DEVELOPMENT OF AN XRF METROLOGY METHOD FOR COMPOSITION AND THICKNESS OF BARIUM STRONTIUM TITANATE THIN FILMS

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ABSTRACT

Thin films of barium strontium titanate (BST) are being investigated as the charge storage dielectric in advanced memory devices, due to their promise for high dielectric constant. Since the capacitance of BST films is dependent upon both stoichiometry and thickness, implementation into manufacturing will require precise metrology methods to monitor both of these properties. This is a challenge, since the BST film thicknesses are 60 nm or less. A metrology method was developed based on wavelength dispersive x-ray fluorescence and applied to the measurement of both stoichiometry and thickness of BST thin films.

INTRODUCTION

The continually increasing demand for more memory and the trend towards higher operating speeds of integrated circuits dictates the need for high density memory accessible at rapid rates. The time-proven bit cell design of DRAMs (dynamic random access memories) relies upon the storage of charge in an integrated capacitor. To date, the dielectric used in this capacitor has been SiO₂; the challenge of maintaining sufficient charge storage density as the bit cell size decreases has historically been met by decreasing the SiO₂ thickness. However, this approach is reaching its limit and although nitridation of SiO₂ affords some increase in dielectric constant, radically higher dielectric constant films are required to replace SiO₂. Barium strontium titanate (BST) is particularly attractive because of its very high dielectric constant, low leakage, thermal stability, low dissipation factor and promising fatigue behavior [1-4].

The dielectric constant of Ba₁₋ₓSrₓTiO₃ is dependent upon both the Ba/Sr ratio and the A/B [(Ba+Sr)/Ti] site ratio [5-8]. For example, a 10% deviation in A/B ratio from 1.0 can result in a 30% decrease in the dielectric constant of the film. Since the capacitance per unit area is a function of both the dielectric constant and the film thickness, implementation of BST into manufacturing requires precise metrology methods to monitor both the stoichiometry and thickness of the films. This is no small challenge, considering that BST film thicknesses are 60 nm or less and that control of the stoichiometry to better than 1% relative will be required. In addition, the metrology method needs to be rapid, non-destructive, non-invasive, wafer-fab compatible and capable of handling wafers up to 300 mm in diameter. The ability to measure across-wafer variations is also desirable.
Several measurement methods were considered as potential metrology options, including wavelength dispersive x-ray fluorescence (WDXRF), energy dispersive x-ray fluorescence (EDXRF), Rutherford Backscattering Spectrometry (RBS), Fourier Transform Infrared Spectroscopy (FTIR), Spectroscopic Ellipsometry (SE), Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES), Glow Discharge-Optical Emission Spectroscopy (GD-OES), Glow Discharge Mass Spectroscopy (GD-MS), and small spot XRF. The inability of EDXRF to resolve the peaks of interest from interfering peaks in BST precluded its use for this work. The utility of SE for film thickness measurement is well accepted; however composition measurement via SE is doubtful. FTIR shows some promise as an indirect "fingerprinting" method for BST film process monitoring; however, the ability of FTIR to directly measure BST film stoichiometry has not yet been proven. RBS was ruled out due to its high cost and lack of wafer fab compatibility; ICP was not considered due to its destructive nature, lengthy analysis time, poor spatial resolution and lack of fab compatibility. GD-OES, GD-MS and small spot XRF were also not considered viable options for various technical reasons. WDXRF was chosen as the preferred method because it satisfied most of the criteria, is already an accepted, fab-compatible tool and offers a high degree of maturity in quantitative analysis of thin films. The weakest attribute of WDXRF is a rather large analysis area, 35 mm on our instrument; however this still affords the ability to measure film composition and thickness at several locations across a wafer. Apertures can be used to reduce the analysis area to as small as 5 mm in diameter; however, with this area reduction comes an associated reduction in count rate and a decrease in statistical precision of the measurement method. To compensate, analysis time can be increased substantially, but the time penalty is usually too high to be feasible except in unusual cases.

EXPERIMENTAL METHOD

For x-ray analysis of BST on a Si wafer, several of the elements have characteristic x-ray lines with wavelengths in close proximity to one another; thus the motivation to use WDXRF rather than EDXRF. On the XRF system utilized in this work, a fixed channel was used for measurement of the Ti-Kα line and a scanning channel for both the Ba-Lβ and Sr-Kα lines, whereas oxygen was not measured.

To quantify stoichiometry and thickness from x-ray intensity, calibration of the XRF is required through the use of appropriate standards. Two series of Ba$_{1-x}$Sr$_x$Ti$_x$O$_3$ standards were created: (1) initially, a set of MOD (metal-organic-decomposition) films made from mixtures of strontium titanate (STO) and barium titanate (BTO) precursors, spun onto 6" Si wafers and subsequently baked to drive off the volatiles; and (2) a series of BST films sputtered from different composition targets. The MOD films ranged from 50 to 200 nm in thickness, had an A/B ratio of 1.0, and included 7 different stoichiometries that covered the range from x = 0 to 1.0. Later on, standards with sputtered films were created, which included nominal stoichiometries of x = 0.3, 0.5 and 0.75 and had A/B ratios of about 1.1. All films were deposited on oxidized <100> Si wafers. The thicknesses of the BST standard films were measured using SE and x-ray reflectivity.
The stoichiometries of the MOD standard films were independently determined using three methods: (1) weight ratios of the STO and BTO precursors; (2) RBS; and (3) ICP-AES; only RBS was used on the sputtered films. The results from RBS and ICP analyses validated the precursor weight ratio values of the MOD films, as shown in Fig. 1. Considering the uncertainties associated with ICP and RBS analyses of these films, it was decided that the stoichiometries as calculated from the weight ratio values would be accepted as the calibration values for the MOD standard films.

All standard films were analyzed using XRF to obtain the x-ray intensities for Ba, Sr and Ti, and then empirical relationships were derived between these intensities and BST stoichiometry. Since the absorption of the Ba, Sr and Ti characteristic x-rays is negligible for thin BST films, relationships of the form:

\[ \text{Sr/Ti (stoichiometry)} = A \times \text{Sr/Ti (x-ray intensities)} + B \]

were derived for both Sr/Ti and Ba/Ti. The empirical calibration curve of Sr/Ti for the MOD standard films is shown in Fig. 2, and the linear fit is excellent; similar correlation was obtained for Ba/Ti. In applying these empirical relationships to calculate the stoichiometry of unknown BST films, we used the convention whereby the sum of (Ba + Sr) stoichiometry was normalized to 1.0 to yield the Ti stoichiometry \((y)\) in \(\text{Ba}_{1-x}\text{Sr}_x\text{Ti}_2\text{O}_3\).

For thickness measurement, an empirical calibration of the form:

\[ t = A \times \text{Ba (net kcps)} + B \times \text{Sr (net kcps)} + C \]

was also derived. The results are plotted in Fig. 3 against film thickness as measured by SE. The agreement between the two methods is very good. Note that knowledge of the density of the
BST films is required when determining film thickness via XRF. The density of the MOD films was determined to be about 4.2 g/cm$^3$, whereas BST films deposited by other methods will result in films with different densities. For example, densities of 5.1-5.6 g/cm$^3$ have been measured (using x-ray reflectivity) for sputtered BST films, depending upon process conditions.

**REPEATABILITY**

The repeatability of the XRF method for measuring BST film stoichiometry and thickness was determined by repetitive analysis of a nominal Ba$_{0.25}$Sr$_{0.75}$TiO$_3$ film over a 15 month time frame. Shown in Figs. 4-6 are the results of this gauge capability study for Ba stoichiometry, A/B ratio and film thickness, respectively.

**FIGURE 3.** Film thickness calibration for MOD BST films. Thickness derived from Ba and Sr x-ray intensities; BST density 4.0 g/cm$^3$.

**FIGURE 4.** XRF measurements of Ba on the same Ba$_{0.25}$Sr$_{0.75}$TiO$_3$ film over a 15 month period. Mean value is 0.258, sigma=0.003.

**FIGURE 5.** XRF measurements of A/B ratio on the same Ba$_{0.25}$Sr$_{0.75}$TiO$_3$ film over a 15 month period. Mean value is 0.967; sigma=0.008.

**FIGURE 6.** XRF measurements of BST film thickness on the same Ba$_{0.25}$Sr$_{0.75}$TiO$_3$ film over a 15 month period. Mean value is 48.2 nm; sigma=0.44.
One challenging aspect of developing metrology methods is the transfer of the method to other labs and the ability to achieve inter-lab agreement among results. This has been accomplished with the BST XRF metrology method. Shown in Fig. 7 is a comparison of A/B ratios between two different labs on a combination of similar and identical BST films. The agreement between the two labs is within the ± 2% precision of the method for A/B ratio measurements.

**MEASUREMENT OF ACROSS-WAFER STOICHIOMETRY**

As noted previously, the XRF method, with its 35 mm diameter analysis area, is capable of measuring across-wafer variations in film stoichiometry and thickness. This has been used extensively during development for process optimization, since uniformity of BST film properties across the wafer is critical to yield functional and reliable devices. It can also readily be used as a process monitoring tool, to ensure process control. Shown in Fig. 8 is an example of the results from measurement of the A/B ratio across a 200 mm wafer. In this case, “overlapping” measurements were taken every 15 mm, from the wafer center to within a few mm of the edge, along orthogonal x- and y-directions relative to the wafer flat. (The XRF tool has an r-θ stage, so across-wafer measurements involve the wafer being rotated 90, 180 and 270 degrees between radial measurements taken center-to-edge). The results in Fig. 8 show relatively good across-wafer uniformity in A/B ratio for the BST film. The analysis time for measurements such as those shown in Fig. 8 is on the order of 1.5 hours/wafer, of course, simultaneously yielding across-wafer data for Ba/Sr ratio and BST film thickness variations.

**FIGURE 7.** Inter-laboratory comparison of A/B ratio measurements of BST films on similar and identical wafers.

**FIGURE 8.** Across-wafer measurements of the A/B ratio of a BST film on a 200 mm wafer.
A fundamental question that existed after the initial calibration using MOD standards was whether those standards were valid for analyzing sputtered BST films; thus the second set of calibration wafers were created composed of sputtered BST from different composition targets. After calibrating with the sputtered standards using a manner identical to the MOD films, a third set of BST films was analyzed using both MOD and sputtered calibrations. A comparison of these results are shown in Figs. 9 and 10. The excellent agreement between these two calibration methods verified the validity of using the MOD standards for sputtered film analysis; the sputtered films also provided a second set of BST reference films over a narrower range of thicknesses and stoichiometries.

Although the empirical methodology for BST quantification was developed from x-ray intensities, this approach requires time consuming off-line data processing to obtain stoichiometries. It would be preferable to utilize the data processing capability of the XRF tool itself, and thus the attempt was made to apply the vendor-provided fundamental parameters (FP) [9, 10] treatment to the data to achieve on-line quantification. A comparison of the results for Ba and Sr stoichiometries, using both empirical and fundamental parameters approaches anchored on the MOD calibration wafer set, reveals that the agreement between the two analytical approaches for Ba and Sr was excellent. However, when comparing the two methods for A/B ratio measurement, the agreement was not as good. This is depicted in Table I, where the A/B ratios of the entire matrix of MOD standard films are shown as calculated using the empirical and fundamental parameters methods of quantification. The A/B ratios for these films should be 1.0; however, the results indicate that the fundamental parameters method yields A/B
ratios that deviate from 1.0 and show a trend of understating the A/B ratio for thin, Ba-rich BST to overstating the A/B ratio for thick, Sr-rich BST. No such bias is evident in the empirical results on the same data set. One can simulate this trend in A/B ratio as a function of film thickness in the empirical approach by using incorrect values for the background count levels for Ba and Sr. It is postulated that the fundamental parameters approach is not properly compensating for the high background levels encountered in our analyses.

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<th>Ba:Sr Composition</th>
<th>60 nm FP</th>
<th>60 nm Empirical</th>
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Table I. Comparison of A/B ratios for the MOD BST standards set calculated using empirical versus fundamental parameters analysis methods for three different BST film thicknesses.

**ERRORS DUE TO SUBSTRATE DIFFRACTION**

There are several sources of error in the analysis of films using XRF, including the accuracy of the calculation algorithm (discussed previously), the accuracy of the standards, the quality of the calibration process, counting statistics, instrument stability and knowledge of the background count levels. Particularly problematic for WDXRF analysis of BST films is the issue of substrate diffraction, which impacts the background levels [11]. Substrate diffraction refers to diffraction of the incident radiation by the single crystal substrate. This diffracted intensity, which is dependent upon the geometrical arrangement of the radiation source, substrate and the x-ray detector, will vary as a function of crystallographic orientation of the substrate and its angular position and manifests itself as additional background x-ray intensity.

In WDXRF, with fixed position detectors, it is not possible to scan the spectrometer wavelength to measure backgrounds levels; additionally, for scanning channels, measurement of background levels can increase the analysis time by 3X or more. Therefore background levels were measured on BST film-free wafers (for Ti) or measured for Ba in STO films and for Sr in BTO films. These "element free" background levels were then assumed to be applicable to the unknown films. However, substrate diffraction can contribute to these background level measurements and therefore must be well characterized from wafer to wafer. As an added complication, to achieve full wafer coverage, many XRF tools use an “r-θ” stage to reach all locations on a wafer rather than an x-y stage. This introduces the added variable of angular geometry (θ) for each measurement location.
shown in Fig. 11 is a plot of the x-ray intensity collected by the Ti-Kα channel measured for a bare Si <100> wafer (no BST), as a function of θ. Note the strong substrate diffraction effect; although there is no Ti present, the background x-ray levels vary by as much as an order of magnitude as a function of θ. The maximum background levels are as high as 10% of the maximum Ti intensity measured in typical BST films. The repeating pattern with angular rotation is due to the four-fold symmetry of the Si <100> wafer. Although diffraction effects are significant for Ti, they can generally be minimized by performing analysis at an angular position having a slowly varying and minimal substrate diffraction intensity, such as near 0, 90, 180 and 270° as shown in Fig. 11. However, the diffraction effect is much more complicated for Sr; for which the diffraction intensity for the Sr channel from a bare Si <100> wafer is shown in Fig. 12 as a function of angular rotation. For Sr, these background levels are 30-50% of the peak intensities measured in typical BST films. As is evident in the graph, the selection of a slowly varying, minimal intensity angular position for Sr is nearly impossible.

The impact of substrate diffraction on the quantification of a BST film is shown in Fig. 13. In this example, across-the-wafer measurements were performed on a BST film; however, the calculated A/B ratios for the same location at the center of the wafer varied considerably when rotating the wafer 180 degrees. This is depicted in Fig. 13 as the apparent “discontinuity” in A/B ratio values at the wafer center. The explanation of this effect is apparent when examining the diffraction effect for this wafer, as shown in Fig. 14. Here the Ti x-ray peak intensity was measured at the center of the BST/SiO2/Si <100> structure as a function of angular rotation. The diffraction effect on the Ti intensity is readily apparent; however, the repeating pattern, four-fold symmetry seen in Fig. 11 is not apparent in this plot. After pole figure analysis using XRD, it was determined that the <100> test wafer substrate was cut 7 degrees off-axis, which explains the loss in symmetry in the diffraction scan shown in Fig. 14. The A/B ratio anomaly at the wafer center is attributable to the difference in Ti background levels at 0 versus 180 degrees angular rotation. Note that there is no difference in Ti intensity between the 90 and 270 degree angles.
Angular rotation, which explains why the A/B ratio anomaly was only observed in one orthogonal direction on this wafer.

DISCUSSION AND CONCLUSIONS

WDXRF has been shown to be a viable method for measurement of the composition and thickness of BST films. Accuracy and precision have been measured through comparison with other measurement methods and repeatability studies. Current limitations to the WDXRF method include substrate diffraction effects, counting statistics, accuracy of the independent measurement techniques for validation of the standards and accuracy of the quantification algorithm. The discrepancies between the empirical and fundamental parameters methods are not fully understood. Accuracy improvements can be achieved through the acquisition of optimized x-ray detectors for Ba and Sr, a more thorough understanding of the substrate-to-substrate variability of the diffraction contribution and improved standard validation.

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