Investigation of Multi-Layer Thin Films for Energy Storage

Timothy Jerome Renk and Todd Monson

Prepared by
Sandia National Laboratories
Albuquerque, New Mexico 87185 and Livermore, California 94550

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy’s National Nuclear Security Administration under Contract DE-AC04-94AL85000.

Approved for public release; further dissemination unlimited.
Investigation of Multi-Layer Thin Films for Energy Storage

Timothy Jerome Renk
Beam Applications and Initiatives

Todd Monson
Nanomaterials Sciences

Sandia National Laboratories
P.O. Box 5800
Albuquerque, New Mexico 87185-MS1182

Abstract

We investigate here the feasibility of increasing the energy density of thin-film capacitors by construction of a multi-layer capacitor device through ablation and redeposition of the capacitor materials using a high-power pulsed ion beam. The deposition experiments were conducted on the RHEPP-1 facility at Sandia National Laboratories. The dielectric capacitor filler material was a composition of Lead-Lanthanum-Zirconium-Titanium oxide (PLZT). The energy storage can be increased by using material of intrinsically high dielectric constant, and constructing many thin layers of this material. For successful device construction, there are a number of challenging requirements including correct stoichiometric and crystallographic composition of the deposited PLZT. This report details some success in satisfying these requirements, even though the attempt at device manufacture was unsuccessful. The conclusion that 900°C temperatures are necessary to reconstitute the deposited PLZT has implications for future manufacturing capability.
ACKNOWLEDGMENTS

The authors wish to thank Gerard A. Torres for technical assistance in the RHEPP-1 deposition experiments, and Donald L. Overmyer for his help in collecting X-ray diffraction (XRD) data.
CONTENTS

1. Introduction. .......................................................................................................................... 7
2. Description of RHEPP-1 and Experimental Setup.................................................................12
3. Experimental results ..............................................................................................................15
   3.1 Deposition and analysis of initial PLZT film .................................................................15
   3.2 Addition of separate lead target and formation of second PLZT film .......................18
   3.3 Attempt to form a capacitor device by multilayer deposition ..................................24
4. Discussion and Conclusions ..................................................................................................26
5. Distribution.............................................................................................................................29

Figure 1. Conceptual Drawing of a multilayer capacitor..........................................................10
Figure 2. RHEPP-1 Marx and pulse-forming line.....................................................................12
Figure 3. RHEPP-1 LIVA and vacuum tank............................................................................12
Figure 4. Schematic side view of RHEPP-1 diode region......................................................13
Figure 5. XRD Spectra from first set of PLZT films...............................................................17
Figure 6. XRD Spectra from PLZT target ..............................................................................17
Figure 7. Photograph of composite PLZT and lead target.....................................................18
Figure 8. XRD Spectra from PLZT-Pb target.........................................................................19
Figure 9. XRD Spectra from PLZT-Pb target, 650°C post-anneal ........................................20
Figure 10. XRD Spectra from PLZT-Pb target, 900°C post-anneal ........................................20
Figure 11. Comparison of XRD Spectra from PLZT-Pb target with PLZT target alone ....22
Figure 12. Conceptual drawing, multi-layer geometry of filler and electrode layers ..........24
**NOMENCLATURE**

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOE</td>
<td>Department of Energy</td>
</tr>
<tr>
<td>FIB</td>
<td>Focused Ion Beam</td>
</tr>
<tr>
<td>LIVA</td>
<td>Linear Induction Voltage Adder</td>
</tr>
<tr>
<td>MAP</td>
<td>Magnetically Injected Plasma</td>
</tr>
<tr>
<td>PLD</td>
<td>Pulsed Laser Deposition</td>
</tr>
<tr>
<td>PIBD</td>
<td>Pulsed Ion Beam Deposition</td>
</tr>
<tr>
<td>PLZT</td>
<td>Lanthanum-doped lead zirconium titanate</td>
</tr>
<tr>
<td>PVD</td>
<td>Physical Vapor Deposition</td>
</tr>
<tr>
<td>RHEPP-1</td>
<td>Repetitive High Energy Pulsed Power</td>
</tr>
<tr>
<td>RTBF</td>
<td>Readiness in Technical Base and Facilities</td>
</tr>
<tr>
<td>RT</td>
<td>Room Temperature</td>
</tr>
<tr>
<td>SNL</td>
<td>Sandia National Laboratories</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>XTEM</td>
<td>Cross-sectional transmission electron microscopy</td>
</tr>
</tbody>
</table>
1. INTRODUCTION

There is at present considerable interest in raising the energy density of electrical storage devices such as capacitors. Applications are diverse, and range from shrinking the size of cell phone batteries, to reducing the on-board footprint of energy storage for electromagnetic launchers. Electric car design is limited by the weight of on-board batteries. Electric cars could be made significantly lighter, and multi-stage accelerators could be made significantly smaller, if the energy storage density of batteries and capacitors could be reduced. Current storage limits are on the order of a few Joules per cubic centimeter (cc). To make significant progress in advancing a number of technologies, the state of the art in energy storage must be not merely 10 or 50% better than this, but factors of 3 to 20. New forms of energy storage need to be developed, not just incremental improvements in current technology such as dielectric film capacitors.

There are three general approaches to increasing the energy density of capacitors: 1) use of capacitor materials with an intrinsically higher dielectric constant, 2) increasing the capacitor standoff voltage, and 3) altering the capacitor geometry so as to increase the effective capacitance. One way to achieve the latter is to combine numerous sub-layers of very thin dielectric material (as little as 10 nm thick) separated by metal layers and energize them in parallel. This can be as follows: The capacitance of a multi-layer capacitor of n layers each of area A is

\[ C = n \varepsilon A / d \]

where \( \varepsilon \) is the dielectric constant of each layer of capacitor filler material of thickness d. Consequently, the capacitance can be increased by increasing the number of layers, and by decreasing each layer thickness (as long as electrical breakdown of each individual layer does not occur). Current approaches to capacitor construction have difficulty scaling down to the 10 nm per layer thickness. Liquid processing (e.g. solgel) cannot achieve this level of thinness. Conventional physical vapor deposition (PVD) techniques such as magnetron sputtering can lead to layers as thin as 10 nm each. But deposition rates for sputtering (Å per second) are relatively slow, and if layer heating is required during the deposition process, the result can be inter-diffusion of the layer materials. The microstructure of sputtered layers also tends to exhibit columnar grain growth. Both of these effects can lead to reduced voltage standoff or otherwise compromised performance of the multi-layer capacitor structure.

An alternate approach to thin film layer formation is investigated in the project described in this report. A pulsed high-power ion beam impinges on various target materials. The beam power is sufficient to vaporize the surface and create a blow-off plasma, which then deposits some distance away on a chosen substrate.
The ion beam is generated by the 800 kV RHEPP-1 facility at Sandia. The advantage of this Pulsed Ion Beam Deposition (PIBD) process over magnetron sputtering lies in the volume of deposited material, the rate of deposition, and the resultant microstructure of the deposited layer. Each ion beam pulse can lead to layer thicknesses from 1 to 100 nm over tens of cm² area. Previous PIBD deposition experiments using RHEPP-1[1] have yielded high-quality thin layers of fine-grain or amorphous microstructure, and in particular lacking the columnar structure seen on sputtered layers. This can be attributed in part to the high-kinetic energy of the ablation plasma, estimated at tens of eV compared to fractions of an eV for plasmas formed by magnetron sputtering. Another deposition approach, which uses lasers to pulse-ablate surface materials, also produces high-kinetic energy ablation plasmas. However, the high laser power density needed to ablate materials requires a highly focused beam (~ few mm²) for lasers of reasonable size. This small spot size leads to low deposition rates even for repetitively pulsed lasers (~ Å/sec), similar to that produced by sputtering. By contrast, the high-power RHEPP ion beam delivers a focused beam of up to 1 kJ of energy to a target material, leading to ablated materials produced over ~ 30 cm² of target area and layer deposition rates over two orders of magnitude higher than with PLD. The RHEPP-1 PIBD process then combines the high-kinetics of laser ablation with potentially high-volume production.

The thin-film materials chosen for this project consist of the following:

1. Dielectric source material: a ceramic material called lanthanum-doped lead zirconium titanate, known by its initials PLZT. This material was chosen because it is the object of current investigation at Sandia, and forms of this material have exhibited energy densities of up to 7 J/cc [2]. The stoichiometry of this material is quite complex, with the highest-performing compositions of proprietary chemical formulation. The high-dielectric properties of this material only occur for highly crystalline microstructure.

2. Electrode material: This is a metal that forms the conductive layers that separate the layers of dielectric material. The metal must have good electrical conductivity, a relatively high melting point (to withstand any post-annealing temperatures without melting or diffusing into the dielectric layer), and in general should have properties of a noble metal to resist oxidation of the electrode tabs which must be connected to external circuitry. We chose rhodium for the electrode material. This was chosen instead of platinum, which is also a good candidate material, because Rh was already acquired, whereas Pt would be very expensive to purchase. Rh actually has a higher melting point and higher electrical conductivity than Pt, and is known to be highly anti-corrosive.

3. Substrate. The substrate chosen was polished sapphire (Al₂O₃), chosen because it has a high
melting point, is electrically insulating, and can be polished to a smooth surface.

The requirements for a high-quality layered capacitor can be separated into two groups:

1) Dielectric material quality. The deposited dielectric material must be of the correct stoichiometry, i.e. the proportion of the constituent elements must be correct. The crystalline structure of the dielectric material must match what is known for a high-performing PLZT film. The material must be fully dense and free of pinholes, so as to hold off applied voltages without electrical breakdown.

2) Multilayer mechanical quality. The dielectric filler material must demonstrate good intra-layer adhesion with the alternating electrode layers. The interfaces between filler and electrode material must be clean and free of interdiffusional phase material. The electrode materials must be connectable to external circuitry for delivery of input voltage and power. The multi-layer film must be stably attached to the substrate, and the resulting structure must exhibit a high dielectric constant and breakdown strength.

These are a challenging group of requirements. The chemical composition of PLZT is complex, as already mentioned. Furthermore, while pioneering Japanese work in use of pulsed ion beams to deposit thin films [1,3] emphasized the ability of PIBD to preserve film stoichiometry compared to target material, prior thin film experiments on RHEPP-1 [4] demonstrated that this need not be so. In addition, the high-kinetic process of PIBD virtually ensures that the target material will be dissociated upon vaporization. That is, molecular and microstructural attributes of the target material will likely be lost. It then is possible that the volatile oxygen and lead components of PLZT will end up in deficient proportion in the resulting film. If this occurs, then ways must be found to restore the correct stoichiometry. Prior RHEPP-1 experiments have also shown that adding heat either during the deposition process (substrate heating) or afterwards (post-annealing) is necessary to recover microstructural properties such as crystallinity. Depending upon the level of heating necessary, this may in turn affect the stoichiometry, as high vapor pressure constituents such as lead may diffuse out of the film. Phase changes that occur upon heating may change the volumetric properties of the dielectric filler material, which may in turn affect the intra-layer adhesion and integrity as these phase changes occur.

Prior RHEPP-1 experiments aimed at reconstituting ablated material have been successful, but the
techniques have proven to be specific to each thin film system under investigation. Furthermore, due to the use of PLZT as a dielectric filler material, the reconstitution here was judged likely to be more difficult than any film composition previously investigated. We decided to focus on a composition of PLZT for which a prepared target material was readily available, with the chemical formula \((\text{Pb}_{0.92}\text{La}_{0.08}\text{Zr}_{0.65}\text{Ti}_{0.35})\text{O}_3\).

A second change to our original deposition plan concerns the formation of the individual electrode and filler thin film layers. A conceptual drawing of the multilayer capacitor structure is shown below:

![Fig. 1](image)

Note that a) the filler material must extend beyond the boundaries of the electrode material, or else shorting between the electrodes will occur, and 2) each electrode must include a tab for connection to external circuitry. In addition, each alternating tab must extend in opposite directions, to allow the left and right side of the capacitor shown above to be attached to different external circuit components. Thus there are three differently shaped beam masks that must be utilized to construct the multi-layer circuit.

We at first investigated the possibility of engineering an in-situ motorized mask support, with each mask being rotated into position with control circuitry outside the deposition vacuum chamber. It became quickly apparent that the engineering for this would be challenging and costly, and we decided to make the films necessary for this project by manual masking using stainless steel cutouts placed close to the substrate surface. This approach requires changing out of the masks with each deposited layer, and hence the necessity of bringing the vacuum chamber up to normal air pressure to change the masks. The result is an increase in deposition time, and a slight additional risk of intralayer contamination by repeated exposure to atmospheric conditions.
The project experimental plan that we developed is divided into several sections which will be discussed in detail in Section III below:

1) After obtaining the target PLZT material and sapphire substrates, we deposited an initial PLZT layer without electrode material under several different conditions intended to investigate the ability of heating mechanisms to reconstitute the PLZT material in the thin film. These include: a) in-situ heating at 350°C during the deposition process (about 45 minutes), b) post-anneal in vacuum at 550°C after deposition (about 45 minutes), and c) removal of the film followed by post-annealing in an external oven located in Bldg 897.

2) Post-analysis of the film layer by X-ray diffraction (XRD) showed that none of the heating techniques resulted in film reconstitution. The oven post-anneal showed promise, but only at a post-anneal temperature of 1100°C. This high heating level led to a serious deficiency in deposited lead fraction in the deposited film. This might be expected given the low melting point and high vapor pressure of lead.

3) We then obtained a separate lead target for the ion beam, and added it to the PLZT target material to form a composite PLZT-Pb target. A second film was then deposited, followed by post-analysis which showed a good match to the PLZT target material, when it was post-annealed at 900°C for 10 min. using a double crucible technique (to minimize Pb loss)

4) At this point, near the end of the FY08 funding period and nearly out of funds, we made a single attempt at a multi-layer capacitor configuration, with a total of three layers of dielectric filler material, and subjected the candidate capacitor to the 900°C post-anneal conditions for 10 min. Subsequent electrical measurements resulted in an electrical short.

Follow-on investigation of the multi-layer concept are being carried out in a separate project being funded through the Readiness in Technical Base and Facilities (RTBF) Program, and discussion of that work will be the subject of a future report.

Section II below begins with a short description of the RHEPP-I ion beam and the geometry for the
deposition experiments, followed by a detailed discussion of the four points listed above in Section III.

2. DESCRIPTION OF RHEPP-1 AND EXPERIMENT SETUP

The RHEPP-1 pulsed ion beam facility is located in the Bldg. 970 Medium Bay at Sandia National Laboratories. RHEPP-1 consists of a 5 kJ Marx and pulse-forming line (Fig. 2) feeding a 4-stage Linear Induction Voltage Adder (LIVA). The LIVA transfers pulsed power to an Applied-B

magnetically insulated diode with a MAgetically injected Plasma (MAP) gas-breakdown ion source. The ion beam propagates downward into a 1-meter long vacuum chamber. The LIVA can be seen in the top potion of Fig. 3, while the vacuum chamber appears in the bottom portion of the same Figure. The RHEPP-1 beam generation process has been discussed in detail elsewhere [1, 5], and we give only the highlights of
that discussion here. A schematic side-view of the diode with MAP ion source and beam transport region is given in Fig. 4. The geometry is cylindrically symmetric, with a gas plenum mounted on the center-line behind the inner Cu anode (red). When the plenum is energized (with nitrogen for these experiments), gas flows radially outward in a gap region towards the space between the inner and outer Cu anode. Two magnetic field coils are built into the cathode-side hardware (blue), and are energized well before the gas plenum is opened and power pulse arrives. The insulation field provided by the cathode (‘slow’) coils insulates the anode-cathode (A-K) gap from electron loss current. Before the gas plenum is energized but long after the ‘slow’ field coil is fired, a ‘fast coil’ is triggered. The rising fast coil waveform has a superimposed RF ringing cycle. When the plenum gas arrives at the fast coil location, the RF field ionizes the gas, and the interaction between the ‘slow’ and ‘fast’ magnetic fields pushes the now-plasma into position for acceleration when the power pulse arrives. The annular-shaped beam is brought to a soft focus due to the 20 degree pitch in the anode design, and Faraday cups can be mounted in the focal region to measure the beam fluence. A beam can be generated every 15 seconds.

Fig. 4
For deposition of the multilayer films, two ablation targets are mounted on a rotatable fixture at a 45-degree angle to the oncoming beam, as shown at the bottom of the Figure. The fixture allows for in-situ ablation from different targets without breaking vacuum. For the studies discussed here, the two targets would be PLZT and Rh. In practice, a third Ti target is used for the first few depositions, to improve film adhesion to the substrate. The depositional substrate is located on the center-line of the ablation plume formed by the impinging of the RHEPP-1 beam on the ablation targets. The substrate can be heated up to 350°C during film deposition, and as high as 450°C in vacuum after deposition. The diode region and the ablation targets are separated by 45 cm, and the distance between target(s) and substrate is typically 30 cm. The beam fluence at the center of the ablation targets is approximately 6-8 J/cm². Additional details of RHEPP-1 experiments can be found in References 6 and 7.
3. EXPERIMENTAL RESULTS

3.1. Deposition and Analysis of Initial PLZT film

A PLZT target of composition (Pb_{0.92}La_{0.08}Zr_{0.65}Ti_{0.35})O_{3} was obtained and used to deposit an initial set of dielectric films. These films were then examined using X-Ray Diffraction (XRD) and compared to the target material. XRD is a non-destructive analytical technique in which X-rays are scattered off the material to be examined. The reflected signal gives information about the crystallographic structure and chemical composition.

The RHEPP-1 nitrogen beam was used to make this set of samples. The beam was intentionally attenuated so that the deposited layers would be thin, and 80 pulses were used (RHEPP-1 shots TJR25339 to TJR25421). Four dielectric films were made from this first deposition:

a) room temperature (RT) deposition, substrate distance 30 cm.

b) room temperature deposition, followed by in-vacuum post-anneal at 465°C for one hour

c) room temperature deposition, followed by oven post-anneal at 1100°C for 10 minutes

d) deposition at 360°C substrate temperature.

The resulting XRD spectra are shown in Fig. 5. The top part of this figure shows the spectra for the 4 samples, and the bottom shows the expected spectral lines for the PLZT and the sapphire substrate. Fig 6, from additional analysis, shows a (Pb_{0.92}La_{0.08}Zr_{0.65}Ti_{0.35})O_{3} spectral scan produced from shavings from the ablation target itself. (For our purposes, the y-units or intensity for these plots can be taken to be arbitrary.) Comparison of the spectra shows that none of the deposited films matches the target material very well. The sapphire substrate shows clearly due to the thinness of the deposited films. None of the peaks at 22°, 44.5°, 55° are evident in the deposited films. The prominent peak at 31° is most evident in the 465° post-annealed film. But additional analysis shows that this in-vacuum post-annealed film still consists mostly of constituent oxide materials like lead oxide. Further analysis shows the 1100°C – annealed film to be very deficient in lead. This is probably due to the high post-anneal temperature. Evidence for this lead loss can be seen in the measured film thicknesses after processing, which were
measured by 1-D Dektak profilometry. The RT film measured 1.6 µm thick, as was the 465°C-annealed film, but the 1100°C post-annealed film measured only 1 µm in thickness, a substantial decrease. This is not entirely attributable to Pb loss, since when ceramics are annealed, there can be a substantial volume change due to phase changes and densification. But this is a larger step-height decrease than is typically seen for these kind of RHEPP-generated films.

We concluded then from this first series of PLZT films that 1) heating to 465°C does not lead to the required crystallographic structure required for PLZT capacitor films, at least using the techniques outlined above. It could be that modifications to these techniques, e.g. extended post-anneal in vacuum, may achieve success, but we concluded that this is unlikely; and 2) The 1100°C oven post-anneal is potentially promising, in that there was considerable shift in several of the lines that did not occur for the lower-temperatures. But clearly the Pb loss was unacceptable.
Figs 5 (above) and 6 (below)

[PLZT_target.MDI] PLZT from Target, from Praxar Surface Tech 6/20/08

00-046-0336> (Pb$_{0.9}$La$_{0.1}$)(Zr$_{0.65}$Ti$_{0.35}$)O$_3$ - Lead Lanthanum Titanium Zirconium Oxide
One option to address the Pb loss is to add additional Pb to the ablation target, in the form of a separate lead target. But because the target stoichiometry would be deliberately altered, this procedure could lead to lengthy delays in reaching an acceptable film composition. An initial estimate of Pb addition was made, and then additional XRD analysis completed. Iteration of the Pb amount would probably be necessary. In view of the lack of success with the other processing techniques, we opted to try this approach.

3.2. Addition of separate lead target and formation of second PLZT film

A separate high-purity lead target was purchased from Kurt J. Lesker (3 inch round, 99.99% pure). Since Pb can have exposure risks, Health Physics personnel participated in close-air monitoring of RHEPP-1 experimenters during the first deposition experiments with the lead target. They determined that any personnel exposure risks were far below SNL standards for maximum Pb exposure. One change to normal RHEPP-1 film deposition procedure was that the Al foil that normally is used to line the vacuum chamber was changed out after each series of experiments involving films containing Pb.

Fig. 7 below shows the additional Pb target (right-side) mounted directly on top of the original PLZT target. The Pb surface is roughened by the PIBD process. Clearly the PB target can be placed on the larger PLZT in any number of positions. Preliminary deposition experiments showed that the Pb ablates at a much higher rate per pulse than the PLZT. The relative position showed was picked as a first-cut. It was anticipated that the amount of Pb in the deposited film would be substantially increased.
We made a second deposition using this composite PLZT-Pb target. The RHEPP-1 nitrogen beam was used for 60 pulses (RHEPP TJR28228 to TJR28289). Since oven post-anneal was the only depositional method we chose to continue investigating, only room temperature films were deposited. One RT sample was then oven post-annealed at 650°C for 1 minute, a second sample was annealed at 900°C for 10 minutes, and a third at 1100°C for 10 minutes. The 650°C sample was then annealed for an additional periods of time (5 and 10 minutes, and one hour), and examined by XRD after each anneal time increase.

![Graphical representation of the XRD results](image)

Fig. 8. Top shows RT spectra (blue), with strong Pb peaks. The 650°C 1-minute post-anneal (gray) shows appearance of PbO peaks.
The XRD spectra from the RT deposition and 1-minute post-anneal at 650°C are shown in Fig. 8. The RT spectra show strong evidence of Pb metal. The Pb lines are attenuated in the 1-minute Post-anneal (gray), and lines for PbO appear. The spectra for the extended 650°C post-anneal times are shown in Fig. 9 below. Extending the post-anneal time to one hour at 650°C results in some reduction of PbO, but there is still no real evidence of PLZT crystalline structure.

Fig. 9. Variation in post-anneal time of PLZT/PB film at 650°C.

The increase in post-anneal temperature to 900°C, in comparison with the 650°C anneal, produced more promising results. The 900°C anneal with the additional Pb added resulted in a highly crystalline PLZT state. The 900°C post-anneal spectra, as well as a comparison to the
PLZT target spectra, are shown in Figs. 10 and 11, respectively. (Note the difference in vertical scale compared to Fig. 9.)

Fig. 10. Spectra for 900°C post-anneal for 10 minutes.
Fig. 11. Comparison of 900°C 10 minute post-annealed film with target PLZT.

This shows that raising the temperature to as high as 900°C seems to be a necessity to fully transition the material to a perovskite PLZT phase. This does not necessarily mean that removal from vacuum and post-annealing in an external oven is necessary. The in-vacuum heater setup used here was not capable of reaching this temperature. It may be that a different setup using in-situ 900°C annealing during the deposition might be as promising.

The indication that 900°C heating is required has significant implications for the manufacturing process. Such a high temperature excludes the use of many substrates, including all plastics. It is also evident that post-anneal after assembly of all the filler and electrode layers is likely to be problematic. This is because differential thermal expansion rates for the various layer constituents likely would lead to distortion of the layer geometry and intra-layer stress as the
filler material undergoes phase transformations during the heating. However, 900°C is still considerably less than the 1100°C temperatures often required in tape-casting thick films of PLZT.
3.3. **Attempt to form a capacitor device by multilayer deposition**

The option of in-situ heating to 900°C was not available to us for this Project. We chose however to attempt a final coating of a capacitor device, in which successive filler and electrode layers would be deposited and then the assembly would be oven post-annealed at 900°C. This can be expected to be challenging conditions for the performance of the final device. In addition to the layer distortions described above which may be introduced by the post-heating process, the masking required to produce the electrode and filler layers may compromise electrical properties of the capacitor.

To understand this, imagine that the first electrode is deposited on the sapphire substrate. The first PLZT/Pb filler layer is then deposited on top of this layer. But the boundary of the PLZT/Pb layer extends beyond the edge of the Rh electrode. Viewed from the side, as the filler layer approaches the Rh electrode edge, the filler material must ‘drop down’ onto the substrate a distance equal to the Rh electrode layer beneath it. This is illustrated in Fig. 12 below. (The individual layer heights have been exaggerated in this conceptual side drawing.) The first Rh electrode layer is shown in dark blue. The first PLZT/PB layer (orange) extends beyond the Rh left-hand edge. The ‘drop down’ is indicated by the orange step. Then the second Rh electrode layer (light blue) extends beyond the PLZT/Pb layer to its left. That layer is separated into 3 step heights. Since the PIBD layer deposition process is line-of-sight, there may be insufficient material to ‘bridge’ the step, and thus the light blue Rh may short to the dark blue layer when voltage is applied. In addition, there may be separate edge effects at each layer boundary that can distort fields and lead to shorting.

![Fig. 12](image-url)
A multi-layer capacitor was constructed using this masking technique. It consisted of 4 Rh electrode layers bounding 3 PLZT/Pb filler layers. A total of 71 sub-layers was deposited, followed by the oven post-anneal at 900°C. When voltage was applied to the capacitor to check its electrical properties, the result was an immediate short. The reason for this is not clear, but could be due to any of the possible mechanisms cited above, or some combination.
4. Discussion and Conclusions

The goal of this project was to investigate the feasibility of constructing a multi-layer thin-film capacitor that exhibits high energy storage for its volume. The approach was to form a number of very thin dielectric layers that due to its geometric construction, shows increased energy storage density. The layers are formed by ablation and redeposition by the RHEPP-1 pulsed intense ion beam of candidate material used as an ablation target. It was found that the candidate material must be augmented with additional Pb on an ad hoc basis, and then must be subjected to a high post-anneal temperature to reconstitute the PLZT filler to a form that could be used as capacitor material. A first attempt at multi-layer construction which includes the capacitor oven post-anneal at 900°C resulted in an immediate device failure.

Work is continuing in this investigation, funded by SNL RTBF for FY09. A preliminary examination of the failed multi-layer film by Focused Ion Beam (FIB) and cross-sectional transmission electron microscopy (XTEM) indicates that the high post-anneal heat may have caused a complete breakdown of the multi-layer structure. The various layers, once deposited, can be expected to exhibit different coefficients of thermal expansion (CTE), leading to significant intra-layer stresses. It may be that in-situ heating to 900°C is necessary to form the multi-layers. Such a temperature is not possible in the RHEPP-1 vacuum tank, which contains diode hardware formed from plastic which could not withstand such temperatures. In that case, successful capacitor manufacture may require a future dedicated facility.

Apart from the post-anneal temperature requirement, additional work will be ongoing to determine scaling behavior, e.g. capacitor layer performance with single-layer thickness, followed by increasing the number of layers. There may be mechanical or adhesion issues limiting the ultimate number of multi-layers or their area.
5. REFERENCES

2. Bruce Tuttle, Private coversation.
DISTRIBUTION

4 Lawrence Livermore National Laboratory
  Attn: N. Dunipace (1)
  P.O. Box 808, MS L-795
  Livermore, CA 94551-0808

1 | MS0431 | Leonard Lorence | Org. 0511 |
---|--------|----------------|----------|
1 | MS1164 | William Guyton | Org. 5400 |
1 | MS1181 | Larry X. Schneider | Org. 1181 |
1 | MS1182 | Bob N. Turman | Org. 5440 |
1 | MS1182 | Bob N. Turman | Org. 5440 |
1 | MS1182 | Ronald J. Kaye | Org. 5445 |
5 | MS1182 | Timothy J. Renk | Org. 5445 |
1 | MS1415 | Diane E. Peebles | Org. 1112 |
5 | MS1415 | Todd Monson | Org. 1112 |
1 | MS1415 | Donald L. Overmyer | Org. 1112 |
1 | MS1816 | Bruce A. Tuttle | Org. 1816 |
1 | MS0123 | D. Chavez, LDRD Office | 1011 |
1 | MS0899 | Technical Library | 9536 (electronic copy) |