Chapter 2. Composition

Using spectroscopic ellipsometry to detect second phase Bi$_2$O$_3$
and explain leakage current in SBT films.

A general method of analyzing VASE spectra using EMA principles was
developed which estimated the amount of second phase Bi$_2$O$_3$ in SBT thin films made by
MOD. In films with nearly identical x-ray diffraction patterns, Bi$_2$O$_3$ contents were
measured from 5% to 16% with an estimated error of ±3%. Since Bi$_2$O$_3$ is 10 orders of
magnitude more conductive than SBT, second phase Bi$_2$O$_3$ produced elevated leakage
currents. Equivalent circuits and percolation theory were applied to predict leakage
current based on Bi$_2$O$_3$ content and connectivity. Ellipsometry provided a vital method of
characterizing the quality of SBT films. This optical analysis showed why sufficient
refluxing of the Bi precursor solution was critical to develop high remnant polarization,
low leakage current, and ferroelectric crystal structure. In this context, the complex role
of excess Bi$_2$O$_3$ in the crystallization of SBT was reviewed from a processing perspective.

INTRODUCTION

An optical method of measuring the amount of second phase Bi$_2$O$_3$ in SrBi$_2$Ta$_2$O$_9$
(SBT) is developed and shown to be more sensitive than x-ray diffraction (XRD) for SBT
films made by metal-organic deposition (MOD). Bi$_2$O$_3$ is an important additive in SBT
films. To achieve acceptable grain growth and ferroelectric behavior, excess Bi$_2$O$_3$ is
required in the MOD precursor solutions. However, the appearance of Bi$_2$O$_3$ in the final
crystallized film is associated with smaller grains and high leakage current. In ferroelectric
capacitors, leakage current causes noise that degrades performance for non-volatile
memory and infrared detector applications. To help optimize MOD processing conditions
for low conductivity, variable angle spectroscopic ellipsometry (VASE) was used to
monitor Bi$_2$O$_3$ levels. Since Bi$_2$O$_3$ and SBT were found to have significantly different
extinction coefficients, k, over the wavelength range from 300 nm to 500 nm, the optical dispersion of MOD films was modeled as a mixture of appropriate SBT and Bi₂O₃ reference materials. The optically determined Bi₂O₃ concentrations were compared to leakage currents measured at 100 kV/cm. Since Bi₂O₃ has a conductivity 10 orders of magnitude higher than SBT, higher than normal leakage currents were attributable to the second phase Bi₂O₃ levels. To test whether or not the observed leakage current versus Bi₂O₃ content behavior was realistic, upper or lower bounds on leakage current were calculated assuming Bi₂O₃ formed continuous paths or isolated particles, respectively. Percolation theory was then applied to estimate the critical Bi₂O₃ volume fraction that would cause the sharpest increase in leakage current for SBT films made by MOD.

**EXPERIMENTAL METHOD**

**Sample Preparation**

Thin films of SBT were spin-coated onto Pt/Ti/SiO₂/Si substrates in seven layers by metal-organic deposition (MOD). All of the films in this study were prepared using the same organic components, the same film heat treatment (750°C for 1 hour in O₂), and the same solution stoichiometry (1 mole of Sr, 2.46 moles of Bi, 2 moles of Ta to make SBT with 23 % excess Bi₂O₃).

The only processing parameter that was varied was, t*, the total length of time that the Bi precursor solutions were stirred prior to use. For the Bi precursor, ~1.5 g of Bi₂O₃ powder (99.99% pure) was added to 10 ml of 2-ethylhexanoic acid. Each Bi solution was stirred uncovered at 25°C for 0.5 hours to dissolve the Bi₂O₃ powder, then stirred uncovered at 125°C for 1.5 hours until the solution became milky white, then stirred uncovered at 170°C for 2 hours until the solution was transparent. Finally, the Bi solution was refluxed by covering it loosely and stirring at 170°C for at least 2 hours to form a transparent yellow solution containing Bi₂-hexanoate. The minimum stirring time was therefore 6 hours, but the reflux step was lengthened for longer durations of t*. The
The purpose of the reflux step was to drive off water vapor and complete the reaction which produces Bi$_2$-hexanoate.

For the Sr precursor, ~0.5 g of Sr acetate (assay grade) was added to 5 ml of acetic acid, then this solution was sealed and stirred for 0.5 hours at 25°C. To avoid reactions with ambient humidity, ~2 g of Ta ethoxide (99.999% pure) was mixed with 3 ml of 2-methoxyethanol, sealed immediately, stirred for 30 seconds, added to the Sr precursor, and stirred for 2 minutes. Then the refluxed Bi precursor was added to the Ta and Sr mixture, and the resulting solution was sealed and stirred for 1 hour at 25°C. In this way, MOD solutions were made in ~20 ml batches containing ~ 0.0025 moles of SBT.

In addition to the SBT samples, Bi$_2$O$_3$ bulk and thin film samples were prepared as reference materials. To make the bulk Bi$_2$O$_3$ reference pellet, Bi$_2$O$_3$ powder was mixed with water and no binder, cold pressed, and sintered at 770°C for 12 hours in air. XRD confirmed that the bulk sample had the crystal structure of Bi$_2$O$_3$. Other bulk Bi$_2$O$_3$ pellets sintered at 800°C lost their shape, while those sintered at 750°C did not consolidate. The Bi$_2$O$_3$ thin film reference was made by MOD, using a solution of Bi 2-ethylhexanoate in hexanoic acid. After spinning and drying 6 MOD layers onto a Pt/Ti/SiO$_2$/Si substrate, the sample was annealed at 350°C for 30 minutes in air, resulting in a smooth, yellow, crystallized film with no visible surface patterns. XRD showed that this film contained both Bi$_2$O$_3$ and Bi$_2$O$_2$.33 phases. Annealing other Bi$_2$O$_3$ films in O$_2$ at 600°C for 1 hour converted the surface of the Pt substrate into a blue insulative material, while annealing in O$_2$ at 650°C for 1 hour created a reaction layer about 100 nm thick composed of Bi$_2$Pt according to XRD.

**Optical characterization**

The optical dispersion of SBT films was initially characterized by modeling VASE spectra from 275 nm to 1000 nm using Lorentz dispersion and following the standard procedures outlined in chapter 1. Smooth single-layer models were sufficient, since
surface roughness and substrate interaction layers did not significantly improve the fit. Later, these samples were treated as Bruggeman effective-media approximations (EMA) containing a mixture of SBT and Bi$_2$O$_3$ reference materials. This EMA theory is also summarized in chapter 1.

Many of the reference material properties were obtained using a point-by-point fitting method. In this case, estimates of the refractive index, n, and extinction coefficient, k, were made one wavelength at a time, without the constraints of a dispersion formula. Starting with initial values for n and k from Lorentz fits, the dispersion of bulk Bi$_2$O$_3$ was accurately determined by a point-by-point fit. Since VASE measures the polarization of spectrally reflected light, and the sample was polished with an optically flat surface, this bulk characterization did not involve any model of the subsurface structure. However to achieve accurate optical constants from thin film samples, the film thickness had to be determined, but it could not be fit, since the same thickness value applied to data at all wavelengths. Therefore, a series of fits were performed using different film thickness values. The mean squared error (MSE) of each fit was plotted versus thickness to find the minimum MSE, which was assumed to occur at the best thickness estimate. The sets of n and k values obtained from the best thickness estimates were used as reference files for Bi$_2$O$_3$ and standard SBT in subsequent EMA analysis of SBT samples.

RESULTS AND DISCUSSION

Tracing film quality to a key processing step

By analyzing two SBT films, (#A16 = normal SBT with t* = 16 hours) and (#A6 = defective SBT with t* = 6 hours), it was discovered that refluxing the Bi$_2$-hexanoate solution longer produced more desirable ferroelectric properties in the final films. As a secondary effect, longer reflux durations resulted in thinner films, probably from lower viscosity in the SBT solutions. Figure 2-1 compares the thin film properties of these normal and defective SBT films. According to atomic force microscopy (AFM), this
normal SBT film had acceptable grain size (~150 nm), and the remnant polarization, Pr, of the well saturated hysteresis loop was 8 µC/cm². In the defective SBT film, grains were half the normal size, and the leakage current, J*, at 100kV/cm was 20,000 times higher than normal. Integrated leakage current rather than integrated change in polarization resulted in an "eye-shaped" hysteresis loop. To find a cause for these widely different properties, the films were analyzed using x-ray diffraction (XRD) and variable angle spectroscopic ellipsometry (VASE). As seen in Figure 2-1, both films exhibited essentially the same x-ray diffraction patterns. The main XRD peaks matched the powder diffraction patterns of SBT, while trace amounts of Bi₂O₃ could account for several small peaks. The random variation of Bi₂O₃ peak heights showed no consistent trend. Therefore both films were predominantly SBT, and XRD could not detect any significance difference in Bi₂O₃ content. The similar refractive index values indicated similar densities and void fractions. However, the defective film had a significantly higher optical extinction coefficient, k, (near λ = 350 nm) than the normal film. Although crystallographically similar, these defective and normal SBT films were optically very different.

Comparing the optical properties of standard and defective SBT films

To further explore the optical differences between defective and normal SBT films, the VASE spectra from a wide variety of SBT films were modeled using Lorentz dispersion with up to three resonance energies as needed to best fit the data. In Figure 2-2, the resulting optical dispersion characteristics (n and k versus λ) of a defective SBT film are compared to a standard SBT film. The absorption coefficient, α, was calculated as a function of photon energy, E, based on (1), where λ is the wavelength, h is Plank's constant, c is the speed of light, and hc = 1240 eV nm.

\[ \alpha = 4\pi k / \lambda \quad \text{and} \quad E = hc / \lambda \]  

The optical absorption of each film can be characterized by a dominant absorption peak energy \( E_{\text{g, Lorentz}} \) and the absorption edge energy \( E_{\text{g, optical}} \) of that peak. One way to
estimate the absorption edge is by plotting $\alpha^2$ versus photon energy and using linear extrapolation to find the energy where $\alpha^2$ goes to zero. All films shared a resonance energy in the range 5.5±0.5 eV, which was expected since SBT has a wide band gap, theoretically at 5.1 eV. In Figure 2-2, the top film was chosen as a standard for our MOD thin films of SBT because it had excellent ferroelectric properties (high Pr and low $J^*$), and because the low optical absorption could be attributed to a single resonance energy at the band gap ($E_g^{\text{Lorentz}} = 5.4\pm0.1$ eV). The absorption edge of this standard SBT film was 4.5±0.6 eV.

In addition to band gap absorption at 5.4±0.2 eV, a defective SBT film (#C10 at the bottom of Figure 2-2) also showed an anomalous strong absorption peak near 3.9±0.2 eV. The absorption edge of this peak was 3.4±0.2 eV. The absorption edge in the defective SBT film was significantly lower than in the standard SBT film. These absorption features were not characteristic of standard SBT; however, very similar behavior was found in Bi$_2$O$_3$.

**Optically identifying Bi$_2$O$_3$ as a second phase material**

To find the cause of anomalous optical absorption in defective SBT films, the properties of Bi$_2$O$_3$ were investigated, since XRD had suggested that defective SBT films might contain trace amounts of Bi$_2$O$_3$. Figure 2-3 shows the optical dispersion of bulk and thin film Bi$_2$O$_3$. The shape of $k$ versus $\lambda$ for Bi$_2$O$_3$ mimics that seen in defective SBT films made by MOD. The strongest absorption peak in the near ultra-violet range was consistently 4.0±0.1 eV, and the absorption edge of this peak was 3.5±0.2 eV for bulk and 3.45±0.08 eV for thin film Bi$_2$O$_3$. All of these features match the behavior of the anomalous absorption in defective SBT films. Furthermore, since the values of $k$ in defective SBT were generally between those of Bi$_2$O$_3$ and standard SBT, it was reasonable to hypothesize that the defective SBT film was a mixture of SBT and Bi$_2$O$_3$. 

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Estimating Bi$_2$O$_3$ content from optical dispersion

The VASE spectra of each sample was modeled by assuming the film was a homogeneous Bruggeman type effective-media approximation (EMA) mixture of Bi$_2$O$_3$ and SBT reference materials. The optical properties of bulk Bi$_2$O$_3$ were taken from a point by point fit. By using a Lorentz model of the standard SBT film discussed earlier as the SBT reference, it was assumed that the SBT samples to be tested would have homogeneous porosity and shallow surface roughness similar to that of the standard SBT film. This was a reasonable assumption because all SBT films in this study were prepared by MOD using the same precursors, concentrations, spin-coating method, and heat-treatments. For optimum compositional resolution, spectra were modeled over the wavelength range from 300 nm to 500 nm, where the optical properties of SBT and Bi$_2$O$_3$ are significantly different. The only variables in the model were film thickness, $t$, and the volume fraction of Bi$_2$O$_3$, $X$.

In an attempt to improve the sensitivity of the EMA method described above for films with very small Bi$_2$O$_3$ levels, all VASE spectra were refit using a new set of reference material files. The new references were a Bi$_2$O$_3$ film and the standard SBT film, both modeled using point by point fits of VASE spectra over the $\lambda$ range from 300 nm to 500 nm. Comparing the EMA results obtained using different reference materials provided an additional estimate for the EMA method's margin of error. The new $X$ values for the % of second phase Bi$_2$O$_3$ obtained using a thin film Bi$_2$O$_3$ reference material were 1 % to 3 % lower than the original estimates of $X$ obtained using a bulk Bi$_2$O$_3$ reference material. This shift makes sense, since the bulk Bi$_2$O$_3$ sample was a little denser (according to higher n values) than the thin film sample. Both Bi$_2$O$_3$ references had nearly identical $k$ values. In general, this EMA method should work for other systems with optically distinguishable components, if appropriate reference samples could be made.

As a typical example of the EMA method, Figure 2-4 shows $k$ versus $\lambda$ for a defective SBT film (#C10). The point by point data for the extinction coefficients of film
#C10 fell between the two reference materials and was reasonably approximated by a homogeneous mixture of the standard SBT film material and 8.2±2 % bulk Bi$_2$O$_3$.

**Correlating Bi$_2$O$_3$ content with leakage current**

The presence of a more conductive second phase should increase the leakage current of defective SBT films. Leakage current was measured as a function of applied electric field, as shown in [Figure 2-5]. To compare the samples under the same conditions, the leakage current, J*, at 100 kV/cm was determined by linear interpolation. The current density through the reference Bi$_2$O$_3$ film was 10 orders of magnitude higher than through standard SBT, and reached the upper current limit of the detector at a field of only 13.5 kV/cm. Therefore the observed linear behavior at low fields was extrapolated to 100 kV/cm. As expected, the leakage current density in defective films, such as #C10, with 8.2 ± 2 % second phase Bi$_2$O$_3$ (according to VASE) was generally several orders of magnitude higher than in standard SBT.

To see if ellipsometry could be used to screen SBT films and predict leakage current, J* was plotted versus X in [Figure 2-6]. For films with 5 % to 10 % Bi$_2$O$_3$, J* was 0 to 3 orders of magnitude higher than in standard SBT. Two films made using Bi solutions that were only stirred for 6 hours contained about 15 % Bi$_2$O$_3$ and had leakage current densities that were 2 to 6 orders of magnitude higher than standard SBT. Although the EMA method was able to attribute higher than normal leakage currents to second phase Bi$_2$O$_3$, J* could not be accurately predicted based on X alone.

Samples with similar Bi$_2$O$_3$ levels often exhibited significantly different conductivities, indicating the importance of other factors such as particle geometry. In [Figure 2-6], the entire shaded region of J* values is possible depending on the second phase microstructure. From first order approximations of the possible microstructures, simple equivalent circuits shown in [Figure 2-7] were used to derive upper and lower limits on the leakage current through a composite film. If Bi$_2$O$_3$ formed continuous paths
(possibly along grain boundaries), then the maximum current would be proportional to the amount of more conductive material, which yields equation (2), where \( J_{\text{net}}^* \) is the leakage current at 100 kV/cm (or some other fixed electric field for all \( J^* \) values), \( X_{\text{Bi}_2\text{O}_3} \) is the volume fraction of second phase \( \text{Bi}_2\text{O}_3 \), \( X_{\text{SBT}} \) is the remaining volume fraction of SBT, \( J_{\text{SBT}}^* \) is the leakage current of the standard SBT film, and \( J_{\text{Bi}_2\text{O}_3}^* \) is the leakage current of the \( \text{Bi}_2\text{O}_3 \) reference material.

\[
J_{\text{net}}^* = X_{\text{Bi}_2\text{O}_3} J_{\text{Bi}_2\text{O}_3}^* + X_{\text{SBT}} J_{\text{SBT}}^* \quad (2)
\]

However, if \( \text{Bi}_2\text{O}_3 \) formed isolated particles (perhaps at triple points between SBT grains\(^2\)), then resistance would be proportional to the amount of insulative material, and the minimum current would be given by (3).

\[
\frac{1}{J_{\text{net}}^*} = \frac{X_{\text{Bi}_2\text{O}_3}}{J_{\text{Bi}_2\text{O}_3}^*} + \frac{X_{\text{SBT}}}{J_{\text{SBT}}^*} \quad (3)
\]

The wide variation in \( J^* \) that can be caused by particle geometry can be appreciated by considering two points. A film containing only 1% \( \text{Bi}_2\text{O}_3 \), all in a continuous network, could have \( J^* \) as high as 2 A/cm\(^2\), which is 1% of \( J^* \) for a \( \text{Bi}_2\text{O}_3 \) film. On the other hand, a film containing 99% \( \text{Bi}_2\text{O}_3 \) in layers separated by SBT would have 1% of the resistance of SBT, so \( J^* \) would be \( 10^{-6} \) A/cm\(^2\), which is only 100 times higher than \( J^* \) for the standard SBT film.

Between these two extremes, percolation theory describes how leakage current would follow a transition from the lower limit to the upper limit if isolated \( \text{Bi}_2\text{O}_3 \) particles formed conductive links at some critical volume fraction, \( X_c \). As discussed in Appendix B, the actual SBT and \( \text{Bi}_2\text{O}_3 \) particle morphology is influenced by many factors including bulk and surface free energies, chemical composition, physical distribution, and processing conditions. For \( X < X_c \), \( X > X_c \), and for \( X = X_c \), the leakage current is predicted by equations (4), (5), and (6), respectively, where the power, \( p \), is usually \( \sim 1.3 \).\(^3\)
for $X < X_c$  \[ J_{net}^* = \frac{J_{SBT}^*}{(X_c - X)^p} \]  \hspace{1cm} (4) 

for $X > X_c$  \[ J_{net}^* = J_{Bi_2O_3}^* (X - X_c)^p \]  \hspace{1cm} (5) 

for $X = X_c$  \[ J_{net}^* = \left( J_{Bi_2O_3}^* J_{SBT}^* \right)^{1/2} \]  \hspace{1cm} (6)

Consistent with percolation theory for small values of $X$, the $J^*$ versus $X$ data stayed closer to the lower limit than to the upper limit. Therefore, when $X$ was less than 10 %, $Bi_2O_3$ seemed to form isolated particles. In Figure 2-6, the percolation theory curves calculated for $X_c = 7$ % and 18 % seem to bracket most of the data. This suggests that the composite leakage current might be more than 5 orders of magnitude higher than in standard SBT if the $Bi_2O_3$ content exceeded 18 % in MOD films of SBT made by this process.

**Reviewing grain size effects**

The EMA method of analyzing VASE spectra discussed above was able to identify and measure the amount of second phase $Bi_2O_3$ appearing in SBT films made by MOD. Ellipsometry was particularly useful in this system because XRD did not show any significant differences in $Bi_2O_3$ content, even between films with drastically different electrical properties. Perhaps the concentration and size of $Bi_2O_3$ particles were both so small that $Bi_2O_3$ peaks were obscured by background noise. It is well known that diffraction peaks become wider and shorter for smaller grains. If $Bi_2O_3$ was constrained to grain boundary regions only 2 nm thick (according to TEM evidence discussed in Appendix B, Figure B2), then this would explain why XRD might not be sensitive to $Bi_2O_3$ content in these films.

Effects of second phase $Bi_2O_3$ in MOD films of SBT include anomalous optical absorption, unacceptably high leakage current, and smaller than normal SBT grains in this study. Related TEM results discussed in Appendix B also showed that wherever second
phase Bi$_2$O$_3$ was detected locally, it inhibited grain growth in SBT films made by MOD. Ironically, even though 30% excess Bi$_2$O$_3$ in the MOD solutions nearly optimizes grain growth under ideal conditions, the presence of Bi$_2$O$_3$ in the crystallized films is consistently associated with small grains and poor electrical properties.\(^4\)

In this study, insufficient refluxing of the Bi precursor solutions seems to have been the primary cause of increased second phase Bi$_2$O$_3$ content detected optically in the crystallized films. Identifying mechanisms by which refluxing longer decreases the concentration of second phase Bi$_2$O$_3$ is beyond the scope of this study. Perhaps a chemical transformation that proceeds during refluxing facilitates a more homogeneous distribution of Bi$_2$O$_3$ throughout the dried MOD film prior to crystallization. Obviously, if the local Bi$_2$O$_3$ concentration exceeds the solubility limit of the SBT phase, then excess Bi$_2$O$_3$ may precipitate out as a second phase. Mechanisms by which uniform or non-uniform excess Bi$_2$O$_3$ may promote or inhibit grain growth are discussed in Appendix B. It is clear that more research is needed to understand the complex role of Bi in this system.

**CONCLUSIONS**

Using EMA analysis, VASE can estimate second phase volume fractions in material systems like Bi$_2$O$_3$ in SBT films made by MOD, with optically distinguishable components. The leakage current through Bi$_2$O$_3$ films and standard SBT films was $10^2$ A/cm$^2$ and $10^{-8}$ A/cm, respectively. When the volume percentage of Bi$_2$O$_3$ in crystallized SBT films increased to 10% or 15%, due to variations in the Bi precursor solutions, the leakage current increased several orders of magnitude. However, leakage current could not be accurately predicted based on Bi$_2$O$_3$ alone, since particle connection could strongly influence net conductivity. In MOD precursor solutions, the traditional benefits of excess Bi$_2$O$_3$ disappeared as second phase Bi$_2$O$_3$ appeared in the crystallized SBT films.
ACKNOWLEDGMENTS

I would like to thank Tirumala Shridhar, Sang O. Ryu, Pooran C. Joshi, and Allen Matthys for making the samples used in this study. Tirumala Shridhar diligently prepared most of the SBT samples and performed careful leakage current measurements. Sang O. Ryu pioneered the chemistry used in this MOD process. Pooran C. Joshi had the "golden touch" to make the standard, against which other SBT films were compared. Allen Matthys shared his expertise on Bi reactions by making the Bi$_2$O$_3$ bulk and thin film references. My advisor, Seshu B. Desu, strongly encouraged this project, and suggested several of the optical analysis tricks which proved to be critically important. Related TEM work was done at ORNL under the guidance of Edward A. Kenik with TEM sample preparation training provided by Wade Jones.

This research was sponsored by the U.S. Department of Energy, Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Industrial Technologies, Advanced Industrial Materials (AIM) Program and Division of Materials Sciences, under contract DE-AC05-96OR22464 with Lockheed Martin Energy Research Corporation as an AIM Scholarship administered by the Oak Ridge Institute for Science and Education. Research utilized the Shared Research Equipment (SHaRE) User Facilities at Oak Ridge National Laboratory.

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