Thin Film Bi-based Perovskites for High Energy Density Capacitor Applications

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Chapter 1 – Introduction

1.1 Motivation and Objective

Sustainable energy sources require efficient energy storage mechanisms to be useful. Many sustainable energy sources under development are striving to efficiently produce electric energy. However, current electrical energy storage approaches can either store a lot of energy in a small volume or quickly release energy for use, but not both at once as shown in Figure 1.

![Figure 1: Energy Storage Device Capabilities (Emerson, 2009)](image)

This research is focused on increasing the energy density of thin-film capacitors to increase their viability as energy storage devices for many applications. New capacitor materials will be investigated to increase this energy density.

1.2 Energy Storage

Electrical energy storage devices store energy in various forms, and release that energy by providing a current. There are two main mechanisms for storing electrical energy:
electrochemical devices, such as batteries, and electrostatic devices, such as capacitors. These energy storage devices are characterized by their energy density, power density, temperature dependence, and lifetime.

Batteries convert chemical energy into electrical energy. Some are single-use only in which the chemical energy is stored in the battery on construction, and some allow for repeated uses through converting electrical energy back into the chemical energy that is stored in the battery. Batteries generally have a high energy density capability, but are limited by long discharge times and a limited number of charge/discharge cycles.

Capacitors consist of two conducting plates separated by an insulating material. When connected to an electrical energy source charge builds up on the conducting plates and energy is stored in the electric field running through the insulating material. Capacitors have much higher discharge rates and lifetimes than batteries, but are limited by their energy density capacity. Table 1 shows some comparative values for batteries and capacitors.

**TABLE 1: Batteries/capacitors table**

### 1.2.1 Capacitors

The characteristics of a capacitor are determined by the insulating material between the conducting plates, called the dielectric. The conducting material does not affect the energy storage capabilities of the capacitor and therefore is usually gold or silver to maximize conductivity for a maximum discharge rate.

The energy per unit volume, W, stored by a capacitor is a function of the dielectric constant, K (also called the relative permittivity, \( \varepsilon_r \)), and the electric field, E, across the capacitor as shown in Equation 1 (Jensen, Energy Storage):

\[
W = \frac{1}{2} K \varepsilon_0 E^2 \quad (Eq. 1)
\]
To maximize the energy density of the capacitor a material with a high dielectric constant and the ability to withstand a high electric field must be chosen.

1.2.2 Thin Film Capacitors

There are four main types of capacitors in use today: polymer-film, electrolytic, ceramic, and thin film capacitors. Thin film capacitors allow for thinner capacitors, which increases the electric field for a given voltage. The thin film geometry also works with many high dielectric constant materials, making thin film capacitors a good option for high energy density applications.

Current status of thin film capacitors (applications, materials, etc.)

1.3 Dielectric Materials

A dielectric material is an electric insulator that becomes polarized when subjected to an electric field. There are four methods of induced polarization: atomic polarization in which the electrons are displaced from the nucleus, ionic polarization, in which the anions and cations are displaced, dipolar polarization which aligns the dipolar molecules with the electric field, and space charge polarization, in which charges are transported until they hit a potential barrier like a grain boundary (Moulson and Herbert). Figure 2 shows the various polarization processes.

Fig 2.25 from Moulson and Herbert

In a capacitor the polarization of the dielectric material leads to a higher buildup of charge on the two conducting plates, which increases the energy storage capability of the device.

The two properties that affect a dielectric material’s ability to store energy in a capacitor are its dielectric constant and dielectric strength. The dielectric constant is a measure of the level of polarization induced in a material by a given electric field. Predicting the dielectric constant of
a material is very complex. This leads to using materials with known high dielectric constants and adding substituent materials to generate the desired properties.

The resistance of a dielectric material to dielectric breakdown is its dielectric strength, and is measured in terms of the maximum electric field the material can withstand. Dielectric breakdown occurs through one of three mechanisms: intrinsic, thermal, or discharge. Intrinsic breakdown occurs when the electric field gets large enough to ionize atoms by ejecting electrons. When the energy of the field gets high enough the electrons are ejected with enough kinetic energy to ionize adjacent atoms. This results in a cascading effect of ionized atoms which turns the dielectric into a conductor. Thermal breakdown occurs when enough thermal energy is created to raise the temperature of the material to the point that the conductivity is increased enough to cause breakdown to occur. Discharge breakdown results from defects in the material having a higher electric field than other locations due to the different dielectric constant. The higher field in the defects results in breakdown occurring at a lower electric field than it would if no defects were present.

**Add dielectric loss to this discussion**

### 1.3.1 Ferroelectrics

Ferroelectric materials have an intrinsic polarization even when no electric field is present. This polarization can be aligned with an applied field if the field is strong enough. The behavior of a ferroelectric in response to an applied field is demonstrated using a polarization vs. electric field hysteresis loop as shown in Figure 4.

**Figure 4: Buchanan, p. 145**

Ferroelectric behavior is temperature dependent. Above a certain temperature, termed the Curie temperature, the material enters a non-polarized paraelectric state (Bokov 2006). The
transition at the Curie temperature also produces a sharp maximum in the dielectric properties. This produces a large dielectric constant, but only in a very small temperature range.

Relaxor ferroelectrics are a special set of ferroelectric materials that are characterized by polarizations extending above the Curie point, a more linear P-E behavior, and most importantly a dielectric constant peak that extends over a broader temperature range. Figure 5 summarizes the differences between a regular ferroelectric and a relaxor.

**Figure 5: Samara/Venturini Fig. 2**

In searching for an ideal dielectric material several factors are important. A linear P-E response is desired to reduce the loss during the charge/discharge cycle of the capacitor. A broad permittivity vs. temperature dependence provides the capacitor with a broad temperature range at which it performs optimally. When these characteristics are combined in a material with a high dielectric constant a feasible thin film capacitor can be created. Certain perovskites have shown the potential to demonstrate all of these characteristics.

### 1.4 Perovskites

Perovskite materials have the ABX$_3$ structure. The unit cell consists of a small B cation at the center with the X anions on the faces and the large A cations on the corners, as shown in Figure 2.
Barium titanate (BaTiO$_3$) was the first ceramic material discovered to show ferroelectric behavior (Moulson).

### 1.4.1 High-K Perovskites

General overview of perovskites used for thin film capacitors. Cover Pb-based materials (PZT, etc.)

### 1.4.2 Bi-Based Perovskites

Current research on Bi-based perovskites. Cover bulk properties of BZT-BT measured by Cann, explain goal of producing those properties in the thin-film geometry

### 1.5 Deposition Techniques

Many techniques exist for depositing material in a thin layer on a substrate. For depositing ceramics the preferred methods are sputtering, pulsed laser deposition (PLD), and metal-organic chemical vapor deposition (MOCVD) (Norton, 2004). MOCVD is a complex process that is applicable for depositing large areas of thin films in industrial applications.
Sputtering and PLD are the most common methods for depositing thin films in laboratory environments.

The differences between these two techniques are central to the research being conducted. Sputtering has produced BZT-BT films that withstand high voltages but have a low dielectric constant, while PLD films exhibit high dielectric constants but breakdown at a relatively low voltage.

1.5.1 Sputtering

Sputtering deposition uses an ionized background gas to drive atoms from the target to the substrate. The target has a negative potential applied to it to attract the negatively charged ions in the background gas. When these ions strike the target atoms are ejected and land on the substrate.

Sputtering does not necessarily produce a stoichiometric deposition as different elements in the target can have different sputtering rates (Norton, 2004). This is normally compensated for by adjusting the stoichiometry of the target.

1.5.2 Pulsed Laser Deposition

The PLD setup is very similar to that of sputtering. Instead of ejecting atoms from the target using accelerated ions, however, a laser is used to boil atoms off the surface of the target. This creates a plume of atoms that deposits the desired material on the substrate. A schematic diagram of the PLD system is shown in Figure 3.
Figure 3: Pulsed Laser Deposition Schematic

The PLD system has many deposition variables that can be examined to determine the optimum method for creating a film with the desired characteristics of a high dielectric constant and a high breakdown voltage. Some of the available deposition variables are the substrate temperature, the laser energy and frequency, the target-substrate distance, and the pressure of the background gas in the chamber.

The substrate temperature affects the diffusion rate within the film and thus the order of the crystal that is formed (Ashfold, Claeyssens, Fuge, & Henley, 2004). Higher temperatures result in more order in the film, but can also create deficiencies of certain elements (Lai, Lu, & Zhu, 2005).

The energy of the laser affects the deposition rate as well as the quality of the film. Higher laser energy will increase the deposition rate by increasing the number of atoms ejected with each pulse but also increase the number of micron-sized particles that are ejected from the target (Norton, 2004). A higher laser frequency will decrease the time between pulses resulting in a higher deposition rate. However, this also has the effect of limiting the ability of previous layers to diffuse and thus reducing the level of crystallization.
The target-substrate (T-S) distance affects the number of atoms deposited with each laser pulse as well as the energy with which the atoms strike the surface. The smaller the T-S distance is the higher the energy of the depositing atoms, which results in more stresses in the film. These stresses result in a less-ordered crystal structure through the introduction of defects (Norton, 2004).

A background gas is used in the chamber as the oxidizing species for the creation of the film. This is necessary to produce the correct stoichiometry in the crystal. The background gas can also have the effect of lowering the intensity of the ablation plume to decrease the defects created in the crystal structure (Norton, 2004).
Chapter 2 – Methods

2.1 Thin Film Preparation

Films were prepared using pulsed laser deposition (PLD). The laser (KrF, Lambda Physik Compex 201, \( \lambda = 248 \text{ nm} \)) was used at a power output of 300 mJ/pulse which provided an energy density of 3 J/cm\(^2\). The chamber was first pumped down to 1 x 10\(^{-7}\) Torr and then filled with an O\(_2\) atmosphere of 200 mTorr. The substrate was adhered to a heater using silver paint and placed at a distance of 6.5 cm from the target. Both the target and the substrate were constantly rotated to create an even film deposition. After deposition samples were cooled in an O\(_2\) atmosphere.

The target composition was 0.1-Bi(Zn\(_{0.5}\)Ti\(_{0.5}\))O\(_3\) – 0.9-BaTiO\(_3\) with 10% excess Bi to maintain stoichiometry after losses during the deposition process. Polycrystalline films were deposited on platinized-silicon substrates. The effects of temperature and deposition rate were examined by creating films at temperatures of 550 \(^\circ\)C, 600 \(^\circ\)C, 650 \(^\circ\)C, 700 \(^\circ\)C, and 750 \(^\circ\)C with deposition rates of 2, 5, and 10 Hz. Deposition times were varied to keep the number of pulses constant: 50 minutes at 2 Hz, 20 minutes at 5 Hz, and 10 minutes at 10 Hz.

To create epitaxial films all layers must be perovskite materials. SrTiO\(_3\) substrates were used, but SrTiO\(_3\) is not a conductor so a conducting layer of LaNiO\(_3\) was deposited first. This layer was deposited at 650 \(^\circ\)C for 20 minutes at 5 Hz. The BZT-BT layer was then deposited on top of the LaNiO\(_3\) using the same variable deposition parameters as for the polycrystalline films.

2.2 Film Characterization

The electrical characteristics of the films were measured to determine the viability of these materials as dielectrics for thin film capacitors. Other data was taken in an attempt to understand the relationships between film structure and the resulting electrical performance.
2.2.1 Surface Structure

The surface structure was primarily examined to determine grain size. These measurements were performed using scanning electron microscopy (SEM).

2.2.2 X-Ray Diffraction

X-ray diffraction (XRD) was used to determine the crystal structure present in the film. Grazing incidence XRD was also performed to determine the orientation of the perovskite structure. XRD was performed using a Bruker D8 Discover system with a Cu Kα source at 40 kV and 40 mA.

2.2.3 Ellipsometry

Layer thicknesses were determined using spectroscopic ellipsometry. The system was a JA Woollam M-2000F.

2.2.4 Electrical Measurements

Addition of electrodes and etching to reveal bottom layer conductor (platinized Si for polycrystalline, LaNiO₃ for epitaxial films)

Low voltage AC current dielectric response measurements performed first

High voltage breakdown test performed next
Chapter 3 – Results

3.1 Polycrystalline Results

Good results here…

3.2 Epitaxial Results

More results…
Chapter 4 – Discussion

4.1 Polycrystalline Films

4.2 Epitaxial Films
Chapter 5 – Conclusion

5.1 Future Research
Bibliography


