Chapter 1. Microstructure

Characterizing material optical properties and microstructure of ferroelectric $SrBi_2Ta_2O_9$ thin films using multi-layer ellipsometric modeling

Process dependent microstructural effects in $SrBi_2Ta_2O_9$ (SBT) thin films were characterized and distinguished from material dependent optical properties using a systematic multi-layer modeling technique. Variable angle spectroscopic ellipsometry (VASE) models were developed by sequentially testing Bruggeman effective-media approximation (EMA) layers designed to simulate microstructural effects such as surface roughness, porosity, secondary phases, and substrate interaction. Cross-sectional analysis by atomic force microscopy (AFM), transmission and scanning electron microscopy (TEM) and (SEM) guide and confirm the structure of multi-layer models for films produced by pulsed laser deposition (PLD), metal-organic chemical vapor decomposition (MOCVD), and metal-organic deposition (MOD). After accounting for microstructural effects, the optical properties of SBT in the MOVCD film matched bulk polycrystalline properties. From 300 nm to 1000 nm, the wavelength dependence of SBT optical constants followed Lorentz dispersion dominated by band-gap absorption at 5.2 ± 0.3 eV. At 630 nm, the refractive index, n, was 2.371 ± 0.002 and the extinction coefficient, k, was 0.060 ± 0.005 for randomly oriented polycrystalline SBT.

INTRODUCTION

Ellipsometry has been used in the semiconductor industry to monitor the thickness and quality of insulating thin films. For a smooth uniform film of a well-known material and substrate, monochromatic measurements at one incident angle were sufficient. In this case, film thickness was determined unambiguously using precalculated plots. With the development of affordable computers and regression software, variable angle spectroscopic ellipsometry (VASE) has been developed with the potential to characterize inhomogeneous films of new materials. However, VASE analysis can become frustrating, slow, and subjective unless proper guidelines are followed. The purpose of this paper is to present a systematic VASE modeling method, to characterize $SrBi_2Ta_2O_9$ (SBT) thin films using this method, and then to test the results.

VASE data must be interpreted through a model, which assumes how the optical constants of a film vary with depth (the optical profile) and with wavelength (the optical dispersion). The sets of parameters that govern the optical profile and the optical dispersion both depend on each other. Therefore, obtaining reliable optical characteristics from a thin film sample requires an accurate description of the film's microstructure. On the other hand, if each component's optical properties are well determined, then each component's concentration profile can be estimated. It will be demonstrated that the modeling method employed below can extract both the optical properties of a new material and the process dependent microstructure of a thin film.

To separate material properties from physical structure, the model assumes that a film contains one new material with Lorentz dispersion mixed with a small number of well characterized components, like empty space, secondary phases, or substrate related materials. The fraction of each component may vary with depth in the film. Therefore multi-layer models were developed by sequentially testing Bruggeman effective-media approximation (EMA) layers designed to simulate microstructural effects such as surface roughness, substrate interaction, porosity, and secondary phases.

To demonstrate how this multi-layer modeling technique accounts for structural defects that arise during processing, unoptimized films were selected which featured different dominant microstructural effects from several deposition methods. Under certain conditions pulsed laser deposition (PLD) produces films with sharp grain tips protruding from a dense film; therefore, a PLD film was selected to exemplify surface roughness. Since metal-organic chemical vapor decomposition (MOCVD) is capable of producing smooth dense films, a MOCVD film was included so that minor substrate interaction could be the main structural defect. When films made by metal-organic deposition (MOD) are annealed, amorphous material may segragate into denser grains leaving voids throughout the film. Additionally, since film thickness is increased by spinning on more layers by MOD, the concentration of voids between layers may be different than that within layers. Therefore, a MOD film with three thick layers was chosen to clearly show homogeneous and layered porosity.

To test the reliability of the multi-layer modeling method, thin film optical dispersion results are compared to bulk dispersion, and thin film optical depth profile results are verified by cross-sectional microscopy.

Many researchers are working to optimize SBT thin film processing, especially for random access memory applications. Achieving optimal ferroelectric properties in SBT thin films requires large grains,[1] minimal voids,[2] and smooth interfaces. Since these microstructural features affect a film's optical properties, semiconductor research and production facilities are increasing using nondestructive optical methods such as ellipsometry for on-line and in-situ monitoring of film quality.[3] Therefore VASE evaluation of SBT thin films is a subject of current interest. Of course, multi-layer EMA modeling can be applied to other dielectric or ferroelectric materials in isotropic polycrystalline thin films.

THEORY

During VASE data acquisition, linearly polarized light reflects off the sample and becomes elliptically polarized. The change in polarization state can be characterized by two angles, Δ (delta) and Ψ (psi). The ellipsometer measures Δ and Ψ as a function of wavelength, λ, for several incident angles, θ. The shape of the ellipse is described by Δ, the phase shift between the s and p components of polarization. The p component of polarization is in the plane of incidence, while the s component is perpindicular to the plane of incidence. Ψ describes the orientation of the ellipse. At the extremes, Δ is 0° for linear polarization or 90° for circular polarization. As Δ goes to 0°, Ψ approaches the angle to the major axis of the ellipse.

For a homogeneous film on a known substrate, equation (1) describes how Δ and Ψ are a function of the film properties, refractive index, n; negative extinction coefficient, k; and film thickness, t, for each given λ and θ.[4] Here R_p and R_s are the Fresnel coefficients for p and s components of polarized light, respectively. The Fresnel coefficients characterize the net amplitude reflectivity of the whole air-film-substrate system. At each interface, $r_{p\,ab}$ and $r_{s\,ab}$ are the p and s amplitude reflectivities, which are given by equations (2) through (5). The subscripts a and b indicate the layer above and below each interface, respectively, (0 for air, 1 for film, and 2 for substrate). Within each layer, N_a is the complex refractive index and θ_a is the angle from the normal to the path of light. Then $N_0 = 1\text{-}i0$, $N_1 = n\text{-}ik$, and $N_2 = n_{substrate}\text{-}ik_{substrate}$. The refracted angles θ_1 and θ_2 are determined from Snell's law in (6) and (7). The factor β is the phase thickness (8).

$$tan(\Psi)\, e^{i\Delta} = [R_p] \;/\; [R_s] = \tag{1}$$

$$[(r_{p01} + r_{p12}\, e^{-i2\beta})/(1 + r_{p01}\, r_{p12} e^{-i2\beta})] \;/\; [(1 + r_{s01}\, r_{s12} e^{-i2\beta})/(r_{s01} + r_{s12}\, e^{-i2\beta})]$$

$$r_{p\,01} = (N_1\, cos\theta_0 - N_0\, cos\theta_1) / (N_1\, cos\theta_0 - N_0\, cos\theta_1) \tag{2}$$

$$r_{p\,12} = (N_2\, cos\theta_1 - N_1\, cos\theta_2) / (N_2\, cos\theta_1 - N_1\, cos\theta_2) \tag{3}$$

$$r_{s\,01} = (N_0\, cos\theta_0 - N_1\, cos\theta_1) / (N_0\, cos\theta_0 - N_1\, cos\theta_1) \tag{4}$$

$$r_{s\,12} = (N_1\, cos\theta_1 - N_2\, cos\theta_2) / (N_1\, cos\theta_1 - N_2\, cos\theta_2) \tag{5}$$

$$\theta_1 = arcsin(N_0 \sin\theta_0/N_1) \tag{6}$$

$$\theta_2 = arcsin(N_1 \sin\theta_1/N_2) \tag{7}$$

$$\beta = 2\pi\, (t/\lambda)\, N_1 \cos\theta_1 \tag{8}$$

Unfortunately, equation (1) cannot be solved explicitly for n, k, or t. So VASE can only estimate film properties by modeling the Δ and Ψ spectra. With the aid of several mathematical tools, Δ and Ψ can be calculated at each λ and θ by assuming a model, which describes how the optical constants vary as a function of wavelength and film depth.[5] By incrementally adjusting model parameters, iteration software tries to improve the fit between measured and simulated spectra. With advanced personal computers and fitting algorithms, VASE has become a powerful analytical tool, with one key limitation. VASE results are only meaningful if the model has a realistic form. Therefore, "complementary" cross-sectional methods such as transmission electron microscopy (TEM), scanning electron microscopy (SEM) and atomic force microscopy (AFM) should be used to guide the development and verify the final structure of VASE models for thin films.[6]

EXPERIMENTAL METHOD

Sample preparation

To make the bulk $SrBi_2Ta_2O_9$ target for PLD, stoichiometric ratios of $SrCO_3$, Bi_2O_3, and Ta_2O_5 were ball-milled and then calcined for 1 hour at 1120°C in air following the solid-state method. This material was reground, ball-milled, pressed at 15 MPa into a pellet, and sintered in air for 1 hour at 1230°C.

Thin films of SBT were fabricated by PLD, MOCVD, and MOD, and all were crystallized at 750°C in O_2 to achieve similar grain size.

The PLD target was ablated by 725 mJ pulses onto an n+ Si (100) substrate held at 750°C in 0.3 Torr of O_2, using a Lamda Physik (Germany) Lasertechnik LPX 300, KrF laser with λ=248 nm. To encourage the formation of an epitaxial SBT/Si interface, the native oxide was etched away by HF before deposition. This film was not annealed after deposition.

The detailed process used to make the MOCVD film has been published. [7, 8]. Liquid and solid precursors were combined in one solvent and deposited at 550°C onto a Pt/Ti/SiO_2/Si substrate. This film was annealed at 750°C for 1 hour in O_2. The vaporized solution contained excess Bi to compensate for losses during annealing, and the final crystallized composition was assumed to be near stoichiometric $SrBi_2Ta_2O_9$ since only perovskite peaks were detected by XRD.

The MOD film was formed on a p-type Si (100) substrate by spin-coating and drying 3 layers of a solution containing metal-organic precursors in the following molar proportions:1 part Sr, 2.6 parts Bi and 2 parts Ta. This level of excess Bi has generally produced the best ferroelectric properties. The organics were pyrolized at 450°C in O_2 for 3 hours, and the film was crystallized in O_2 by annealing in a tube furnace at 750°C for 1 hour.

Cross-sectional analysis

Film thickness, void profiles, and substrate interactions were determined through cross-sectional SEM, TEM, and AFM. The fracture profiles of cleaved films coated with gold were observed on a Hitachi SEM equipped with a field emission gun. Cross-sectional TEM specimens were prepared using traditional film to film bonding, slicing, dimpling, and ion milling techniques prior to analysis on a Philips CM12 with a LaB_6 gun operated at 120 kV. AFM images were acquired by a Digital Instrument Dimension 3000 in tapping mode within 5 μm by 5 μm regions, then raw and integrated z-height histograms were obtained by bearing analysis.

Ellipsometric characterization

Samples were optically characterized using a Woollam spectroscopic ellipsometer with WVASE software (Lincoln, NE). Because Δ and Ψ spectra tended to exhibit a shift at about 340nm, more data was acquired near that wavelength; the bulk SBT sample was probed every 1 nm from 270 nm to 360 nm, and every 4 nm from 364 nm to 1000 nm. VASE data is most sensitive if the incident angles are chosen so that Δ is near 90° somewhere in the spectrum.[9, 4] Therefore incident angles of 66.0°, 67.2°, 68.4°, and 69.6° were used for the bulk sample.

Increasing the number of carefully selected incident angles makes VASE data more sensitive to variations in n and k at various depths in a film.[10] However, large data sets slow iteration. As a compromise between speed and accuracy, thin films were probed every 5 nm from 300 nm to 1000 nm, with θ at 70°, 75°, and 80°.

To estimate the band-gap energy of SBT, VASE models used Lorentz dispersion, governed by equation (9), to calculate the complex optical dielectric constant, ε, as a function of wavelength, λ, given the following fit parameters: baseline optical dielectric constant, ε_o ; absorption energies, E_j ; line breadths, B_j ; and amplitudes, A_j.[5] The product of Plank's constant and the speed of light, hc, equals 1240 eV nm.

$$\varepsilon = (n - ik)^2 = \varepsilon_o + \sum_j \left[A_j / \{1 - (hc/\lambda E_j)^2 + (hc/\lambda B_j)\} \right] \qquad (9)$$

Porous microstructural layers were modeled as Bruggeman EMA mixtures of SBT and some fraction, f, of empty space. In this case, ε_1 is the optical dielectric constant of SBT, and ε_2 is the optical dielectric constant of empty space (ε_2=1). With round voids, the net complex optical dielectric constant, ε, of the mixture is given by (10), where A and B represent dimensionless expressions (11).[11]

$$\varepsilon = \left(1 - AB + \frac{A^2}{3B}\right)\varepsilon_2 \qquad (10)$$

$$\text{where } A = \frac{(1-f)(1-\varepsilon_1/\varepsilon_2)}{(\varepsilon_1/\varepsilon_2)^{1/3}} \text{ , and } B = \left\{\frac{1}{2}\left[1 + \left(1 + \frac{4A^3}{27}\right)^{1/2}\right]\right\}^{1/3} \qquad (11)$$

To emphasize the importance of realistically simulating film profiles, multi-layer effective media approximation (EMA) models were developed from and compared to single-layer models.

Starting with single layer models, parameters were initially adjusted manually as follows to provide the software with a reasonable starting point for modeling. Since absorption dampens Δ and Ψ oscillations, the Lorentz parameters, E_j, B_j, and A_j were varied to mimic observed peak-to-peak envelopes. Then ε_o was increased from 1 until the center of oscillation of fit Ψ values agreed with data for all θ. As the modeled thickness was increased, peaks in the fit Ψ and Δ spectra became more numerous and moved away from the band gap energy. Therefore, coarse thickness adjustments were performed until the number of fit peaks agreed with the data;[4] then fine changes in thickness values further aligned the modeled peaks with observed peaks. The model parameter "thickness nonuniformity"[5] was increased only enough to round sharp features in the fit spectra to match the observed spectra at long wavelengths, where absorption was minimal for these wide bandgap materials.

VASE models with progressively more detailed structures were developed by introducing sets of EMA layers in three locations: first at the top, second at the base, and third in the interior of the films.[12, 4] These EMA layers accounted for both the SBT grains and the empty space between grains in the form of surface roughness or interior porosity. At each location (top, base, and interior) modeling first assumed sharp transitions between layers, and then tested whether graded transitions to the neighboring composition improved the model fit.

At every step of development, subsequent models included only those layers which reduced the mean squared error (MSE)[4] by more than 10%. According to Jellison, although χ^2 is a better statistical measure of the quality of fit, "the MSE can often be a good indication of fit improvement."[5] Layers were omitted if their thickness approached zero, or if any of their parameters became unrealistic, overcorrelated, or highly uncertain.

Parameters were consolidated to achieve the best fit with the simplest possible model. A flowchart for the interactive procedure used to develope VASE models is included in Appendix A.

RESULTS AND DISCUSSION

Summary of optical results

Optical dispersion curves which estimate the material properties of dense polycrystalline SBT were obtained by VASE from a bulk PLD target, a rough PLD film on Si, a smooth MOCVD film on Pt, and a layered MOD film on Si. The results from multi-layer EMA models were more reliable than the results from single layer models.

The average optical properties calculated from single-layer models (Figure 1-1a) varied significantly with the synthesis method, largely due to variations in film density. The refractive index values obtained from single-layer models of PLD and MOD films were significantly lower (by 23% and 16%, respectively) than from the bulk sample. Most of this apparent reduction in n came from surface roughness or interior voids. However, for more typical films that are dense and smooth, such as the MOCVD sample in this paper, single-layer models do fit VASE spectra reasonably well and provide a good first approximation of the film structure. In the MOCVD sample, the single-layer modeled refractive indexes were only 11% lower than the bulk refractive indexes.

Nonetheless, even with fairly dense and homogenous films, multi-layer EMA models were more accurate than single-layer models. When minor imperfections present in the MOCVD film were accounted for by a multi-layer VASE model, the estimated refractive index values of the SBT in this film were within 1% of bulk values over wavelengths from 550 nm to 750 nm, as shown in Figure 1-1b (rather than appearing 11% lower, as in the single-layer model mentioned above, Figure 1-1a). In general, the optical properties extracted from multi-layer EMA models were closer to measured bulk properties and less dependent on the synthesis method than single-layer models were. (Figure 1-1b and Table 1-1)

Despite the unique depth profiles of films made by different methods, multi-layer models were able to reveal that SBT material in each sample had comparable optical dispersions. For example, the refractive index values of SBT from multi-layer models of MOD and PLD films were only 11% and 9% lower than in the bulk sample respectively. These differences between bulk and thin film dispersion could originate from either compositional or structural effects not included in the multi-layer models described in this paper, such as deviations in bismuth stoichiometry, secondary phases, grain size effects, preferred orientation, defect or grain boundary concentrations, and residual stress.

Using EMA models, SBT material properties estimated from all samples were described by Lorentz dispersion, with a primary absorption peak at 5.2 ± 0.3 eV and a secondary absorption peak at 3.75 ± 0.07 eV. This primary absorption was consistent with a 5.1 eV band-gap, estimated from tight binding principles.[13]

In SBT samples the secondary absorption peak near 3.75 eV did not correspond to any band-to-band transitions or shallow traps (< 0.2 eV) in SBT.[13] This absorption was responsible for sharp discontinuities in Δ and Ψ spectra near $\lambda = 340$ nm, which have been observed in many materials that contain bismuth and oxygen including Bi_2O_3. In contrast to thin film SBT samples, bulk SBT had no excess Bi, was annealed at much higher temperatures, contained much larger grains, and exhibited less absorption near 3.75 eV (See "Amplitude #2" in Table 1). The bulk sample was probably more like pure SBT than the films. Therefore absorption near 3.75 eV in SBT samples might originate from bismuth oxide contamination. The role of bismuth oxide in SBT will be discussed in chapter 2.

Bulk polycrystalline SBT

The bulk PLD target was modeled as a single material with Lorentz dispersion. Optical microscopy showed less than 2% voids (in the size range less than 2 μm) between randomly oriented grains ranging from 2 μm to 11 μm in size. Only voids less than 2 μm in size were assumed to contribute to the optical properties of the polished bulk sample measured from specular reflections, as in VASE. Without backside reflections or secondary phases, this bulk sample provided an ideal opportunity to characterize the optical dispersion of dense isotropic polycrystalline SBT. The overall shapes of observed Δ and Ψ spectra in Figure 1-2 were accurately predicted (MSE = 6.2) by a primary absorption peak at 5.25 ± 0.19 eV. The discontinuities in all bulk spectra at 340 nm were explained by a sharp secondary absorption peak at 3.688 ± 0.002 eV. Both features of bulk SBT were described by the Lorentz parameters in Table 1-1. The secondary absorption peak could be located more accurately because it occurred within the spectral range of the ellipsometer, while the primary peak location, which occurred just beyond the range, had to be extrapolated from the observed shape of the curve.

Consistent with the widely distributed nature of states forming the band-gap in SBT,[13] the absorption near 5.25 eV could be separated into peaks at 5.88 ± 0.06 eV and 4.40 ± 0.02 eV. The latter peak may explain why Chen estimated the SBT absorption edge at 4.55 eV by plotting the absorption coefficient versus energy.[1] Chen's ellipsometry work modeled SBT dispersion with a single Lorentz oscillator at 5.47 ± 0.03 eV.[1] Separations of the band-gap absorption peak were not pursued since they resulted in more complicated models with about the same fit of the data and with about the same dispersion curve for SBT.

PLD film on Si

A 1 μm thick pulsed laser deposition film was studied in which the surface roughness depth was significant even though it represented only 10% of the film thickness. Under conditions which produce supply-limited growth, surface roughness in PLD films can be minimized by providing incoming material with enough mobility and time to find the most stable crystallization sites,[14] if the fastest growing crystallographic direction is not oriented perpendicular to the surface.[15] However, this rough SBT film was selected so that surface roughness would be a dominant effect.

Because AFM provided fairly direct measurements of surface roughness, it was a useful tool for testing the validity of the VASE model of the free surface of a film. AFM showed that the surface height had a normal distribution with a full width at half maximum (FWHM) of 50.7±7 nm. Statistically, 98% of a normal distribution spans 2 FWHM; so in this case, 98% of the film surface was within a region 101.5±14 nm deep, according to AFM. When surface roughness was modeled as a linear transition from SBT to empty space in model A (Figure 1-3b), VASE estimated the surface roughness layer was 108±16 nm thick, which was close to the AFM value of 101.5±14 nm. This agreement between VASE and AFM was not surprising, since the AFM cross-section in Figure 3b showed a "zig-zag" pattern of grain tips at the film's surface. If the cross-sections of all SBT grain tips were equally tall triangles, the transition from SBT to empty space in such a surface roughness layer would be exactly linear.[15]

When the surface roughness profile was measured, AFM showed that SBT grain tips formed pyramids with a distribution of heights. Integrating the AFM surface height histogram yielded an S-shaped empty space profile (Figure 1-4). The fraction of empty space, f_{space}, at any height, Z, was found by integrating the surface z-height probability distribution, p(z), from the lowest surface point, z_{min}, upward:

$$f_{space}(Z) = \int_{z\,min}^{Z} p(z)\,\partial z \tag{12}$$

Equation 12 is derived in the Appendix and facilitates the comparison of AFM data with VASE models.

VASE models with S-shaped surface transitions were tested but did not improve the fit of the VASE spectra or provide any new, accurate information, compared to the linear model discussed above. In fact, S-shaped transitions tended to become linear during

VASE iteration. Perhaps if VASE spectra had been acquired at more than three incident angles, greater depth profile resolution could have been obtained.

Model A provided a simple, justifiable, and accurate method of characterizing the surface roughness and the SBT optical properties of the PLD thin film. Compared to a single-layer model (MSE = 90), model A improved the fit of VASE spectra and reduced the MSE to 33 (Figure 1-3a). To follow the sharp stair-step in Δ and Ψ near λ = 340 nm, a secondary Lorentz absorption peak was required at 3.75+.03 eV in addition to the primary absorption peak at 5.38 +.03 eV. The refractive index values obtained from model A for thin film SBT were only 8% lower than bulk values (from λ = 300 nm to 1000 nm). Obtaining similar optical properties for SBT made by different methods increases confidence in both the characterization and deposition processes.

If a single-layer model was used for the entire PLD film, the apparent n values were 23% lower than in the bulk sample. Considering that empty space in the rough surface of this film only represented 5% of the whole film's volume, the optical behavior of this film was disproportionally sensitive to empty space near the surface. As shown below, VASE can also detect void space at the base and in the interior of a film, where other nondestructive methods are not possible.

MOCVD film on Pt

The chemical vapor deposition (MOCVD) thin film of SBT on a Pt/Ti/SiO_2/Si substrate was dense enough that even a 1-layer model fit the VASE spectra reasonably well (Figure 1-5a) and yielded refractive index values only 11% lower than bulk. However cross-sectional SEM revealed shallow surface roughness and kernel-shaped columnar grains (Figure 1-5c). Several authors have noted that conical grains growing taller and wider and often leave voids between nucleation sites at the base of the film.[12,2] When these features were included in model B as a linearly graded surface roughness layer and a sub-film layer with 34 ± 3% voids (Figure 1-5b), the MSE was reduced from 59 to

27 (Figure 1-5a), and the refractive index dispersion curve of the film interior matched that of the bulk sample within 2% over visible wavelengths (Figure 1-1b). These results showed that bulk optical properties were achievable in dense thin films of SBT made by MOCVD.

MOD film on Si

Using metal-organic deposition, a thin film of SBT was formed on Si by spin-coating three layers. Cross-sectional TEM (Figure 1-6c) revealed three dense layers (with occasional voids) separated by thin porous layers. Based on VASE and TEM evidence presented in Appendix B, it is proposed that during the drying step second phase Bi_2O_3 became concentrated between each layer and inhibited grain growth and consolidation during annealing, so that these regions became more porous than the rest of the film. MOD techniques (involving thinner layers and proprietary solvents) have been developed which facilitate SBT grain growth across spin-coated layers,[16] perhaps by achieving a more homogeneous distribution of excess Bi_2O_3. This MOD film was selected because it showed clearly delineated layers and thus tested the capabilities of VASE.

The thickness and porosity of each layer was accurately simulated by model C, illustrated in Figure 1-6b. For comparison, the TEM profile is displayed on the same scale in Figure 1-6c. When comparing model C with TEM, the following points should be considered. Model C represents the average properties of a region 1000 times larger than the area examined by cross-sectional TEM. For samples this small to be representative of the average implies this structure is present throughout the film. The only constraints on the structural parameters of model C were that they all be positive and that the two thin, most porous layers be identical. TEM was used to suggest the general form of VASE models, but not to fix their properties.

The void fraction and thickness of each layer in model C were in remarkable agreement with TEM and AFM. On the top of the film, VASE estimated that a graded surface roughness layer was 38 ± 12 nm thick, and AFM agreed that 98% of the surface was within a layer 34 ± 6 nm thick. The base of the film was best modeled as a linear transition from SiO_2 to SBT. TEM showed that SiO_2 formed a smooth interface with the Si substrate and a rough interface with SBT grains, so it was realistic for the SBT fraction to increase away from the substrate in this graded layer. Model C included two porous regions between denser layers of SBT; the upper and lower porous regions had 41 ± 8 % voids and 40 ± 10 % voids, respectively. The fit was improved considerably if the top two dense layers of SBT were allowed to contain 13 ± 3 % voids. The position, thickness, and porosity of these layers estimated by VASE were consistent with TEM cross-sections. As described above, model C used multiple EMA layers to accurately simulate surface roughness, substrate interaction, and interior porosity.

Model C was structurally more accurate than a 1-layer model, and therefore generated more realistic VASE spectra and optical dispersion. In Figure 1-6a, the 1-layer model did not predict Δ peak heights or shapes, resulting in a poor fit (MSE = 103). Model C followed the sharp high Δ peak near 420 nm and the double-humped structure of Δ peaks between 500 nm and 1000 nm, so the MSE was reduced to 33. The refractive index values obtained from model C were 11% lower than those of bulk SBT, (rather than 16 % lower as from the single-layer model).

In this MOD film, SBT material properties were extracted from EMA layers simulating mixtures of SBT grains (86±38 nm long by 40±14 nm wide) and voids (16±4 nm). In all thin films presented here, the grains and voids were smaller than the probing wavelengths and Bruggeman EMA models yielded valid results. Model C achieved a significant level of accurate detail regarding the component profile without becoming overcorrelated by too many parameters.

Confirming the physical structure of a VASE model

The results of modeling the films in this paper did not support the notion that introducing enough parameters to a VASE model could arbitrarily decrease the fit MSE to zero. As more layers and variables were tested, generally only parameters which provided a better approximation of the structure or optical dispersion of the film produced a better fit. Every model discussed here, including the SBT/Si film by MOD, had a characteristic lowest achievable MSE, (Figure 1-7) which marked a point of diminishing returns. Beyond this stage, additional variables increased correlation and uncertainty without improving the fit. When parameters were strongly correlated, changes in one parameter could be offset by modifications of its counterpart, and iteration would not find a unique solution. Even when parameters are not strongly correlated, it is well known that a variety of similar models can be designed that will fit the data reasonable well.[4] Therefore, a low MSE alone was insufficient justification of a model's structure. Cross-sectional analysis was required to guide the formation and test the validity of VASE models. VASE should not be used as a substitute for other more direct methods of estimating microstructural composition profiles. VASE is better suited as a quality assurance tool. If there are a series of films that have been made under the same conditions and should have very similar structure, then it may be sufficient to examine only one of the films using cross-sectional TEM (for example). In this case, small variations in structure can be detected by VASE as variations in parameter values taken from a consistent model with a verified form.

In these films, with grains smaller than 200 nm, the Bruggemen EMA theory realistically simulated interior void profiles, and graded sets of Bruggeman EMA layers accurately predicted surface roughness depths. This justified Jellison's confidence in Bruggeman simulations of rough surfaces.[5]

SUMMARY

In SBT films with lateral features smaller than 200 nm, surface roughness, substrate interaction, and interior porosity were realistically described by multi-layer

Bruggeman EMA structures. At the top of a film made by pulsed laser deposition (PLD), surface roughness was simulated by a linear transition from SBT to empty space, and the thickness of the roughness layer was confirmed by atomic force microscopy (AFM). At the base of a film prepared by liquid delivery metal-organic chemical vapor decomposition (MOCVD), subfilm porosity in the multi-layer model represented gaps between the nucleation sites of kernal-shaped columnar grains seen by scanning electron microscopy (SEM). In a film made by spinning on three layers via metal-organic deposition (MOD), voids within and between each layer were included in a void profile that was justified by cross-sectional transmission electron microscopy (TEM). Because multi-layer models account for how n and k vary with depth, they estimate more accurately how n and k vary with wavelength. Compared to 1-layer models, multi-layer EMA models with physically verifiable component profiles extracted refractive index values from thin film SBT samples that were significantly closer to bulk material properties ($n=2.371\pm.002$ and $k=0.060\pm.005$ at 632 nm). Over wavelengths from 300 nm to 1000 nm, bulk and thin film SBT samples exhibited Lorentz dispersion with band-gap absorption at 5.2 ± 0.3 eV.

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