

## EDXRF Characterization of BST Films

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### Abstract:

High dielectric constant and other electrical properties of (Ba, Sr)TiO<sub>3</sub> (BST) thin films have resulted in increasing interest by the semiconductor manufacturing industry to develop these films for use in capacitors for ultra-large scale integrated dynamic random access memories (ULSI-DRAMs). The development and eventual production of these devices requires characterization and control of the BST thin film composition and thickness. X-ray Fluorescence Spectrometry is a widely accepted technique for such characterization of thin-film structures.

The methodology and data presented herein demonstrate the application of Energy Dispersive X-ray Fluorescence (EDXRF) spectrometry to the compositional and thickness characterization of BST films, parameters that are so important to the films electrical properties. EDXRF characterization is rapid, accurate and nondestructive. With analytical precision comparable to that predicted by counting statistics, BST film thickness and composition measurements within  $\pm 2\%$  are made with an analysis time of approximately 8 minutes. Y-theta stage automation enables multiple point analyses of BST films deposited on Si wafers, and the evaluation of deposition uniformity.

EDXRF data comparisons to other analytical techniques are presented.

### Introduction:

Over the past few years, ferroelectric compounds have received wide attention in the semiconductor manufacturing industry for use in capacitors for ULSI-DRAMs. The interest in these compounds is primarily the result of the high dielectric constant that these compounds exhibit. Although, other electrical properties of these compounds, such as, low dielectric dissipation loss and low leakage current, are also very important to the application. BST is a particularly strong candidate. The high dielectric constant,  $>300$  [1] provides the capacitance required for small geometry, high density ( $>1$  G) DRAM.

Researchers have shown that composition plays an important role in the resulting dielectric constant of BST films having thicknesses greater than 700 Å [1]. Therefore, development and ultimately production control of these films requires close monitoring of film composition and thickness.

X-Ray Fluorescence is widely accepted as an analytical technique for thickness and composition measurement of deposited films in semiconductor and other industries. Modern EDXRF equipment is commercially available in compact designs and with Peltier-cooled solid state detectors that are compatible with semiconductor manufacturing parameters of high FAB area costs and cleanliness. The goal of the analytical development presented herein is to demonstrate the applicability of modern EDXRF equipment to the characterization of BST film thickness and composition. Parameters important to such evaluations and presented here are analytical accuracy, precision and analysis time.

#### Experimental:

#### **Film Deposition**

Two BST films deposited on 4" silicon wafers were provided by LG Corporate Institute of Technology, Seoul, Korea for our EDXRF method development. The films were deposited using a Metal Organic Chemical Vapor Deposition (MOCVD) process. MOCVD is widely accepted as the most appropriate process method for BST DRAM production due to the good step coverage, thickness and composition uniformity, and high deposition rate that can be achieved. The deposition conditions for these two films are given in Table 1.

| <u>MOCVD Parameter</u> | <u>BST Film No. 1</u>   | <u>BST Film No. 2</u>   |
|------------------------|---|---|
| Temperature:           | 625 °C  | 550 °C  |
| Pressure:              | 1 m Torr  | 1 m Torr  |
| Atmosphere:            | O <sub>2</sub>  | N <sub>2</sub> O + O <sub>2</sub>   |
| Flow rate:             | 250 sccm  | 400 sccm  |
| MO precursors:         | Ba(thd) <sub>2</sub> -tetraglyme,<br>Sr(thd) <sub>2</sub> -tetraglyme,<br>Ti(O-iPr)(thd) <sub>2</sub> | Ba(thd) <sub>2</sub> -tetraglyme,<br>Sr(thd) <sub>2</sub> -tetraglyme,<br>Ti(O-iPr)(thd) <sub>2</sub> |

Table 1: MOCVD conditions.

#### **EDXRF Method Development**

EDXRF method development was done with the TN-Spectrace QuanX spectrometer. This is a bench-top spectrometer that features a Peltier-cooled lithium-drifted Silicon [Si(Li)] detector, and a Y-theta stage for automated multi-point analysis of semiconductor wafers. Analytical considerations that need to be addressed in using this kind of spectrometer for BST film characterization include: the availability of standards, which in turn may influence the quantitative algorithm employed; deconvolution of Ti K lines from Ba L lines; the use of Ba L lines or Ba K lines to determine Ba concentration; and diffraction of incident X-rays by the crystalline Si substrate that may interfere with the analyte lines.

Empirical XRF requires "type-standards". These are standards that are of the same type as the unknown materials that are to be analyzed. This usually means that compositionally, the standards will have compositions bracketing those of the routine sample. In the case of thin-film characterization, type standards must be similar in composition and thickness to the routine sample. Standards of this kind typically do not exist, particularly when dealing with developmental films. Fortunately, X-ray physics are well understood and algorithms exist that employ X-ray

fundamental parameters (first principals of X-ray physics) for quantification of composition and thickness. Such programs permit analytical standardization of the X-ray spectrometer with dissimilar standard materials. For our method development, pure metal and binary compounds that are deposited on Mylar film and weighed to determine mass thickness were used for standardization (Micromatter Co., WA). Three thin-film standards were used as follows:  $42.9 \mu\text{g}/\text{cm}^2$   $\text{BaF}_2$ ,  $48.1 \mu\text{g}/\text{cm}^2$   $\text{SrF}_2$ , and  $37.5 \mu\text{g}/\text{cm}^2$  Ti. The thin-film software supplied with the TN-Spectrace spectrometer is a fundamental parameters based program for the determination of composition and thickness of single and multi-layer structures [2]. The program reports wt. % composition, and mass thickness (mass per unit area).

EDXRF employs the resolving ability of the X-ray detector to separate the analyte lines that are fluoresced from the sample. Si(Li) detector based EDXRF spectrometers provide the best resolution of those commercially available. This is typically between 150 - 175 eV Full Width Half Maximum for the Mn  $K\alpha$  emission at 5.9 keV. With this kind of detector, peak overlaps are fairly few, nonetheless, some exist. One of these overlaps is between the Ti K lines and Ba L lines. Spectra acquired from BST Film No. 2 presented in Figure 1 show this overlap. These peaks are deconvoluted to extract net peak intensities using a multiple-regression least-squares fit to reference spectra [3]. L-line intensity ratios have been noted to vary with the mass thickness of the sample and excitation potential. To optimize the accuracy of the Ba L - Ti K deconvolution, the Ba L reference spectrum was acquired from the  $\text{BaF}_2$  standard using the same tube potential as that used for the BST acquisitions.

The probability of K emission is much greater than L emission, however, for this application, we found that we were able to optimize our spectrometer for the Ba  $L\alpha$  emission to yield twice the intensity of the Ba  $K\alpha$  under optimum conditions (70 counts/second and 35 counts/second respectively). Given this higher sensitivity in conjunction with the need to acquire Ti  $K\alpha$  intensities for the  $\text{TiO}_3$  component, we chose to utilize the Ba  $L\alpha$  emission for Ba composition, thereby, limiting spectrum acquisitions to two for the application. Spectrometer acquisition parameters are given in Table 2.

| <u>Acquisition Parameter</u>     | <u>Analyte Line(s)</u>      |
|----------------------------------|-----------------------------|
| Tube potential: 13 kV            | Ti $K\alpha$ , Ba $L\alpha$ |
| Tube current: 1.98 mA            |                             |
| Beam filter: 0.13 mm thick Al    |                             |
| Beam collimator: 7.8 mm diameter |                             |
| Dead time: 40%                   |                             |
| Live-time: 200 seconds           |                             |
| Tube potential: 33 kV            | Sr $K\alpha$                |
| Tube current: 1.00 mA            |                             |
| Beam filter: 0.13 mm thick Pd    |                             |
| Beam collimator: 7.8 mm diameter |                             |
| Dead time: 40%                   |                             |
| Live-time: 100 seconds           |                             |

Table 2: Instrument acquisition parameters

Our spectrometer uses an X-ray tube as the excitation source. The tube emits X-rays characteristic of the anode material and a continuum, referred to as Bremsstrahlung over the range of the tube potential setting. So, for the excitation cases presented in Table 2, X-rays from the tube are emitted from very low keV to 13 keV for the Ba and Ti acquisition and to 33 keV for the Sr acquisition. When a broad energy range of X-rays impinge on highly crystalline materials, like silicon wafers, there is a very good probability that the Bragg condition will be met and incident X-rays diffracted. This is only a problem if the diffraction should interfere with analyte peaks. Incident beam filters are frequently used in EDXRF to remove Bremsstrahlung from the analyte peak area, thereby, lowering background and improving detection (the peak-to-background ratio). By removing the Bremsstrahlung from the energy region of the analyte lines, the probability of diffraction in that region is also removed. Figure 1 shows overlaid spectra from our Ba and Ti acquisitions that were acquired from BST Film No. 2. At certain orientations of the wafer a small diffraction peak occurred at about 5.8 keV, which slightly overlapped the Ba  $L\gamma$  emission. Some Bremsstrahlung radiation passed through the aluminum beam filter at this energy and was diffracted, however this did not interfere with our ability to extract the net Ba  $L\alpha$  and Ti  $K\alpha$  intensities. No diffraction occurred in the Sr acquisitions.

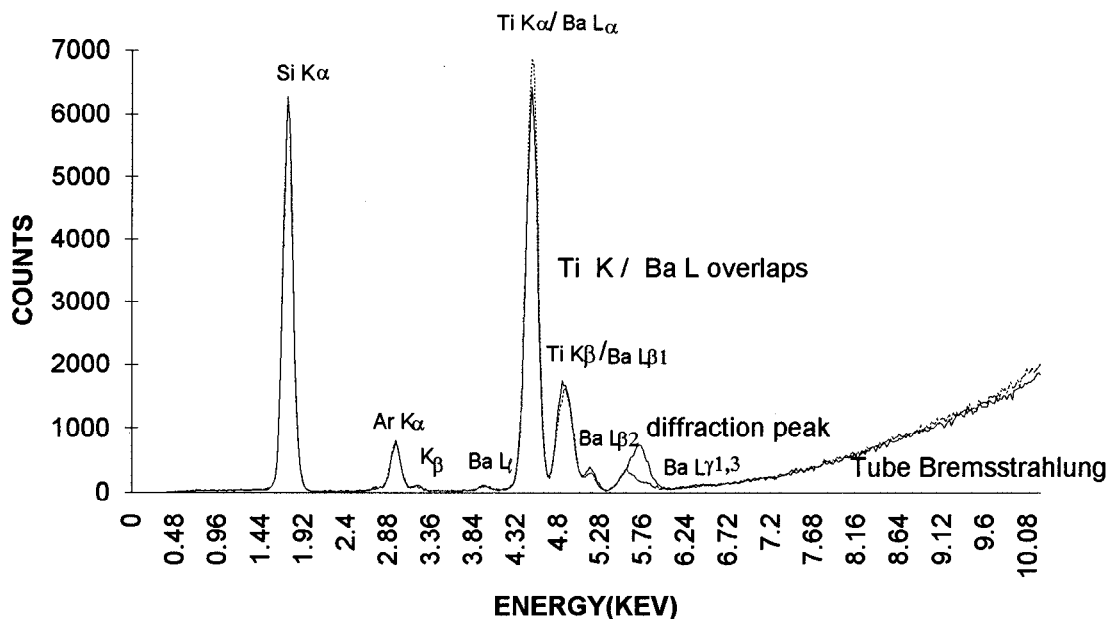


Figure 1: Overlay of spectra from two Ba L, Ti K acquisitions from BST Film No. 2. The two spectra were acquired from the wafer having a  $90^\circ$  theta orientation difference. A diffraction peak was evident in the one orientation, but did not interfere with net peak extractions of the Ba  $L\alpha$  and Ti  $K\alpha$  lines used to quantify composition of the film.

## Results:

### Precision & Film Uniformity

Spectrum acquisition times were established based on counting statistics to achieve better than or equal to 2% relative for the compositional components of the BST films. To determine the actual analytical precision of our EDXRF methodology, thickness and composition measurements were

made at the center and four compass points around BST Film Sample No. 1. Five measurements were made at each point. Standard deviations for each of the 5 analyses at each point were calculated and averaged. The averaged relative standard deviations were within the precision predicted by peak counting statistics, Table 3. The total analysis time to achieve this precision was approximately 8 minutes per analysis.

| <u>Wafer/Test</u>                              | <u>Ba, %RSD</u> | <u>Sr, %RSD</u> | <u>Ti, %RSD</u> | <u>Thickness, %RSD</u> |
|--|-----------------|-----------------|-----------------|------------------------|
| BST Film 1 - Analytical Precision <sup>1</sup> | 1.9%            | 1.0%            | 0.6%            | 0.6%                   |
| Predicted by Counting Statistics               | 2.0%            | 1.0%            | 0.6%            | 0.6%                   |
| BST Film 1 - Uniformity <sup>2</sup>           | 1.9%            | 1.4%            | 1.0%            | 4.3%                   |
| BST Film 2 - Uniformity <sup>2</sup>           | 3.7%            | 2.4%            | 1.4%            | 4.5%                   |

RSD = Relative Standard Deviation

1 Average RSD (5 analyses each) at 5 positions on the wafer (compass positions and center).

2 RSD of 48 different positions over each wafer.

Table 3: Analytical precision and film uniformity comparisons

Film uniformity, both thickness uniformity and composition uniformity, were evaluated by making multiple point analyses of the films over the two sample wafers. This process was automated by using a motorized Y-theta stage, which is controlled via the instrument software. Spectra were acquired at 10 mm steps across the wafers, on the spectrometer Y axis, with 30° theta increments. This amounted to 48 data points over each wafer. Calculating the relative standard deviations for these 48 data points for each component allows for direct comparison to the analytical precision and a measure of compositional and thickness uniformity (Table 3). In making this comparison, it is immediately evident that the compositional uniformity of BST Film No. 1 is quite good, but not so for BST Film No. 2. Whereas, thickness distributions are obviously off. Graphical views of the thickness measurements give a conical image with thicker deposition in the middle of the wafer and thinning towards the edges.

Uniformity in the semiconductor CVD community is defined as follows:

$$\% \text{ uniformity} = [(\text{maximum value} - \text{minimum value}) / (2 \times \text{average})] \times 100\%$$

Utilizing this definition we obtain the uniformities presented in Table 4.

| <u>Sample</u> | <u>BST Thickness Uniformity</u> | <u>BST Composition Uniformity</u> |
|---------------|---------------------------------|-----------------------------------|
| BST Film 1    | 7.9%                            | 6.0%                              |
| BST Film 2    | 8.7%                            | 8.1%                              |

Table 4: Film uniformity, thickness and composition.

## Comparative Results

Composition and thickness measurements that were determined by the EDXRF methodology described in this paper are presented in Table 5 and compared to ICP-MS composition and thickness determinations for 1 cm x 1 cm pieces taken from the same wafers, and TEM cross sectional thickness measurements made on several pieces sectioned from these wafers.

Compositions are reported in terms of atomic % and atomic ratios. Yamamichi et al., reported that the dielectric constant of BST films is stoichiometrically dependent for films thicker than 70 nm [1]. For these thicknesses, they report that (Ba + Sr)/Ti ratios of ~1 yield higher dielectric constants with a maximum resulting in 5% (Ba + Sr) rich films, or a ratio of 1.05 [1].

It was expected that ICP-MS analysis would corroborate our EDXRF technique. As presented in Table 5, there was EDXRF - ICP-MS corroboration of relative components (stoichiometry), but total composition of the ICP-MS analyses, reported as mass thickness, were inconsistent.

Although reported in different terms, we feel that thickness consistency between BST Film No. 1 and BST Film No. 2 of TEM measurements corroborates the EDXRF analyses (Table 5). This is further supported by relative thickness changes, center to edge of the wafers, as measured by EDXRF and TEM (Table 6).

| Sample  | Technique           | Ba, atomic% | Sr, atomic% | TiO <sub>3</sub> ,<br>atomic% | (Ba+Sr)/Ti<br>Ratio | mass<br>thickness<br>μg/cm <sup>2</sup> | linear<br>thickness<br>Å |
|---------|---------------------|-------------|-------------|-------------------------------|---------------------|---|--------------------------|
| BST # 1 | EDXRF               | 17.01       | 27.86       | 55.13                         | 0.81                | 51                                      |                          |
|         | ICP-MS <sup>1</sup> | 23.8        | 23.8        | 52.4                          | 0.91                | 40                                      |                          |
|         | ICP-MS <sup>2</sup> | 18.7        | 26.1        | 55.2                          | 0.81                | 87                                      |                          |
|         | TEM                 |             |             |                               |                     |   | 1213                     |
| BST # 2 | EDXRF               | 16.67       | 17.49       | 65.84                         | 0.52                | 52                                      |                          |
|         | ICP-MS <sup>1</sup> | 15.9        | 16.4        | 67.7                          | 0.48                | 25                                      |                          |
|         | ICP-MS <sup>2</sup> | 10.6        | 13.7        | 75.7                          | 0.32                | 61                                      |                          |
|         | TEM                 |             |             |                               |                     |   | 1195                     |

Table 5: EDXRF, ICP-MS, TEM analysis comparisons. ICP-MS<sup>1</sup> and ICP-MS<sup>2</sup> analyses were performed in different laboratories. Inconsistencies in the ICP-MS results are not systematic laboratory to laboratory.

XRF thickness measurements are in terms of mass thickness, mass/unit area. To convert mass thickness to linear thickness, it is necessary to know the density of the deposited film. CVD processes incorporate carrier gases that can be entrapped in the film, and affect the density of the film. The effect is a lower density relative to the densities measured for like compounds that are synthesized using sintering techniques. Calculated densities ( $\rho$ ) from the EDXRF and TEM data reported here are as follows:  $\rho$  BST Film No. 1 = 4.20 g/cm<sup>3</sup>;  $\rho$  BST Film No. 2 = 4.35 g/cm<sup>3</sup>.

| Sample  | Technique | mass thickness<br>at center<br>$\mu\text{g}/\text{cm}^2$ | mass thickness<br>at edge<br>$\mu\text{g}/\text{cm}^2$ | linear<br>thickness at<br>center $\text{\AA}$ | linear<br>thickness<br>at edge $\text{\AA}$ | relative<br>change center<br>to edge % |
|---------|-----------|--|--|---|---|--|
| BST # 1 | EDXRF     | 53   | 47   |   |   | -10.6                                  |
|         | TEM       |  |  | 1213  | 1135  | -6.4                                   |
| BST # 2 | EDXRF     | 54   | 46   |   |   | -14.8                                  |
|         | TEM       |  |  | 1195  | 1049  | -12.2                                  |

Table 6: Center to edge EDXRF and TEM thickness measurement comparisons.

X-ray diffraction patterns were acquired from nine pieces taken from the X axes and nine pieces from the Y axes through the center of each of the BST covered wafers. Only the BST phase was detected in the BST Wafer No. 1 samples. Three phases - BST,  $\text{TiO}_2$  (rutile), and trace amounts of  $(\text{Ba},\text{Sr})\text{CO}_3$  were detected in the BST Wafer No. 2 samples, with increased levels of  $\text{TiO}_2$  toward the edges of the wafer, which is consistent with lower  $(\text{Ba} + \text{Sr})/\text{Ti}$  ratios determined for this film using the EDXRF methodology described here.

#### Conclusions and Future Work:

EDXRF provides a rapid and precise method for determining the thickness and composition of BST films. Film uniformity of thickness and composition is evaluated by making multi-point scans over sample wafers with an automated Y-theta stage.

Of the ferroelectric compounds under consideration for use in ULSI-DRAM and new nonvolatile memory, BST represents the most challenging from an EDXRF perspective, because of the Ba L / Ti K line overlaps. The next step in EDXRF method development for monitoring BST and other ferroelectric films for high density memory applications will be the analysis of the ferroelectric film on various electrode materials to determine thickness and composition of the ferroelectric layer and thickness of the electrode layer simultaneously. Candidate electrode materials include Pt, Ru, and Ir.

#### References:

1. S. Yamamichi, H. Yabuta, T. Sakuma and Y. Miyasaka, (Ba + Sr)/Ti Ratio Dependence of the Dielectric properties for  $(\text{Ba}_{0.5}\text{Sr}_{0.5})\text{TiO}_3$  Thin Films Prepared by Ion Beam Sputtering, *Applied Physics Letter*, Vol. 64 No. 13, pp. 1644 -1646, 28 March 1994
2. J.E. Willis, Simultaneous Determination of the Thickness and Composition of Thin Film Samples Using Fundamental Parameters, *Advances in X-Ray Analysis*, Vol. 31, pp. 175-180, 1988.
3. J.J. McCarthy, Analysis of X-Ray Spectra by Filtered Least-Squares Fitting, *Scanning Electron Microscopy*, pp. 259-270, 1980, II, SEM Inc., AMF O'Hare (Chicago), IL.