gives:

\[
\frac{\langle J \rangle}{J_0} = \frac{1}{2N\pi} \int_0^{2N\pi} \sqrt{1 + \frac{4\pi^2 A^2}{L^2} \cos^2 \theta} \, d\theta 
\]

(4.27)

The normalized leakage current density is a function of the ratio \( A/L \). Figure 4.7 shows the variation of the normalized leakage current density as a function of \( A \) for different values of \( L \). Thus, a shorter wavelength, and rougher electrode morphology is expected to increase the leakage current in a given area of the device.

![Figure 4.7: Normalized leakage current of type II capacitors as a function of amplitude of unevenness A, for different values of wavelength of roughness, L.](image-url)
4.4 Finite Element Modeling of Idealized Microstructure Defects

The effect of electrode defects on electric field distributions was investigated using the finite element method. The average dielectric layer thickness of the model was 10 µm. The software package ANSYS was used to solve for electric field and potential distributions in the dielectric layer. The element type chosen for the analysis was SOLID231 and the average mesh size of the model was 2.5 µm with some local refinements around defect features. The Laplace equation for electrical potential \( \phi \), denoted by equation (4.28) was solved, with the potential difference across electrodes as the boundary condition.
\[
\nabla^2 \phi = 0 \quad (4.28)
\]

4.4.1 Curvature-induced Local Electric Field Enhancement due to Electrode Roughness

The simple analytical model presented above does not take into account any field enhancement due to curvature of the electrodes. To incorporate this effect into the analysis, finite element method is used. A model section of a parallel plate capacitor is used to represent a local region of MLCC (Figure 4.8). The dielectric layer is assumed to have a dielectric permittivity of 2000. However, these values are arbitrary and theoretically should not affect the relative electric field and potential distributions inside the capacitor.
The electric field distribution in each of these cases is normalized with respect to the field in a perfect flat-plate capacitor. A potential difference of 1V, corresponding to an average electric field of $10^5$ V/m, is applied across the terminals of the MLCC section. The potential and normalized electric field distributions are calculated for type I electrode configuration as shown in figures 4.9(a) and 4.9(b), and for type II electrode configuration as shown in figures 4.10(a) and 4.10(b). In type I, the electric field profile shows bands of high and low electric fields which are $+/−$ 10% of the mean field strength in the dielectric layer. In type II, the electric field in the dielectric layer shows a local increase of $−20\%$ due to the curvature of the electrode surface. Thus, it can be seen that presence of unevenness at the electrode-dielectric interface induces heterogeneities in the electric field inside the dielectric layer.
Figure 4.9: Finite element calculation results for type I capacitor: (a) electric potential in V and (b) normalized electric field distribution.

Figure 4.10: Finite element calculation results for type II capacitor: (a) electric potential in V and (b) normalized electric field distribution.
4.4.2 Effect of Electrode Discontinuity

The electrode discontinuity is modeled as shown in figure 4.11, where one electrode with two identical semi-circular pores is sandwiched in between two dielectric layers and two perfect electrode segments. The distance between the centers of the two semi-circles is fixed at 50 µm and their radii are gradually increased from 10 µm to 40 µm. This is done in order to study the effect of two adjacent pores and their superposition effects on electric field. The normalized electric field distribution is shown for several different pore diameters in figure 4.12. The maximum normalized electric field in the dielectric layer increases as the pores grow larger and thus, get closer. This is significant because, for MLCCs with higher electrode discontinuity, the probability of pores being closer will be higher, thus leading to higher local electric field enhancements. Thus, both the presence of electrode pores and their relative position with respect to each other are critical while calculating the local electric field enhancements in MLCCs.

Figure 4.11: Parallel plate capacitor with electrode pores used for finite element calculations. The inset shows the shape of the pores in the middle electrode. All dimensions are in µm.
Figure 4.12: Normalized electric field distribution for two adjacent pores of diameter (a) 40 µm (b) 25 µm (c) 10 µm.
4.4.3 Leakage Current due to Local Microstructure Effects

Based on the electric field calculation from the finite element analysis, the leakage current density was calculated for type I, type II, and discontinuous electrodes (diameter of pores was 40µm). The calculations were made assuming a Schottky-barrier controlled conduction mechanism. The leakage current density was normalized with respect to that for a perfect flat plate capacitor and is plotted as a function of applied average electric field for each of the three cases (figure 4.13). For lower electric field,
when compared with the two types of electrode roughness, the leakage current was lower for the model with discontinuities due to the smaller electrode area. However, as the electric field is further increased, the leakage current density for the model with discontinuous electrodes is much higher as compared to the model with electrode roughness. Also, the leakage current for type I electrodes is always higher than type II electrodes. Thus, it can be seen that higher electric field around discontinuous electrodes has a significant effect in terms of higher leakage current. Local effects such as electrode curvature also lead to higher leakage current, albeit to a smaller degree as compared to electrode pores.

4.5 Discussion

The present study highlights the ever-increasing problem of the adverse effects of electrode defects on electric field and leakage current in multilayer devices. However, the present model has several simplifications. The two types of capacitors considered in both the analytical modeling and FEM are the most extreme cases. In reality, though, the relative orientation of the electrodes would be intermediate of the two. However, representing the electrode surfaces by sinusoidal functions makes it possible to account for such intermediate cases by a net phase difference. Also, as observed in the SEM micrograph (figure 4.1), the shape of the electrode pores are much more complex as compared to that in the finite element model. In the present study, the electrodes are assumed to be uneven only in two dimensions. However, the three-dimensional surface
profile of the metal-dielectric interface needs to be determined in order to identify the possible regions of failure inside the capacitor more accurately.

The finite element analysis helps in identifying the electrode defects as the regions of field enhancement, which in turn can act as a stimulus to electrical breakdown and a higher leakage current. As observed in the VC-SEM images, local perturbations in electric potential take place due the presence of these electrode pores. The relative effects of electrode roughness and pores can also be assessed. In the present work it is seen that electric field enhancements near electrode discontinuities are considerably higher than those arising out of electrode curvature. The individual effects of electrode roughness and pores on leakage current were analyzed. Due to the higher electric field, the electrode discontinuities have a more significant effect in terms of higher leakage current, as compared to electrode roughness.

4.6 Summary

The study of electrode defects such as porosity and roughness in MLCCs can give vital information regarding the enhancement in electric field and leakage current. This chapter highlighted the role of these defects as sites of electric field enhancement and hence, higher leakage current. In case of a parallel plate capacitor, the relative position of these defects controls the field enhancement factor and thus the leakage current. Also, if the conduction mechanism has an exponential dependence on electric field like in the case of Schottky or Poole-Frenkel, the leakage currents are even higher for the presence
of electrode roughness. These effects are further magnified for decreasing dielectric layer thickness, thus reducing the insulation resistance for thinner layers.

However, further studies would be required to determine the three-dimensional extent of such defect features in order to have better quantitative results. The next chapter discusses quantification of real multilayer microstructures in three-dimension through serial sectioning of MLCCs using focused ion beam milling and imaging analysis. An in-depth quantitative analysis of the relative contribution to leakage current from electrode roughness and porosity is also discussed with the help of the true three-dimensional microstructure of MLCC.
4.7 References


Chapter 5

QUANTITATIVE ANALYSIS OF MICROSTRUCTURAL DEFECTS IN MLCCS AND THEIR EFFECTS ON ELECTRIC FIELD AND LEAKAGE CURRENT*

5.1 Introduction

Developing techniques to better quantify the morphology of the electrodes in MLCCs is necessary in order to evaluate the precise effects of electrode defects on device performance. This can be achieved by reconstructing a three-dimensional microstructure of a given region in the MLCCs, which enables the visualization and quantitative evaluation of various defects in the electrodes such as roughness and discontinuity.1-5 This chapter discusses in detail the various aspects of 3D microstructure reconstruction and modeling, and their applications in understanding the importance of superior electrode morphology. Serial sectioning and imaging was performed using the focused ion beam (FIB). These serial images were combined to form a 3D image using the Avizo software. The 3D data was then converted into a finite element model, which was used to evaluate the electric field distribution in the presence of such electrode defects. The effect of processing on microstructure and subsequently, the field distribution was also studied.

The leakage current was also calculated from the electric field values at the metal-dielectric interface, assuming a Schottky-barrier controlled conduction mechanism. Also, based on the leakage current calculations, the effects of scaling down the dielectric layer thickness on insulation resistance was modeled.

5.2 Three-dimensional Microstructure Characterization

The images collected from serial sectioning process in the FIB were edited and aligned before being used to reconstruct the 3D volume. Figure 5.1 shows such an example where a series of images of an MLCC cross-section were collected, aligned and combined to form a 3D image of the volume, which was milled out in the process. The dark gray regions are BaTiO₃ based dielectric and the lighter regions are the Ni electrodes, which contain pores denoted by the black phase. The average dielectric layer thickness for the MLCCs was 2.2 μm.

Figure 5.1: A series of images collected during serial sectioning in the FIB that are combined to reconstruct a 3D image of the microstructure.
This 3D image can be further cropped to reveal the pores in every electrode layer as shown in figure 5.2. Figure 5.3 illustrates the process of calculating the average electrode continuity from the 3D microstructures.

Figure 5.2: Pores in each of the electrode layers observed by cropping down the 3D microstructure, one layer at a time.

Figure 5.3: Electrode continuity calculation: The electrode images are converted into a binary format and then the total number of black pixels corresponding to the pores are measured for each layer and added to give the net percentage porosity.
5.3 Influence of Sintering Rate on Electrode Morphology

As discussed in chapter 2, processing plays a very important role in governing the microstructure of MLCCs. Earlier work has shown that the rate of sintering green MLCC chips during the co-firing process affects the morphology of electrodes, especially their continuity. The formation of electrode pores is attributed to the mismatch in the densification kinetics of Ni and BaTiO$_3$. Since Ni densifies faster than BaTiO$_3$, this leads to the generation of a tensile stress in Ni, and a compressive stress in BaTiO$_3$. Furthermore, due to the incomplete binder burnout, some amount of residual carbon is always present in the dielectric. This residual carbon leads to a reduction reaction at the Ni-BaTiO$_3$ interface, giving rise to a Ni-Ba-Ti interalloy whose thickness depends on the sintering kinetics. The tensile stress in the Ni layer along with the interfacial alloy layer promote the electrode pore formation, which is a kinetic process controlled by the heating rate. Thus, faster sintering rates lead to more continuous electrodes. In order to study the influence of sintering rate on electrode morphology, MLCC chips already subjected to the binder burnout step were sintered in a custom-built furnace having atmosphere control and rate control capabilities. The sintering was carried out under a reducing atmosphere with a pO$_2$ range of $10^{-12}$ - $10^{-10}$ atm in order to prevent Ni electrode oxidation. The setup of the experiment has been discussed in detail in chapter 3. The MLCCs sintered at different rates were subjected to 3D microstructure characterization using the serial sectioning technique in the FIB. This allowed for the accurate estimation of their electrode continuity. Figure 5.4 shows the sintering profiles and the resulting continuity of Ni electrodes in MLCCs.
Figure 5.4: (a) Different heating profiles applied on the MLCCs and (b) corresponding electrode continuity. Note that, for complete design of dielectric properties, multiple firing stages can be invoked. But the present firing schemes are sufficient for controlling the interface and are representative.
Figures 5.5(a) and 5.5(b) show the 3D microstructures of typical slow-fired (200°C/hr) and fast-fired (3000°C/hr) samples, respectively. The electrode continuities were calculated from these microstructures as previously illustrated and were found to be 79.1% ± 5.8% for the slow-fired samples and 92.1% ± 2.9% for the fast-fired samples. The improvement in electrode continuity with increased firing rate was consistent with the previous results of Polotai et al.\textsuperscript{6} It was also observed that the electrodes were smoother in the case of fast-fired MLCCs.

![Figure 5.5: Three-dimensional microstructure of a typical MLCC processed under (a) slow-fired conditions and (b) fast-fired conditions.](image)

The binary images of the electrodes also allowed for the measurement of the pore sizes with the help of image-analysis. It was found that the pore size distribution (figure 5.6) was broader for slow-fired MLCCs as compared to the fast-fired ones. Also the
average pore sizes were $4.8 \pm 4.4 \, \mu m^2$ for slow-fired samples and $1.7 \pm 1.4 \, \mu m^2$ for fast-fired samples. Larger pores imply a smaller separation distance between them, which is expected to lead to higher electric fields around those regions, as shown from the simulations in the previous chapter. Hence, fast-fired samples reduce the possibility of local electric field enhancement around electrode pores, besides increasing the overall electrode area.

Figure 5.6: Size distribution of pores for fast-fired and slow-fired MLCCs. It is represented in terms of a histogram distribution of discontinuity areas.

5.4 Finite Element Modeling of Three-dimensional Microstructure

In order to calculate the electric field distributions in a given volume, the images of a local region in the MLCC were collected, also using serial sectioning. A part of this
set of images, consisting of only two electrodes was extracted for 3D reconstruction and finite element modeling (figure 5.7(a)). The images were converted to a volume segmented into different phases (figure 5.7(b)), following which a 3D finite element mesh of the volume was generated (figure 5.7(c)). An electrostatic simulation was carried out on this volume in COMSOL. Details related to the meshing techniques are discussed in chapter 3. The dielectric layer was assumed to have a permittivity of 2000 and Poisson’s equation for the electrical potential \( \phi \), denoted in equation (5.1), was solved at each node of the volume.

\[
\nabla^2 \phi = -\frac{\rho_f}{\varepsilon} \tag{5.1}
\]

where \( \rho_f \) is the free charge density, assumed to be zero, and \( \varepsilon \) is the permittivity of the dielectric. The potential values at the surface of the two electrodes were the imposed boundary conditions. The model also consisted of additional areas of the dielectric and pores on the surface of the volume, on which a zero-charge/symmetry boundary condition was used and is given as:

\[
\vec{n} \cdot \vec{D} = 0 \tag{5.2}
\]

where \( n \) is the surface normal vector, and \( D \) is the dielectric displacement vector. Thus, it was assumed that no electric field flux escaped out of this volume. This assumption caused some fringing effects, and hence, the field values at the edge were neglected. Moreover, contact between the different phases (dielectric, electrode, and pores) was established through internal areas, on which the following field continuity condition was imposed:

\[
\vec{n} \cdot (\vec{D}_1 - \vec{D}_2) = 0 \tag{5.3}
\]
where $D_1$ and $D_2$ are dielectric displacement vectors normal to the two areas in contact. The solution gave the potential distribution, which on differentiation provided the electric field value. Note that the electric field was normalized with respect to the average value in the dielectric layer in all parts of the discussion in this chapter.

Figure 5.7: (a) Representative microstructure extracted from the original image. It consists of two electrodes similar to a parallel plate capacitor. (b) Microstructure is converted into a 3D image segmented into different phases; the red phase is the dielectric, the green phase is the electrode and the yellow phase are the pores in the electrodes. (c) This segmented volume is then meshed.
5.4.1 Correlation Between Electrode Morphology and Device Performance

Finite element simulations were carried out on 3D microstructures acquired from both slow-fired and fast-fired samples. The electrodes exhibit higher porosity and roughness for slow firing as compared to fast firing conditions. (Figure 5.8) These electrode defects act as sites of electric field enhancement as shown in figures 5.9(a) and 5.9(b). While the maximum electric field was more than three times the average value for slow-firing conditions, it is only about 1.6 times the average value for fast-firing conditions. Thus, superior electrode morphology limits the local electric field enhancement due to the reduction of microstructural defects such as pores and roughness.

Figure 5.8: Electrode morphology of MLCCs processed under (a) slow-fired conditions and (b) fast-fired conditions.
Figure 5.9: Electric field distribution in the dielectric layer normalized with respect to the average electric field based on average dielectric layer thickness for (a) slow-fired and (b) fast-fired MLCCs.

To further understand the effect of electrode morphology on leakage current, the local leakage current density was calculated at about 1400 different points, which were 0.2 µm apart on the electrode-dielectric interface, assuming a Schottky barrier controlled conduction mechanism given by: \(^8,9\)

\[
J_{sc} = A^* T^2 \exp \left( \frac{\alpha E^{1/2} - \phi_B}{k_B T} \right)
\]

(5.2)

where \(A^*\) is the Richardson constant and was found to be 54 J-m\(^2\)-K\(^{-2}\), \(\alpha\) is a constant which depends on the relative permittivity and was found to be \(2.55 \times 10^{-23}\) J-V\(^{-1/2}\)-m\(^{1/2}\). \(E\)
is the electric field, and $\phi_B$ is the zero-bias Schottky barrier height at the Ni-BaTiO$_3$ interface and is equal to 1.2 eV, and $k_B$ is the Boltzmann constant which is $1.38 \times 10^{-23}$ J-K$^{-1}$. Thus, the local leakage current density as a function of the local electric field, $E_{loc}$ can be calculated as follows:

$$J_{SC,loc} = A^* T^2 \exp \left( \frac{\alpha E_{loc}^{1/2} - \phi_B}{k_B T} \right) \quad (5.3)$$

Also, it must be noted that the interface electric field values at the edges of the model were not considered in order to avoid fringing field effects. Thus, all calculations started 0.2 µm away from the edge into the model. On integrating the local leakage current density over the entire electrode for the two models, it was found to be almost three times for the slow-fired samples as compared to that for the fast-fired samples as shown in figure 5.10.

![Figure 5.10: Leakage current density calculated based on the electric field distribution at the electrode-dielectric interface for slow-fired and fast-fired samples at 80°C.](image-url)
Thus, the high local electric field places severe limitations on device performance due to enhanced local leakage current, and therefore reduces the operating voltage of the devices. Under such conditions, it becomes extremely important to have smoother and more continuous electrodes in state-of-the-art MLCCs.

5.4.2 Scaling Down the Layer Thickness: Effect on Electric Field and Leakage Current

With rapid miniaturization in the electronics industry, there has been a growing demand for increasing the number of dielectric layers and scaling down the dielectric layer thickness in order to increase the volumetric capacitance.\textsuperscript{11, 12} However, such trends are severely limited by the morphology of the metal-dielectric interface and the presence of defects such as roughness and porosity in the metal electrodes.\textsuperscript{6, 9, 13-15} Also notable is the fact that there is a considerable decrease in the insulation resistance of MLCCs with decreasing dielectric layer thickness, which can lead to a higher leakage current.\textsuperscript{16, 17}

In order to study the effect of reducing the dielectric layer thickness on electric field and the leakage current, the 3D microstructure of a MLCC that had been subjected to conventional slow firing was considered. The dielectric layer was progressively cropped down from 2.0 µm to 0.5 µm keeping the morphology of the two electrodes exactly the same as illustrated in figure 5.11. This was done in order to study the impact of electrode morphology on insulation resistance of the device without having to consider other factors such as grain size, dielectric composition, etc.
Figure 5.11: The dielectric layer thickness is progressively scaled down from 2.0 µm to 0.5 µm, keeping the electrode morphology exactly the same.

Figure 5.12: Normalized electric field distribution for models with different dielectric layer thickness. The maximum normalized field increased from 3.1 (corresponding to 2.0 µm) to 3.7 (corresponding to 0.5 µm). Electric field values at the edges were not considered because of possible artifacts due to fringe fields. It must also be noted that the maximum field enhancement values may be sensitive to meshing. Hence, local mesh artifacts in each of the four models can lead to some differences in the maximum field value as seen in the model with average layer thickness of 1.0 µm.
Also, in order to maintain the same value of average electric field in the dielectric layer, a reduction in layer thickness was accompanied by a corresponding reduction of the potential difference across the electrodes in the models. Figure 5.12 shows the normalized electric field distribution in a cross-section of the model for decreasing dielectric layer thickness. The maximum electric field stayed almost the same at about 3 times the average value around an electrode pore until the layer thickness is reduced to 1 μm. However, as the dielectric thickness was further reduced to 0.5 μm, the maximum electric field increased to about 3.7 times the average value, with this maxima occurring at a rough interface rather than a pore. This is due to the fact that the length scale of electrode roughness became comparable to the dielectric layer thickness at 0.5 μm, and hence led to a localized thinning and high electric field around roughness. To further understand the effect of reducing dielectric layer thickness, the local electric field was calculated at the metal-dielectric interface at discrete intervals of 0.2 μm in all the four models and was then used to calculate the local leakage current density using equation 5.3. This local leakage current density was then integrated over the entire electrode area for each of the models. The J-E characteristics for all the four models were plotted as shown in figure 5.13. Notably, for the same average electric field, the leakage current density is almost 50% higher for a dielectric layer thickness of 0.5 μm as compared to that for 2.0 μm. This can be attributed to the more pronounced effect of electrode defects on electric field enhancement and subsequent increase in leakage current. Thus, it can be seen that the influence of the electrode-dielectric interface on MLCC performance becomes more pronounced as the dielectric layer thickness is reduced. Hence, eliminating such extrinsic defects is critical for successful miniaturization of MLCCs.
Figure 5.13: Leakage current calculated as a function of average electric field at 120°C for different dielectric layer thicknesses. The calculations were based on four models with exactly similar meshing parameters and average electric field. The electric fields at the metal-dielectric interface were used to evaluate the local leakage current densities, which were integrated over the entire electrode.

5.4.3 Scaling Down the Layer thickness: Effect on Insulation Resistance

The insulation resistance for a capacitor is defined at the room temperature at the operating voltage, which is determined by the dielectric breakdown strength. At a given value of electric field $E$, the insulation resistance can be denoted by:

$$ IR = \frac{V}{I} = \frac{E}{Ja}d \quad (5.4) $$

where, $V$ and $I$ are the voltage and current, respectively, $a$ is the total area of the electrodes, $J$ is the leakage current density and $d$ is the thickness of the dielectric layer.
between the two adjacent electrodes. Ideally, for a given value of electric field and leakage current density, and for the same electrode area, the insulation resistance should decrease linearly with the decreasing dielectric layer thickness. However, based on the calculations of leakage current density for the four models, it was qualitatively seen that the drop-off in the resistance was much faster than the expected linear drop-off as shown in figure 5.14.

![Graph](image)

Figure 5.14: The insulation resistance calculated based on the leakage current density evaluated from the simulation, drops off faster than expected as the dielectric layer becomes thinner in conventionally sintered MLCCs.

This was consistent with some of the previous studies on correlation between dielectric layer thickness and insulation resistance. Thus, microstructure defects play a very critical role in governing the performance of the MLCCs, especially as the dielectric layer thickness decreases to the scale of the interfacial roughness.
When a similar analysis was done on a 3D microstructure extracted from fast-fired MLCC, the drop-off in the insulation resistance was much closer to the expected linear drop-off (figure 5.15). This shows that superior electrode morphology reduces the extrinsic effects on device performance caused by various defects such as electrode roughness and porosity.

![Figure 5.15](image)

Figure 5.15: The drop in the calculated insulation resistance is much closer to the expected linear trend as the dielectric layer thickness is reduced in fast-fired MLCCs.

As discussed earlier, typical electrode defects such as pores and roughness act as local sites for electric field enhancement. However, the relative impact of porosity and roughness on electric field and leakage current density depends on the dielectric layer
thickness. In order to quantify this relative impact, the local leakage current calculated earlier was categorized into contributions from the regions around the pores and from the continuous, but rough, electrode regions. Although the electrode was absent wherever there were pores, the regions around them witness a significant increase in electric field, and hence were assigned to the local leakage current contribution from pores. The rest of the electrode was rough, and hence accounted for the contributions to leakage current from electrode roughness. As illustrated in figure 15.16, the fractional contribution to the leakage current from discontinuities is more significant for the model with 2.0 µm dielectric layer thickness. However, as the thickness is scaled to 0.5 µm, the impact of electrode roughness becomes more significant due to local dielectric layer thinning. Thus, as the dielectric layers approach a thickness comparable to the roughness of the electrode, roughness has a greater impact in controlling the performance of MLCCs.

Figure 5.16: Percentage contributions to the net leakage current as a function of electric field at 120°C from areas around electrode porosity and roughness for models with dielectric layer thickness of (a) 2.0 µm and (b) 0.5 µm.
5.4.4 Microstructure near Termination of MLCCs

The morphology of Ni electrodes near the termination and its limiting effects on the performance of MLCCs has been a topic of interest for some time. Generally, the electrode tends to disintegrate near the termination due to residual compressive stresses in the dielectric layer in those regions. Figure 5.17 shows the difference in the electrode morphology in the bulk and near the termination of a MLCC using 3D microstructure.

Figure 5.17: Electrode morphology (a) in the bulk and (b) near termination of a MLCC.
As is evident from the figures, the electrode that is terminating is extremely rough and discontinuous in comparison to the second electrode. The electric field is simulated for both these 3D volumes as shown in figure 5.18.

Figure 5.18: Electric field distribution in a 3D volume extracted from (a) the bulk and (b) near the termination of a MLCC.
The maximum normalized electric field was much higher near the termination as compared to the bulk of the MLCC (3.8 versus 1.7). Also, the tip of the terminating electrode witnessed the maximum amount of electric field. Earlier work by Yang et al. had identified the region near the tip of the electrode to be of significantly lower resistance as compared to the bulk.\textsuperscript{21} This can be attributed to the increased flux of oxygen vacancies toward the tip due to higher local electric field. Thus, the imperfect electrode morphology near the termination led to significant amount of perturbation in electric field distribution, and hence these regions acted as weak spots during the operation of these devices.

The 3D microstructure analysis was helpful in accurate estimation of the effect of electrode defects on electric field calculations. The 3D simulation also reveals the superposition effects of various defects on electric field in a given volume. Such an understanding was not possible with 2D microstructures analysis reported in some of the earlier work.\textsuperscript{24, 23}

5.5 Summary

The present chapter identified 3D microstructure modeling and simulation as a powerful technique, which can provide excellent data on the morphological distribution within multilayer structures at the mesoscale. A 3D microstructure of a region inside the MLCC was reconstructed using serial-sectioning and imaging technique via FIB. This 3D microstructure was converted into a finite-element model to solve for electric field distribution in that region of the capacitor. Strong electric field perturbations were
observed around microstructural defects at the electrode interface of MLCCs. Specifically, two different batches of MLCCs, which were subjected to different sintering rates and had different electrode morphology, were compared. Faster sintering rates resulted in more continuous and smoother electrodes as compared to those subjected to the conventional slow-firing steps. Superior electrode microstructure resulted in lesser perturbations in the electric field, which is expected to lower leakage current.

It was also observed that enhanced leakage current resulted from the local high electric field, and increasingly became important as the dielectric layer thickness was reduced. Also, electrode roughness was found to contribute more toward leakage current as the dielectric layer became thinner. A 3D microstructure analysis near electrode termination revealed very high local electric field and hence, confirmed them as potential weak spots during the operation of MLCCs.

Several different aspects of microstructure were explored. Local high electric field can lead to breakdown in any of the weak spots. Thus, in order to maintain the expected levels of insulation resistance of MLCCs during miniaturization, the electrode morphology and continuity must be concomitantly improved. The next chapter offers practical methodologies through the processing to combat challenges discussed in this chapter that limit downsizing of MLCCs. Various electrical characterization techniques were used to evaluate these effects quantitatively.
5.6 References


Chapter 6

EFFECT OF FIRING RATES ON ELECTRICAL PROPERTIES OF MULTILAYER CERAMIC CAPACITORS

6.1 Introduction

Most of the state-of-the art multilayer ceramic capacitors having high volumetric capacitance consist of nickel electrodes and dielectric layers ranging from 2.0 µm to 0.8 µm with more than 500 parallel layers. As the layer thickness has been reduced below 3.0 µm, the electrode microstructure has become a major problem due to the presence of various defects such as porosity and roughness. The root cause of this problem is a stress-induced morphological instability in the electrode layer, which is further facilitated by the formation of a low melting-point Ba-Ti-Ni alloy formed during processing.\textsuperscript{1, 2} This alloy layer is formed because BaO and TiO\textsubscript{2} are highly reduced at the electrode interfaces as a result of the thermo-chemical and catalyzed removal of residual carbon from the dielectric binder.\textsuperscript{3-7} The liquid-phase formation allows for a fast diffusion path and thus leads to electrode instabilities.\textsuperscript{8} To mitigate the formation of the liquid alloy, fast firing, alloyed electrodes or coated Ni powders have all proved to be effective, with the most

important advance being the fast-firing process.\textsuperscript{8,9} Mass manufacturing approaches have recently been modified with new kiln technologies to practice the advantages of fast firing.\textsuperscript{10,11} Even with these technological advancements, the electrode interfaces are not perfectly continuous and planar, and can still limit the capacitor performance in submicron scale dielectric layers.

The previous two chapters discussed the influence of electrode morphology on the electric field distribution and leakage current in MLCCs using finite element modeling. It was shown that electrode defects such as porosity and roughness act as sites of electric field enhancement. It was also observed that faster sintering rates lowered electrode defect concentration, and thus were expected to improve device performance. The present chapter will discuss the influence of microstructure on device properties such as leakage current, capacitance and impedance.

\section*{6.2 Analysis of As-reduced MLCCs for Microstructure and Device Performance}

Two different batches of MLCCs were co-sintered at 1280°C for 2h in a reducing atmosphere with vastly different heating rates of either 150°C/hr or 3000°C/hr in a custom-built furnace having atmosphere control and rate control capabilities. The details of the furnace are discussed in detail in section 3.2. As discussed in the previous chapter, the two heating ramp rates led to markedly different electrode morphologies, with electrode continuities being 79.1\% \pm 5.8\% for the slow-fired samples and 92.1\% \pm 2.9\% for the fast-fired samples. Also, the MLCCs were not given a typical “reoxidation” treatment, which is used to decrease the oxygen vacancy concentrations in the
dielectric.\textsuperscript{12} This step was neglected in order to eliminate the effect of incomplete non-ideal reoxidation reactions in MLCCs and specifically compare the effects of microstructure on device performance. The grain structure of the dielectric layer and the microstructure of the electrode-dielectric interface were characterized by transmission electron microscopy (TEM) using a JEOL-2010 field emission TEM (JEOL, Tokyo, Japan) at an operating voltage of 200 kV.

Various electrical properties such as temperature dependence of capacitance (TCC), current-voltage (I-V) characteristics, and frequency dependence of impedance were measured from the two batches of MLCCs. The TCC was measured in the temperature range of -60°C to 150°C using an HP4284A LCR meter (Hewlett-Packard, Santa-Clara, CA) operated at 1kHz frequency without any DC bias. Since, the MLCCs were prepared in a reducing atmosphere, they maintained high oxygen vacancy concentrations and thus had relatively low resistivity. Current-voltage characteristics were measured at 50°C, 60°C, 70°C and 80°C using a pA meter/DC voltage source HP-4140B (Hewlett Packard) and a DC bias from 1V to 20V. The steady-state leakage current was measured after keeping the sample at a constant bias for four minutes, and permitting relaxation of the depolarization current. The impedance of the two sets of MLCCs were measured over the frequency range of 0.1 Hz to $10^6$ Hz at a $V_{\text{rms}}$ of 40 mV over a temperature range of 240°C to 270°C using a Solartron SI1287 electrochemical interface and 1255B frequency response analyzer. The electrochemical impedance software Z-plot\textsuperscript{TM} and Z-view\textsuperscript{TM} were used for analyzing and fitting the impedance data. Details of the setup for each of these measurements are discussed in chapter 3.
6.3 Experimentally Measured Electrical Properties

6.3.1 Temperature Capacitance Characteristics (TCC)

The electrical properties of both types of samples were significantly different. Figure 6.1 compares the temperature dependence of capacitance (TCC) for the two sets of samples. While the dissipation factor was almost the same over the entire temperature range, the capacitance of the fast-fired samples was higher than that of the slow-fired samples. The improvement in the capacitance was $8.71 \pm 0.35 \text{ nF}$ and correlates directly with the 10% increase in electrode area resulting from the fast firing conditions.

![Figure 6.1: Dependence of capacitance and dissipation factor for the two sets of MLCCs on temperature.](image)
Figure 6.2: Transmission electron microscopy image of MLCCs that were (a) slow-fired and (b) fast-fired.
The TEM analysis (Fig 6.2(a) and 6.2(b)) showed that the average grain size of the dielectric material was 265±46 nm and 251±45 nm for the slow-fired and fast-fired samples, respectively, which was similar within error limit. This ruled out any difference in permittivity of barium titanate due to grain-size effects.\textsuperscript{13-15} In addition, the composition of the powders and the effective dielectric layer thickness were the same. Hence, this improvement in capacitance of the fast-fired samples can solely be attributed to the increase in the electrode area.

6.3.2 Current-Voltage (I-V) Characteristics

Figures 6.3(a) and 6.3(b) show the I-V characteristics at different temperatures for fast-fired and slow-fired samples respectively. The data are represented in terms of leakage current density ($J$) versus the electric field ($E$) applied to each layer. The leakage current increased with increasing temperature for both the samples. Also, the leakage current density was higher for the slow-fired samples as compared to the fast-fired samples. There are several conduction mechanisms possible for metal-insulator systems.\textsuperscript{16-20} Previous works have suggested that the dominant conduction mechanism for BaTiO$_3$ based capacitors is a thermionic emission of electrons from the metal into the dielectric over a Schottky barrier at the metal-dielectric interface, also known as the reverse-bias Schottky emission (equation 6.1).\textsuperscript{12,21-23}

$$J_{SC} = A^* T^{-2} \exp \left( \frac{\alpha E^{1/2} - \phi_B}{k_B T} \right)$$

(6.1)
Here $A^*$ is the Richardson constant, $\alpha$ is a constant which depends on the relative permittivity, $E$ is the electric field, and $\phi_B$ is the zero-bias Schottky barrier height.

![Graph](image)

Figure 6.3: Current density ($J$) versus electric field ($E$) at different temperature for MLCCs that were (a) slow-fired and (b) fast-fired. The current densities have been plotted on similar scales to highlight the difference between the two batches of MLCCs.
Figure 6.4: (a) The Log (J/T²) versus 1/T plot at 3.97 MV/m for MLCCs that were slow-fired and fast-fired was a linear plot whose slope gives $(\alpha E^{1/2} - \phi_B)/k_B$. This slope is also plotted (b) with respect to $E^{1/2}$, which is a linear plot whose intercept on the y-axis would give the zero-field Schottky barrier height $\phi_B$. 

The Schottky conduction mechanism is consistent with observation of a linear log $J/T^2$ versus $1/T$ plot at 3.97 MV/m electric field for both samples as shown in figure 6.4(a). It must be noted that the leakage current density reported did not take the difference in electrode continuity into consideration. However, if this difference were considered, the disparity in the leakage current densities of the two sets of samples would be even larger. Specifically, at 80°C, the measured leakage current density was 80% lower for fast-fired samples as compared to slow-fired samples. This difference in leakage current density was comparable to the 70% lowering predicted by the finite-element simulation results (figure 5.10) and hence, could be attributed to the difference in electrode morphology of slow and fast-fired samples.

The slope of the linear plot in figure 6.4(a) gives the quantity $(\alpha E^{1/2} - \phi_B)/k_B$ at that electric field. The plot of $(\alpha E^{1/2} - \phi_B)/k_B$ versus $E$ (figure 6.4(b)) is linear and its intercept on y-axis gives the values of $\phi_B$ for both kinds of MLCCs. Using the least squares method, the Schottky barrier was calculated to be $1.06 \pm 0.02$ eV for the slow-fired samples and was $1.15 \pm 0.01$ eV for the fast-fired samples.

High-resolution TEM studies revealed the presence of an interfacial alloy layer for both the samples (figure 6.5), although it was thicker for the slow-fired sample as compared to the fast-fired sample, thus confirming that the alloy layer formation is kinetically driven.
Figure 6.5: High-resolution TEM images showing the presence of interfacial alloy layer at the interface between BaTiO$_3$ and Ni in MLCCs that were (a) Slow-fired and (b) Fast-fired. (Courtesy: Dr. W. Qu, Penn State University)
This result was consistent with the earlier findings of Polotai et al., where a correlation was noted between the alloy layer thickness and the measured Schottky barrier height. This reduction in the alloy layer with higher heating rates was thought to be the primary reason for the increased barrier height. The metal work function of the electrode is expected to be lower than that of pure Ni based on the Freeouf empirical model, thus leading to some lowering of the Schottky barrier height. However, the findings from FEM simulations in chapter 5 identified electrode defects such as roughness and porosity as sites of electric field enhancements. This field enhancement reduces the net Schottky barrier $\phi_{net}$ according to the relation:

$$\phi_{net} = \phi_{B} - \alpha E^{1/2} \quad (6.2)$$

This lowering is expected to play a dominant role in increasing the leakage current. Thus, a higher concentration of electrode defects in slow-fired MLCCs leads to a significantly higher leakage current density in comparison to the fast-fired MLCCs as observed from the current-voltage measurements and predicted by FEM calculations in chapter 5.

### 6.3.3 Complex Impedance Spectroscopy (IS)

Figures 6.6(a) and 6.6(b) show the complex impedance spectroscopy (IS) plots over a range of temperatures for slow-fired and fast-fired samples respectively. The shape of the IS plots in the complex plane are distorted semi-circles, typical of reduced Ni-BaTiO$_3$ MLCCs. At all temperatures, the impedance of the fast-fired sample is significantly higher than that of the slow-fired sample.
Figure 6.6: Complex impedance plots at various temperatures measured on MLCCs that were (a) slow-fired and (b) fast-fired. The 3-RC impedance model is also shown in the inset.
The IS plots had a good fit to a 3-RC impedance model (shown in the inset), which had also been reported by both Yang et al. and Chazono et al. These lumped RC components were attributed to the electrode-dielectric interface, given by $R_I$ and $C_I$, the dielectric grain boundaries, given by $R_{GB}$ and $C_{GB}$, and the bulk of the dielectric grains, given by $R_G$ and $C_G$. Typically, the Schottky barriers at the interface and the grain boundaries are responsible for their respective contributions to the net impedance of the MLCCs. From the fitting results, the resistance for each of the components of the 3-RC model is plotted as a function of the temperature (figure 6.7) and shows that the value of resistance from the electrode-dielectric interface is significantly higher than that from the grain-boundary and grain.

![Figure 6.7](image.png)

Figure 6.7: For each of the components of the net impedance, R versus T is plotted. The interface and grain-boundary components have the maximum contribution to the resistance. The error bars were obtained from the 95% confidence levels in the fit to the Z-plot data analysis.
The formation of double Schottky barriers at the grain boundaries due to acceptor and amphoteric doping of n-type BaTiO$_3$ gives rise to a higher grain boundary resistance.\textsuperscript{27-29} Thus, the interface and the grain boundary are responsible for a majority of the insulation resistance. Also, because of the barrier-controlled conduction, the resistance contributions from the interface and grain-boundary are expected to have an Arrhenius dependence on temperature given by:

$$R_i = R_0 \exp \left( \frac{E_{a,i}}{k_B T} \right)$$

(6.3)

where $R_i$ is the resistance from the $i$th circuit element, $R_0$ is a constant, and $E_{a,i}$ is the activation energy for conduction for the corresponding element. Figure 6.8 shows the natural log of the resistance values for interface and grain boundaries as a function of inverse absolute temperature. The data shows a very good linear fit, whose slope gives the values of the activation energies of the corresponding elements. These values are listed in Table 6.1.

![Figure 6.8: Log R versus 1/T for interface and grain boundary resistance.](image)
Table 6.1: Activation energies of resistance contributions from interface and grain boundary for slow-fired and fast-fired MLCCs

<table>
<thead>
<tr>
<th></th>
<th>E_A for Interface (eV)</th>
<th>E_A for Grain boundary (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Slow-fired MLCC</strong></td>
<td>1.27±0.01</td>
<td>1.08±0.01</td>
</tr>
<tr>
<td><strong>Fast-fired MLCC</strong></td>
<td>1.52±0.01</td>
<td>1.02±0.01</td>
</tr>
</tbody>
</table>

The improvement of resistance due to the electrode-dielectric interface from slow-fired to fast-fired samples is almost 80%, which can be largely attributed to the improvement in electrode morphology, as discussed above. The grain boundary resistance also improves by almost 50% from slow-fired to fast-fired samples, possibly due to higher acceptor segregation, although that needs to be ascertained. However, as seen from figure 6.7, the contribution to the net resistance from the interface is almost 65% and hence, superior electrode morphology is found to be the most important factor in increasing the resistance of MLCCs. Also, activation energies of interface are higher than that of grain-boundaries, which translates to a higher insulation resistance.

6.4 Effect of Reoxidation on Leakage Current

Some of the Ni terminated MLCCs subjected to slow-firing and fast-firing were also reoxidized, typically between 400°C and 500°C in air atmosphere for more than 24 h in order to ensure complete reoxidation. Kaneda et al. reported a technique through which the extent of reoxidation can be deduced from the impedance spectra of the MLCCs. Such impedance plots were measured during the reoxidation process until they reached saturation, which indicated complete reoxidation of the MLCCs. The interfacial alloy
layer was present even after the reoxidation as evident from the high-resolution TEM images of the Ni-BaTiO₃ interface (figure 6.9), thus ruling out the formation of any nickel oxide layer at the interface.

Figure 6.9: High-resolution TEM images showing the presence of interfacial alloy layer and no NiO at the interface between BaTiO₃ and Ni in reoxidized MLCCs that were (a) Slow-fired and (b) Fast-fired. (Courtesy: Dr. W. Qu, Penn State University)
These batches of MLCCs were studied for their $I-V$ characteristics. As shown in figure 6.10, after reoxidation, the leakage current decreased by up to three orders of magnitude for both fast-fired and slow-fired MLCCs.

Figure 6.10: Current-voltage characteristics of (a) slow-fired and (b) fast-fired MLCCs before and after reoxidation.
When, for reoxidized MLCCs, leakage current trend with increasing voltage was plotted on a log-log scale in a temperature range of 80°C to 170°C (figure 6.11), it was observed that the trend scales with a parabolic dependence beyond 130°C and can be fitted to a current voltage relation given by:

\[ I = kV^\alpha \] (6.4)

where \( k \) and \( \alpha \) are constants. The values of \( \alpha \) from figure 6.10 are consistent with space charge limited current (SCLC) dominating conduction in the bulk at temperatures above 130°C. Such a mechanism can be strongly affected by the trap density in the dielectric. However, the exact origin of this mechanism in base-metal MLCCs is yet to be understood. Thus, while the interface would affect the leakage current at low temperatures (operational temperatures), the conduction mechanism is expected to be space charge controlled at high temperatures (highly accelerated lifetime testing temperatures). It is also seen that even after complete reoxidation, the leakage current for fast-fired MLCCs was almost 20% lower than that for slow-fired MLCCs at temperatures below 130°C, therefore, re-emphasizing the importance of electrode microstructural control in sub-micron MLCCs.

In industrially manufactured MLCCs, the duration of the reoxidation process is much lower than that used for complete reoxidation. Hence, the insulating properties of the dielectric in commercial MLCCs are expected to be intermediate of the two extreme cases discussed in this chapter, i.e., as-reduced and completely reoxidized MLCCs. Hence, device properties are expected to be significantly affected by the electrode morphology in commercially manufactured MLCCs.
Figure 6.11: Current Vs. Voltage trends on a log-log scale for (a) slow-fired and (b) fast-fired reoxidized MLCCs. At temperatures beyond 130°C, space charge limited current controls leakage.
6.5 Summary

The present chapter correlated the microstructure of internal electrodes in Ni-BaTiO₃ MLCCs with their electrical performance. Two batches of MLCCs sintered under reducing conditions at firing rates of 150°C/hr and 3000°C/hr were compared for their microstructure and electrical properties. As expected from prior studies, the continuity of the electrodes was higher for the fast-fired batch. The TCC measurements showed that the capacitance increase was concomitant with the increase in electrode continuity. Also, as predicted by the finite element simulations in chapter 5, leakage current was considerably higher for the sample with slower sintering rate. The Schottky barrier height was also lower for slow-fired samples, with inferior electrode morphology being identified as the primary reason. Impedance measurements showed that both the electrode-dielectric interface and the grain boundary contributed to the improvement in resistance of fast-fired samples. However, the interface played a much bigger role in this improvement as compared to the grain boundary. All these findings show that fast-firing processes limit the electrode defect concentrations and offer enhanced MLCC performance for thin-layer devices.

Even after reoxidation, at temperatures below 130°C, the leakage current is higher for slow-fired MLCCs, although the difference is smaller due to improved insulating properties of BaTiO₃. However, at higher temperatures, the leakage is bulk controlled and differences in leakage are no longer observed for MLCCs with different firing-rates.

The next chapter will discuss the evolution of various properties of MLCCs during degradation, and the role that interface plays during the process.
6.6 References


10 S. M. Landin and W. A. Schulze, “Rapid thermal processing of Pb(Mg$_{0.7}$Zn$_{0.3}$)$_{1/3}$Nb$_{2/3}$O$_3$ multilayer ceramic capacitors,” J. Am. Ceram. Soc., 73, 909–12 (1990).


Chapter 7

PARTIALLY DEGRADED MLCCS: MICROSTRUCTURAL AND ELECTRICAL CHANGES

7.1 Introduction

The degradation of MLCCs is a direct consequence of their processing and electric field history. As discussed earlier in chapter 2, most of the Ni-BaTiO\textsubscript{3} MLCCs are co-fired in reducing atmosphere (pO\textsubscript{2} $\sim$10\textsuperscript{-10} atm) in order to prevent oxidation of nickel electrodes. This in turn leads to a defect reaction whereby the oxygen escapes the BaTiO\textsubscript{3} lattice and leaves behind an oxygen vacancy that is charge compensated by two electrons as shown in the following defect chemistry reaction:

$$O^{x}_{O} \rightarrow \frac{1}{2}O_2 + V_{O} + 2e'$$  \hspace{1cm} (7.1)

Under reducing conditions, and using Brouwer approximation at low pO\textsubscript{2}, the electron concentration $n$ is related to the oxygen vacancy concentration $[V_{O}]$ as follows:\textsuperscript{1}

$$n \approx 2[V_{O}^-]$$  \hspace{1cm} (7.2)

This leaves the dielectric reduced and n-type semiconducting. A reoxidation annealing treatment at $\sim$800°C and a slightly higher pO\textsubscript{2} of 10\textsuperscript{-8} atm is employed to recover part of the resistivity. However, the dielectric is still considerably reduced. Previously, Waser et al. proposed a model based on mixed electronic-ionic conduction to explain the
degradation behavior of single-crystal or coarse-grained acceptor-doped perovskite titanates.\textsuperscript{2-4} These systems had oxygen vacancy concentration controlled in part by the acceptor concentration. According to this model, a demixing of doubly positively charged oxygen vacancies from the anode to the cathode takes place over time, leading to the formation of a n-type region near the cathode and a p-type region near the anode. The formation of this forward biased p-n junction over time is responsible for the time-dependent increase in the leakage current. Earlier, thermally stimulated depolarization current measurements by Liu et al. showed both in-grain and across grain relaxation of oxygen vacancies in case of degraded polycrystalline Fe-doped SrTiO\textsubscript{3} systems.\textsuperscript{5} Moreover, impedance analysis showed evidences of small-polaron hopping from Ti\textsuperscript{3+} to Ti\textsuperscript{4+} due to the accumulation of oxygen vacancies, which leads to Ti ions trapping excess electrons with the transition of a +4 valence state to a +3 valence state.\textsuperscript{6}

However, in case of donor-doped BME MLCCs, additional factors such as the presence of polycrystalline dielectric material, and higher concentration of oxygen vacancies as compared to the acceptor-doped titanates lead to a different interpretation of the problem. Thus, one can no longer assume the formation of a p-n junction. Rather, during degradation, the regions near the cathode can be assumed to be similar to an n\textsuperscript{+} region. Also, the grain boundaries in the dielectrics would act as barriers to the electromigration of oxygen vacancies.\textsuperscript{7-10}

Studies of the Ni-BaTiO\textsubscript{3} interfaces in completely degraded MLCCs by Yang et al. and Woodward et al. have shown the presence of modulated and ordered defects with significantly reduced BaTiO\textsubscript{3}.\textsuperscript{11, 12} This can be further aggravated if the binder burnout is not complete leading to severe local reduction of the dielectric near the interface.\textsuperscript{13}
The present chapter intends to study the changes that take place in the microstructural and electrical properties of commercial MLCCs during the initial stages of degradation. There is enough evidence to prove that this degradation takes place due to the electromigration and accumulation of oxygen vacancies toward the cathode.\textsuperscript{14} However, what needs to be determined is whether this accumulation is reversible if the applied bias on the capacitors is reversed. Such studies won’t be possible in failed capacitors, hence the partial degradation scheme. Also, changes in properties such as capacitance, impedance, and leakage current will be studied.

7.2 Partial Degradation of MLCCs

MLCCs with a rated voltage of 10V were subjected to a 30V bias at \sim 225°C and their leakage current was allowed to increase over the steady state current by about 50-150% before being stopped. This is known as the step-1 of a highly accelerated degradation process. Some of these capacitors were also allowed to further degrade in an unusual reversing of field direction (-30V), with this being step-2 of degradation. The capacitors were then studied for changes in their microstructure, oxygen stoichiometry and electrical properties. Figure 7.1 illustrates what step-1 and step-2 of degradation imply. The change in leakage current with time was previously shown in figure 3.7 in chapter 3.
Figure 7.1: Schematic of step-1 and step-2 of the partial degradation experiment in MLCCs carried out at 225°C.

7.3 Microstructural Changes during Degradation

7.3.1 Transmission Electron Microscopy (TEM)

The TEM studies were necessary to determine the quantitative changes in the microstructure of MLCCs in the vicinity of the electrodes. Yang et al. demonstrated for the first time a spatial variation in microstructure by quantifying the BaTiO$_3$ stoichiometry in degraded BME MLCCs using electron energy loss spectroscopy (EELS) analysis in the TEM.$^{11}$ A similar approach has been used in the present work to ascertain the changes in the stoichiometry of BaTiO$_3$ near the electrode interfaces during the various stages of degradation.
EELS is a technique that involves electron beam interactions with a given specimen, followed by analysis of the electron energy loss spectrum. There are two electron scattering mechanisms associated with a given specimen – elastic and inelastic scattering. The elastically scattered electrons give rise to a sharp narrow peak in the spectrum, which is called the zero-loss peak (ZLP). The energy resolution of the EELS is measured from the full-width-half-maximum (FWHM) of the ZLP. In the present study, this resolution is about 1.3 eV for the instrument.

The low-loss (<50 eV) region of the EELS has the plasmon peak generated from the electron interactions with the loosely bound outer-shell electrons of the atoms in the specimen. This peak is useful in estimating the specimen thickness.

The core-loss (>50 eV) region of the spectrum results from the inelastic interaction of electrons with the core shells of the atoms in the specimen and contains the elemental information. Specifically, the excitation of the K-shell electron in the 1s orbital gives rise to a K-edge. For the L-shell, the excitation of a 2s electron gives an L$_1$ edge, and that of 2p electrons gives the L$_2$ or L$_3$ edges depending on the spin quantum number of the electron. Figure 7.2 shows a typical core-loss region of the spectrum for BaTiO$_3$ in a MLCC before any degradation. The Ti L$_2$ and L$_3$ (or L$_{2,3}$) edges give information about the oxidation state of Ti. The splitting of the L$_{2,3}$ fine structure occurs due to crystal field splitting and indicates the presence of Ti$^{4+}$ valence state. However, if this splitting is suppressed, it indicates the presence of a mixed Ti$^{3+}$ and Ti$^{4+}$ valence state. Similarly, the fine structure of O K edges contains information about the oxygen content.

The EELS analysis and quantification was done in collaboration with Dr. Weiguo Qu (Penn State University). The local oxygen stoichiometry of BaTiO$_3$ for a given EEL
spectrum is quantified using the K-factor approach, whereby an EEL spectrum obtained from pure BaTiO$_3$ is used as a standard assuming perfect stoichiometry. Yang et al. have outlined the details of this technique in a previous work. The stoichiometry from figure 7.2 was calculated to be BaTiO$_{2.95 \pm 0.04}$.

Figure 7.2: Electron energy loss spectrum for BaTiO$_3$ in a non-degraded MLCC. (Courtesy: Dr. W. Qu, Penn State University)

Figure 7.3 shows the bright field TEM images near two neighboring electrodes, the corresponding stoichiometry of BaTiO$_{3-\delta}$ and the EEL spectra (7.3(c)) for a MLCC subjected to step-1 of degradation. The value of 3-\delta near electrode-1 is 2.84 \pm 0.03, indicating severe reduction due to oxygen vacancy accumulation. Hence, electrode-1 is the cathode. This accumulation effect can be observed till at least one to two grains away from the electrode. The inset in figure 7.3(a) is the selected area electron diffraction
(SAED) pattern in <110> direction near electrode-1 and it does not show the presence of any modulated or ordered defects in the dielectric.

Figure 7.3: Bright-field TEM images near (a) Electrode-1 (cathode) and (b) Electrode-2 for a MLCC degraded in one direction. The inset in (a) shows the diffraction pattern for BaTiO$_3$ near electrode-1. The EEL spectra near both the electrodes and the corresponding dielectric stoichiometry are also shown in (c). (Courtesy: Dr. W. Qu, Penn State University)
Figure 7.4: Bright-field TEM images near (a) Electrode-1 and (b) Electrode-2 for a MLCC degraded in one direction. The insets in (a) and (b) shows the diffraction pattern for BaTiO$_3$ near the two electrodes. The EEL spectra near both the electrodes and the corresponding dielectric stoichiometry are also shown in (c).

(Courtesy: Dr. W. Qu, Penn State University)

Similarly, figure 7.4 shows bright-field TEM images near two neighboring electrodes, the corresponding BaTiO$_3$ stoichiometry, and the EEL spectra for a MLCC
subjected to both step-1 and step-2 of degradation. The value of $\delta$ near electrode-1 is $2.86 \pm 0.06$, and is $2.82 \pm 0.06$ near electrode-2. Thus, the dielectric near both the electrodes is significantly reduced. Hence, no significant depopulation or spatial reversal of oxygen vacancies was observed after reversing the bias on the original cathode in step-1. Also, as shown in the SAED patterns in $<110>$ direction in the inset in figures 7.4(a) and 7.4(b), no modulated or ordered defects were observed near either electrode. Thus, such defects do not form during the initial stages of degradation.

### 7.3.2 Voltage-Contrast Scanning Electron Microscopy (VC-SEM)

Voltage Contrast (VC) SEM operates on the basic principle that the emission of secondary electrons by a surface bombarded with the primary electron beam of a SEM is suppressed or enhanced by the presence of positive or negative polarity on the surface respectively.\textsuperscript{17} Thus, the image contrast varies in a complex way with the potential distribution on the specimen surface, but still can give qualitative information about the degradation process. Figure 7.5 illustrates the principle behind VC-SEM.

![Figure 7.5: Principle of VC-SEM imaging.\textsuperscript{18}](image-url)
Thus, it is expected that if the local electric field in a region is perturbed due to any reason, the VC-SEM image can detect that perturbation.\textsuperscript{18} Earlier, in chapter 4, it was shown that presence of electrode pores led to a noticeable change in the VC-SEM image, with regions around the pores of the positively charged electrodes appearing brighter than other parts of the electrodes (figure 4.2). A similar image was captured from a polished cross-section of a MLCC before being subjected to degradation. Bias voltages of +5V and -5V were applied across the terminations using a DC source connected to the holder with the sample attached. The images of the MLCC cross-section with and without bias are shown in figure 7.6. The electrodes at both the positive and negative bias are clearly visible.

Figure 7.6: SEM images of a non-degraded MLCC cross-section (a) before bias, (b) at +5V bias and (c) at -5V bias
The images of the MLCC cross-section after being subjected to step-1 of degradation are shown in figure 7.7. It is seen that one set of negatively charged brighter electrodes in figure 7.7(b) appear visibly blurred, thus indicating that the dielectric regions around those electrodes are less insulating as compared to the bulk. On the other hand, the other set of negatively charged brighter electrodes in figure 7.7(c) are clearly visible. Thus, it is seen that even during the initial stages of degradation, the insulation resistance of the regions near one set of electrodes drops significantly. Based on earlier studies, that set of electrodes should have been the cathode during step-1 and should correspond to the electrode next to reduced BaTiO$_3$ as shown in the EELS analysis (figure 7.3(a)).

Figure 7.7: SEM images of cross-section of MLCC subjected to step-1 of degradation (a) before bias, (b) at +5V bias and (c) at -5V bias. Brighter electrodes in (b) appear blurred (indicated by circled regions) as compared to those in (c).
The images of MLCC cross-section partially degraded both ways (step-1 and step-2) are shown in figure 7.8. Interestingly, the negatively biased brighter electrodes in both figure 7.8(b) and 7.8(c) appear blurred. This indicates that the insulation resistance near both the sets of electrodes dropped, each after the corresponding degradation process. This is also consistent with the findings from the EELS analysis, which showed reduction in BaTiO₃ near both the electrodes (figures 7.4(a) and 7.4(b)). Thus, it is indicative of the fact that degradation process cannot be reversed with reversal of bias.

Figure 7.8: SEM images of cross-section of MLCC subjected to step-1 of degradation (a) before bias, (b) at +5V bias and (c) at -5V bias. Brighter electrodes in both (b) and (c) appear blurred, indicating drop in resistivity around the electrodes.
While the TEM analysis revealed only one or two grains near the cathode that were heavily reduced, the VC-SEM images show that this resistivity reduction due to degradation percolates much deeper into the dielectric layer, which was consistent with the Kelvin Probe characterization of degraded MLCCs reported by Okamoto et al., and will be discussed later.  

7.4 Changes in Electrical Properties of MLCCs During Initial Stages of Degradation

7.4.1 Temperature Capacitance Characteristics (TCC)

The VC-SEM studies and TEM EELS analysis together confirmed a drop in the resistivity near the electrodes with progressive steps in degradation due to accumulation of oxygen vacancies. Figure 7.9 shows the variation of capacitance with temperature for MLCCs before degradation, after step-1 and after step-2. While the dissipation factor did not change significantly, the capacitance steadily increased with each step of degradation. This increase in capacitance can be attributed to the lowering of the effective dielectric layer thickness due to the drop in resistivity near the electrodes. After step-1 of degradation, the region near the cathode becomes more conductive; while after both step-1 and step-2, the regions near both the electrodes become more conductive.
7.4.2 Complex Impedance Spectroscopy (IS)

The impedance spectra of MLCCs at different stages measured at 375°C are shown in figure 7.10. The IS plots had a good fit to the 3-RC impedance, where the RC components of the impedance are attributed to the electrode-dielectric interface, given by $R_I$ and $C_I$, the grain boundaries, given by $R_{GB}$ and $C_{GB}$, and the grain, given by $R_G$ and $C_G$. The impedance decreased with progressive steps of degradation.
Figure 7.10: Impedance spectra of MLCCs at different stages of degradation at 375ºC.

Figure 7.11 shows the resistance contributions from the interface, grain-boundaries, and grains, plotted as a function of temperature. While contributions from the grain boundary and bulk did not change considerably with degradation, there was a notable drop in interface resistance (figure 7.11(a)) after degradation. This is important because the interface contributed about 70% of the net resistance and is consistent with previous findings of Chazono et al. and Morita et al., which showed deteriorating interface resistance with degradation. This drop in interface resistance can be explained by the accumulation of oxygen vacancies near the cathode.\textsuperscript{20, 21} Thus, in doubly degraded capacitors, the interface resistance is expected to be even lower than those degraded in a single direction. These findings can be easily explained by the severe reduction of BaTiO\textsubscript{3} near the electrodes after degradation as observed through the EELS analysis.
Figure 7.11: Resistance contributions from (a) electrode-dielectric interface, (b) grain-boundaries, and (c) grains at temperatures ranging from 375ºC to 450ºC. Note that the error bars are based upon the 95% confidence of the Z-plot fit.
7.4.3 Current-Voltage (I-V) Characteristics

The capacitance and impedance measurements of degraded MLCCs along with the EELS and VC-SEM analysis, gave a clear indication of the resistance degradation near the electrodes due to accumulation of oxygen vacancies. However, detailed current-voltage studies were necessary to ascertain the relevant conduction mechanism on degradation. It is generally accepted that the Schottky barrier at the metal-dielectric interface controls leakage current in MLCCs.\textsuperscript{20, 22, 23} While electron injection from the cathode to the dielectric is believed to be the rate-limiting step for conduction, that may not always be the case. As demonstrated by Levi et al., in BaTiO\textsubscript{3} thin film layers that were deposited on Ni foils, the presence of extrinsic local defects such as grooves formed by Ni grain boundaries can perturb the electric field distribution in those films to such an extent that the conduction mechanism can change from being controlled by the electron injection from the cathode in the absence of grain-boundaries to being controlled by electron extraction at the anode in their presence.\textsuperscript{24} Discussions in previous chapters of this work also highlighted the effect of local electrode defects such as porosity and roughness in MLCCs on perturbation in electric field and the resulting effect on their electrical performance. These defects are potential weak spots where local leakage current is expected to be high due to enhanced electron injection.
Figure 7.12 shows the leakage current variation with voltage ranging between -20 and +20 V for non-degraded X7R base metal MLCCs, whose operating voltage was 10V. The current-voltage characteristics were measured at temperatures ranging between 90°C to 135°C, and were similar in positive and negative bias before any degradation. The conduction was controlled by thermionic injection of electrons from cathode into the dielectric, which was also the case for MLCCs in section 6.2.2. The Schottky barrier calculated from the current-voltage characteristics was 1.1 ± 0.01 eV.

However, after the first step of degradation, there was a significant asymmetry in the current-voltage characteristics in the positive and negative bias as shown in figure 7.13. There was some increase in the leakage current in the positive bias, which was also
the direction in which the MLCC had been degraded. However, the leakage current was even higher in the negative bias. This asymmetry was clearly induced by the unidirectional degradation. The TEM EELS analysis revealed a significant drop in oxygen stoichiometry near one of the electrodes after step-1 of degradation due to the electromigration of oxygen vacancies toward the cathode during the degradation process. Figure 7.14 also shows the current-voltage characteristics for MLCC subjected to both step-1 and step-2 of degradation. The leakage current is high in both the positive and negative bias after subjecting the MLCCs to both step-1 and step-2. This is consistent with findings from the EELS analysis, which revealed significant drop in oxygen stoichiometry near both electrodes.

Figure 7.13: Current-voltage characteristics from 90°C to 135°C for MLCC subjected to unipolar degradation.
Figure 7.14: Current-voltage characteristics from 90ºC to 135ºC for MLCC subjected to bipolar of degradation.

Figure 7.15: Ratio of leakage current at negative and positive bias as a function of voltage at 135ºC. The leakage current is symmetric for MLCCs before degradation. For MLCCs after degradation, the ratio has a departure from one, thus implying asymmetry.
Figure 7.15 demonstrates the symmetry of leakage current with respect to positive and negative bias before degradation and its asymmetry after both unipolar and bipolar degradation. The asymmetry after unipolar degradation is critical for the study of conduction mechanism.

### 7.5 Conduction Mechanism in Degraded MLCCs

There were a few notable aspects about the current-voltage characteristics of the MLCCs that had been subjected to degradation, both single-step and double-step:

- The leakage current showed a noticeable increase with progressive steps of degradation.
- The leakage current increased with increasing temperature, suggesting a thermally controlled conduction mechanism.
- The asymmetry observed in the current-voltage characteristics for single-step degraded MLCCs along with the knowledge of interface degradation (as observed from TEM and VC-SEM) were all strong indicators toward an interface-controlled conduction mechanism.

These observations rule out the possibility of a temperature independent tunneling such as Fowler-Nordheim conduction. Also, bulk-controlled mechanisms such as Poole-Frenkel conduction cannot explain the asymmetry observed in current-voltage characteristics of MLCCs after a unipolar degradation, even though some studies in the past have suggested it. Thus, the only plausible rate-limiting mechanism is a temperature-assisted transport of charge carriers over an interface Schottky barrier, either
from the cathode to the dielectric or vice-versa. Few studies have reported that air-fired acceptor-doped BaTiO$_3$-based systems exhibit p-type conduction.$^{26, 27}$ But for BME-MLCCs processed under reducing conditions, the BaTiO$_3$ would exhibit n-type conduction. Furthermore, an interface between Ni and p-type BaTiO$_3$ would be Ohmic because the work function of Ni (5.15 eV) is greater than that of BaTiO$_3$ (3.9 eV). Hence, the interface between Ni and n-type BaTiO$_3$ is expected to be rectifying.

If the conduction mechanism were to be governed by the thermionic injection of electrons at the cathode (similar to that of MLCCs before degradation) then for MLCCs degraded in one direction, a higher leakage current is expected in the positive bias as compared to the negative bias. This is so because the local reduction of interface near the cathode would result in higher electron injection from the cathode to the insulator. But, that is not the case as seen from figure 7.13. While the asymmetry in the leakage current characteristic after step-1 degradation is strongly suggestive of an interface-controlled conduction, higher leakage current in the negative bias can only be explained by the thermionic emission of electrons from dielectric into the anode being the rate limiting mechanism. This emission is expected to be higher near the electrode with a higher oxygen vacancy concentration, thus leading to the observed asymmetry. The higher electron injection can be explained by the fact that oxygen vacancies present near an electrode interface act as donors and are expected to cause severe band bending. This increases the probability of electron tunneling through the interface. Figure 7.16 shows the band-structure at an interface with and without oxygen vacancy accumulation.
Figure 7.16: Schematic of band structure near the interface with and without oxygen vacancy accumulation under zero-bias. $V_{\text{bi}}$ is the built-in potential.

When a metal-insulator junction with no excessive donor concentration is under forward bias, the band bending tends to get reduced, thus making it easier for electrons to overcome the barrier at the interface and get injected into the anode. However, the situation is different for a junction with excessive concentration of donors such as oxygen vacancies. At low temperatures and under forward bias, all the conduction takes place via tunneling of electrons close to the Fermi energy of the semiconductor. This phenomenon is also known as “field emission”. However, at higher temperatures electrons are excited to higher energies and the possibility of tunneling increases due to a thinner and lower barrier. This phenomenon is known as “thermionic-field emission” and was first proposed by Padovani et al. The schematic for field and thermionic field emission in a degenerate semiconductor is shown in figure 7.17.
Thus, while the electron extraction process from the anode is solely thermionic in nature for electrodes with no oxygen vacancy accumulation, it can be thermionic-field emission controlled at electrodes with oxygen vacancy accumulation. This would lead to higher electron extraction from an electrode with oxygen vacancy concentration (figure 7.18).

Figure 7.18: Schematic of electron extraction from anode interface (a) without oxygen vacancy accumulation, controlled by pure thermionic emission over the net potential barrier $q(V_{bi}-V)$ and (b) with oxygen vacancy concentration, controlled by thermionic-field emission at an energy $E_m < q(V_{bi}-V)$. $V$ is the forward bias voltage applied.
Evidences of a Schottky conduction at the anode in degraded MLCC have also been observed by Okamoto et al. using Kelvin probe force microscopy (KPFM). In particular, a significant electric field concentration was observed near the anodes of degraded MLCCs, thus indicating the presence of a dominant Schottky-barrier at the anodic interface (figure 7.19). However, no such electric field concentration was observed in MLCCs before any degradation (figure 7.20).

Figure 7.19: Electric field maps (generated through KPFM) of degraded MLCC under external voltages in the (a) opposite and (b) same direction as that during degradation.

Figure 7.20: Electric field maps (generated through KPFM) of non-degraded MLCC under external voltages in the (a) forward and (b) reverse bias direction.
Notably, the electric field concentration near the anodes of degraded MLCCs (figure 7.19(a)) is as high as ~3 times the average electric field values seen in figure 7.20. This factor combined with the effective reduction in dielectric layer thickness is expected to magnify the influence of various extrinsic defects and weak spots such as electrode porosity, roughness etc. due to local field enhancement.

Figure 7.21: Thermal micrograph of a planar Cr-dope SrTiO$_3$ single-crystal cell showing local resistive heating near the anode, which witnesses a significant field concentration.

Further evidence of field concentration near anode is also shown in figure 7.21, which is a resistive switch working on the principle of electroforming. Thus, a filamentary formation at the cathode grows till the anode and depending on the field either creates short-circuit or breaks the circuit. The formation of low conductivity regions near the cathodes of MLCCs and their growth into the dielectric layer is analogous to the electroforming phenomenon in resistive RAMs.
It was shown in chapter 6 that even before degradation, microstructure defects and weak spots led to an increase in the electron injection at the cathode and adversely affected the device performance, although this injection was still the rate-limiting step. However after degradation, the magnification of the influence of these weak spot tends to wipe out the Schottky barrier at the cathode, and leads to significantly high electron injection at the cathode. Under such circumstances, electron extraction from the anode acts as the rate-limiting step. Figure 7.22 shows the schematic of the electrode-interface after the two degradation schemes, and the electron injection at the relevant electrode under a given bias condition.

Figure 7.22: Conduction mechanism through electronic injection at the relevant electrodes under given bias conditions in a parallel plate capacitor subjected to different steps of degradation. The darker regions near the electrodes are weak spots, which under degradation maybe regions with high oxygen vacancy concentration. The curved arrows denote thermionic emission of electrons across the interface, while the straight arrows denote tunneling across those interfaces.
Table 7.1 summarizes the various conduction mechanisms possible in a degraded MLCC and the arguments supporting and opposing them.

### Table 7.1: Various possible conduction mechanisms in degraded MLCCs

<table>
<thead>
<tr>
<th>Conduction Mechanism</th>
<th>Supporting Arguments</th>
<th>Opposing Arguments</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Poole-Frenkel Conduction</strong></td>
<td>• Temperature dependence of leakage current</td>
<td>• Asymmetry in current-voltage trends cannot be explained</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Increase in leakage current with degradation cannot be explained</td>
</tr>
<tr>
<td><strong>Tunneling Conduction</strong></td>
<td>• Significant increase in leakage current with degradation</td>
<td>• Temperature dependence of leakage current cannot be explained</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Asymmetry in current-voltage trends cannot be explained</td>
</tr>
<tr>
<td><strong>p-type Schottky Conduction</strong></td>
<td>• Asymmetric current-voltage trends can be explained by Schottky injection of holes from metal into dielectric, and the that the cathode has a lower barrier due to degradation</td>
<td>• For a Schottky barrier formation, work-function of metal, $\Phi_M$ should be lower than semiconductor/insulator work-function, $\Phi_{SC}$, which is not true for Ni-BaTiO$_3$ interface.</td>
</tr>
<tr>
<td></td>
<td>• Temperature dependence of leakage current</td>
<td></td>
</tr>
<tr>
<td><strong>n-type Schottky Conduction at the cathode (electron injection)</strong></td>
<td>• Temperature dependence of leakage current</td>
<td>• Expected an asymmetry in leakage current but the trend should be opposite, i.e., higher leakage in forward bias because of enhanced electron injection at the cathode as a result of degradation</td>
</tr>
<tr>
<td></td>
<td>• Significant increase in leakage current with degradation</td>
<td></td>
</tr>
<tr>
<td><strong>n-type Schottky Conduction at the anode (electron extraction)</strong></td>
<td>• Temperature dependence of leakage current</td>
<td>• The effect of weak links and electric field enhancement on the electron injection process at the cathode is magnified and needs to be completely understood</td>
</tr>
<tr>
<td></td>
<td>• Significant increase in leakage current with degradation</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Asymmetric current-voltage trend can be explained by Thermionic-field injection of electrons from dielectric into the metal, and that the electrons tunnel through the cathode due to enhanced effects of weak links at the interface</td>
<td></td>
</tr>
</tbody>
</table>
7.6 Different Extent of Degradation

Most of the discussion in the present chapter is about the changes in MLCCs during the initial stages of degradation. It has been shown that the leakage current increases with time during degradation of MLCCs. Thus, the extent of degradation has been defined in terms of the percentage increase over the steady state leakage current as illustrated in figure 7.23. Figure 7.24 also shows the current-voltage characteristics at 120ºC for MLCCs subjected to various extents of degradation. Not only does the leakage current increase in both bias directions with increasing amount of degradation, but the asymmetry in the leakage current about 0V also increased. Thus, the increase in leakage with degradation was much higher in negative bias as compared to the positive bias, indicating further deterioration of interface resistance at the cathode.

Figure 7.23: Extent of degradation defined by the percentage increase in current over the steady-state value for time-dependent degradation of MLCC at 225ºC under 30V bias.
Figure 7.2.4: Current-voltage characteristics at 120ºC for MLCCs subjected to different extents of degradation.

Figure 7.2.5: Variation of capacitance and dissipation factor of MLCCs from -60ºC to +150ºC at 1kHz and 0V d.c. subjected to different extents of degradation. The capacitance and the dissipation factor trends for 100% (green) and 150% (blue) degradation almost coincide due to saturation.
The TCC characteristics (figure 7.25) also witnessed an increase in capacitance till about 100% degradation with respect to the leakage current. However, beyond this, the capacitance tends to saturate. This trend indicates that the regions of reduced interfacial resistance gradually spread over entire the interface with degradation. When this process is complete, the effective dielectric layer thickness tends to saturate. The dissipation factor also showed a small increase with increasing amount of degradation.

7.7 Summary

This chapter discussed the aspects related to partially degraded BME-MLCCs. The various microstructural changes taking place even in the initial stages of degradation were studied using VC-SEM and EELS analysis techniques. It was found that there is a significant drop in the oxygen content near the cathode due to accumulation of oxygen vacancies. Also, this process is not reversible as shown from studies of doubly degraded MLCCs. Moreover, the VC-SEM results show enhanced field perturbations due to degradation of MLCCs, in addition to the morphological defects.

Furthermore, leakage current of partially degraded MLCCs was considerably higher than that of MLCCs before degradation. Also, the current-voltage characteristic for MLCCs degraded in a single bias direction was asymmetric about 0V, with the leakage current being higher in the bias direction opposite to that of degradation. This showed that due the presence of weak spots the Schottky barrier near the cathode interface became ineffective in controlling the conduction. Then, the barrier near the anode controlled the current conduction. Also, due to the lowering of interface resistivity,
as seen from the impedance spectroscopy studies, the effective dielectric layer thickness of degraded MLCCs became lower, thus resulting in an increase in the capacitance. It was also seen that by gradual increase in the extent of degradation, the leakage current of the MLCCs at lower temperatures became higher, thus indicating the deterioration of the interface.

For MLCCs, conclusive evidence of interface-controlled conduction is observed. Typically before degradation, the conduction is controlled by thermionic injection of electrons over an interfacial Schottky barrier at the cathode. However with degradation, the rate-limiting conduction is often controlled at the anodic interface through a field-assisted thermionic extraction of electrons from the insulator. This can be attributed to the field enhanced microstructural and stoichiometric features overriding the electron injection control at the cathodic interface.

The degradation studies in this work are unique in terms of having capacitors, which are degraded in both directions. This is solely possible through partial degradation. These studies conclusively prove that degradation is an irreversible phenomenon.
References


Chapter 8

CONCLUSIONS AND FUTURE WORK

8.1 Conclusions

The effects of various microstructural defects in base-metal multilayer ceramic capacitors were studied. This understanding is critical in achieving successful miniaturization of these devices, because it is known that the adverse effects of these defects would get magnified on reducing the dielectric layer thickness. Some of the important findings from this thesis are as follows:

- A significant enhancement in electric field is caused by electrode defects such as porosity and roughness, which is expected to limit the device performance.
- The enhanced electric fields lead to a significant increase in leakage currents, with this effect becoming increasingly important with reducing dielectric layer thickness.
- Fast firing of MLCCs limits the defect size and concentration at the electrode interface and offers superior performance for thin-layer devices.
• It was also observed that at temperatures above 130°C, reoxidized MLCCs exhibit a space charge limited conduction, which nullifies the influence of interface morphology.
• Even after reoxidation of MLCCs, some non-stoichiometry exists in BaTiO$_3$ due to residual oxygen vacancies, whose electromigration under bias leads to time-dependent degradation and additional field enhancement.
• Through bi-polar degradation schemes it is observed that accumulation of oxygen vacancies at blocking electrodes is only partially reversible and the resulting non-stoichiometry at the interfaces due to degradation is permanent.
• Compelling evidences of interface controlled conduction in n-type BaTiO$_3$ were found, with the rate-limiting conduction being controlled by the defect concentrations at the interface.

8.1.1 Study of Simplified Microstructure Defects

The effect of electrode roughness and porosity was studied on electric field distribution using finite element modeling (FEM). A parallel plated capacitor with simplified electrode defects were analyzed. Even with a simple representation of electrode roughness and pores it was found that the electric field could be as high as twice the average electric field in a dielectric layer. These field enhancements occurred around regions with electrode defects, and were expected to increase the local leakage current. The relative position of these defects was also a key factor in determining electric field distribution. Thus, closer electrode pores lead to higher field enhancement.
Also, the local thinning of dielectric layers due electrode roughness led to high electric fields and concomitantly high leakage current density.

### 8.1.2 Three-dimensional Microstructural Analysis

The exact electrode morphology of MLCCs was necessary to evaluate the impact of electrode defects on perturbations in electric field and leakage current density. Methodologies involving focused ion-beam milling and imaging provided excellent information on the electrode morphology, which was then converted into models for finite element analysis. The electric field distribution was then evaluated for 3D MLCC microstructures and was found to be higher around electrode defects such as porosity and roughness. Some MLCCs were also subjected to faster sintering rates and it was observed that the morphology of the electrodes improved considerably, thus leading to a better uniformity in electric field distribution. The leakage current density was also calculated from the electric field distribution, and it was predicted to be lower for MLCCs with improved electrode morphology.

The effect of electrode morphology on scaling down the dielectric layer thickness was also studied. Three-dimensional models with similar morphology but lower thickness showed increased electric field enhancement around electrode defects. More importantly, as the layer thickness reduced, a higher electric field concentration was detected around the electrode roughness. Thus, it proves that improving the electrode morphology is critical for successfully reducing the dielectric layer thickness without risking the failure of these devices. It was also shown that the electrodes are a lot more disintegrated near
the termination regions, with substantially high electric field concentrations. These considerations are important, especially since the probability of device failure occurring in those regions are high.

8.1.3 Improvement of Electrical Properties with Fast Firing of MLCCs

After having ascertained a significant improvement in electrode morphology of MLCCs with fast firing rates, the electrical properties of as-sintered MLCCs, which had been slow-fired at 150ºC/hr and fast-fired at 3000ºC/hr, were compared. There was an improvement in capacitance with increasing the firing rates, which was consistent with the observed improvement in electrode continuity. The impedance analysis showed that the MLCCs could be represented by 3-RC lumped components, which were contributed by electrode-dielectric interface, grain boundaries and grains. The interfacial resistance component witnessed the most significant improvement with fast firing, thus proving the importance of interface morphology control in MLCCs. The leakage current was improved by almost 70% by switching from slow firing to fast firing of MLCCs. Even after subjecting the MLCCs to complete reoxidation, the leakage current for fast-fired MLCCs was found to be lower than that for the slow-fired MLCCs at temperatures below 130ºC. However, at higher temperatures the conduction is space charge limited, and hence the effect of electrode morphology is nullified.

Thus, it is concluded that improvement of interface morphology becomes very important in order to improve performance and reliability of MLCCs, because of the reduction of potential weak spot in the microstructure failure might happen.
8.1.4 Partial Degradation of MLCCs

Various microstructural and electrical properties of MLCCs were studied after subjecting them to some initial stages of degradation. Also, some MLCCs were subjected to degradation in both the bias directions. Through TEM EELS analysis, it was observed that even during the initial stages of degradation, oxygen vacancy accumulation, as measured from BaTiO$_3$ stoichiometric analysis, took place near the cathodes. For capacitors degraded in a bipolar manner, there is an accumulation of oxygen vacancies near both the electrodes. This result through reversing the polarity suggests that the degradation process is partly irreversible. The typical oxygen stoichiometry of BaTiO$_{3-x}$ in those cases were reduced to somewhere between 2.82 to 2.86, while the average stoichiometry before degradation was 2.95. Voltage-contrast SEM images revealed significant reduction of interfacial resistance accompanied by effective thinning of the dielectric layer. This was further confirmed by capacitance measurements, which showed an increase in capacitance with progressive steps of degradation. The interfacial resistance evaluated from the impedance analysis also showed a marked decrease with degradation.

The current-voltage analysis provided the most insight into the conduction mechanism under these degradation steps. It was observed that as a result of degradation, the dominant conduction mechanism of MLCCs changed from being controlled by the Schottky-barrier at the cathode to being controlled by the Schottky-barrier at the anode. This was attributed to the enhanced electron injection process at the cathode due to
various factors such as oxygen vacancy accumulation, increase in the influence of the weak links in microstructure and effective thinning of the dielectric layer.

Thus, it is seen that the presence of extrinsic defects in microstructure, combined with the interface resistance degradation severely impair the performance and reliability of MLCCs, even during the initial stages of degradation. It was essential to prevent complete failure of MLCCs in order to assess these changes and to get a better insight into the degradation mechanism.

8.2 Future Work

Microstructural defects in MLCCs can affect the device performance quite significantly, especially in thin-layer MLCCs. The present study discussed some of the aspects related to these issues. The degradation mechanism and the changes occurring in the devices gave valuable insight regarding the importance of weak links in MLCCS in controlling reliability.

However, the processed MLCCs are anything but perfect metal-insulator systems. What this implies is that the interface between Ni and BaTiO$_3$ is not pure and can have a lot of surface impurity states, which would affect the band-structure and potential barrier at the interface and lead to Fermi level pinning at those surface states (figure 8.1).
Bardeen first proposed this theory.\textsuperscript{2} This is different from the Mott-Schottky theory which states that the barrier height at a metal-insulator interface should depend on the work-functions of the metal and the insulator.\textsuperscript{3,4} Thus, the Mott-Schottky and Bardeen theories are two extremes, and the actual nature of many real material interfaces is in between these limits. Moreover, there are additional factors such as grain boundaries, which are expected to control conduction.

Ideal depositions on single crystals under would be necessary to fully understand the interfacial conditions. Such studies would be necessary in different crystal orientation and in material systems with different dopant levels and non-stoichiometry.

It was also shown from the work by Okamoto et al. that Kelvin-force probe microscopy is a very useful tool to study the potential and electric field profile in degraded MLCCs.\textsuperscript{5} Figure 8.2 shows a typical topographic image of a cross-section of degraded MLCC and the corresponding electric field map collected in KFPM.
This technique can be very useful in studying the potential profile in partially degraded MLCCs, subjected to both single-step and double-step degradation. With improved resolution, such studies can also give conclusive evidence of electric field perturbations around electrode defects such as porosity and roughness.

The finite element analysis on MLCC microstructures helped in identifying electrode porosity and roughness as sites of electric field enhancement. However, in order to have a quantitative estimate of the effect of these defects on oxygen-vacancy migration and time-dependent degradation, the Poisson’s equation has to be coupled with diffusion equations of charge carriers and oxygen vacancies. Baitu et al. solved the temporal evolution of oxygen vacancy distribution in acceptor-doped SrTiO₃ crystals. However, similar solution are required for MLCCs with high oxygen vacancy concentration and a given complex 3D microstructures.

It is known that the electromigration of oxygen vacancies toward the cathode during degradation is dependent on the applied electric field and its flux is given by:

Figure 8.2: (a) Topographic image of cross section of degraded MLCC sample and (b) electric field map under external bias voltages.\(^5\)
where $\mu_V$ is the mobility of the oxygen vacancy. Thus, with the knowledge that electrode defects have high local electric field, an additional flux of oxygen vacancies is expected around them leading to higher accumulation, and thus very high injection currents. This is also illustrated in figure 8.3.

Figure 8.3: Regions in MLCCs with high local electric field, as calculated from finite element modeling in a cross-section, are expected to witness higher accumulation of oxygen vacancies during degradation.

Phase field modeling is a very powerful technique used to represent complex 3D microstructures in terms of field variables that are continuous across the interfaces and can predict microstructure evolution in materials.\(^7\)\(^8\) This technique can be used to solve coupled complex equations in a system. Thus, oxygen vacancy redistribution can be evaluated by coupling their flux equation (equation 8.1) along with the Poisson equation with a spatial variation of charge density. For such systems, additional complexities such as a real 3D microstructure observed in multilayer devices, grain boundaries, and Schottky barriers at the interfaces can also be incorporated and solved using phase-field modeling. Such solutions would give very useful information regarding the origins of locally reduced regions often observed in multilayer devices.
References


APPENDIX

CALCULATION OF SCHOTTKY-BARRIER HEIGHT FROM CURRENT-VOLTAGE DATA OF X7R MLCCS

The current-voltage measurements give useful information regarding the dominant conduction mechanism in metal-insulator systems. As has been discussed in chapters 6 and 7, the conduction mechanism in MLCCs (before degradation) are generally controlled by electron injection at the cathode, also known as reverse-bias Schottky conduction, and the governing equation for the leakage current density $J_{SC}$ is given as:

$$J_{SC} = A^* T^2 \exp \left( \frac{\alpha E^{1/2} - \Phi_B}{k_B T} \right) \quad (A.1)$$

where $A^*$ is the Richardson constant, $T$ is the temperature in K, $\alpha$ is a constant which depends on the relative permittivity, $E$ is the electric field, $\phi_B$ is the zero-bias Schottky barrier height, and $k_B$ is the Boltzmann constant. Generally it is not necessary to convert a current-voltage data into a current density ($J$) versus electric field ($E$) trend. Thus, equation (A.1) can be rewritten in terms of current ($I$) and voltage ($V$) as follows:

$$I = AA^* T^2 \exp \left( \frac{\alpha (V/d)^{1/2} - \Phi_B}{k_B T} \right) \quad (A.2)$$

where $A$ is the total area of the electrodes and $d$ is the average dielectric layer thickness. The first way to check for reverse-bias Schottky mechanism is to plot $\log I$ versus $V^{1/2}$. If
this is a linear plot, then the conduction mechanism is either reverse-bias Schottky controlled or Poole-Frenkel controlled.

In order to distinguish between these two mechanisms, current-voltage measurements are carried out at several different temperatures. Then, a linearly decreasing trend of \( \log I/T^2 \) versus \( I/T \) plot at any given value of \( V \) is a strong indication of reverse-bias Schottky conduction as being the dominant mechanism. The slope of these plots should give \( (\alpha(V/d)^{1/2} - \phi_B)/k_B \), which if plotted as a function of \( V^{1/2} \) should give a linear trend, which when extrapolated to \( V=0 \) gives the value of \( \phi_B/k_B \). Thus, the zero-field Schottky barrier is extracted from the current-voltage data.

Figures A.1 to A.4 illustrates this data analysis technique for a typical X7R MLCC, for which current-voltage measurements were made in a temperature range of 90ºC and 135ºC.
Figure A.1: Current-voltage data for a X7R MLCC from 90°C to 135°C.

Figure A.2: Linear trend between log I and $V^{1/2}$. Conduction could be either reverse-bias Schottky controlled or Poole-Frenkel controlled due the similarity in their expressions.
Figure A.3: Linear trend between log \((I/T^2)\) and \(1/T\) for several different bias voltages, confirm thermionic emission of electrons over a Schottky barrier as the dominant conduction mechanism.

Figure A.4: The slopes from A.3 are plotted against \(V^{1/2}\) to give a linear fit (fitting equation has also been indicated). The y-intercept of the equation gives \((\phi_B/k_B)\), from which the Schottky barrier height is calculated as shown in the figure.
VITA

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Malay M. Samantaray was born on October 18\textsuperscript{th}, 1983 in the state of Orissa, India. From his school days, Malay had a special inclination toward mathematics and science, which led him to his passion to become an engineer. He enrolled in the Indian Institute of Technology, Kanpur as an undergraduate student in Materials and Metallurgical Engineering, and graduated top of his class in 2006. Having heard about Penn State University and its renowned Materials Science program, Malay decided to continue his doctoral studies under the guidance of Profs. Clive Randall and Elizabeth Dickey, working on microstructure aspects in multilayer ceramic capacitors. He got to work on problems related to mathematics and physics, and in the process completed his doctoral research.