A GRAZING INCIDENCE X-RAY FLUORESCENCE ANALYSIS
OF THE COMPOSITION
OF (Ba,Sr)TiO₃ (BST), AND SrRuO₃ (SRO) STACKED FILMS

Shinichi Terada, Hiroaki Furukawa, Hiroyuki Murakami, and Kazuo Nishihagi

TECHNOS Co., Ltd.

ABSTRACT

Grazing Incidence X-ray Fluorescence (GIXRF) and an X-ray interference (XRI) method were
used to determine the composition and thickness of both (Ba,Sr)TiO₃ (BST) and, SrRuO₃ (SRO)
thin films stacked on a silicon wafer.

INTRODUCTION

BST has an extremely high dielectric constant and is therefore a promising material for the next-
generation of DRAM capacitors. However, the dielectric constant of BST is strongly dependent
on its composition. Therefore, a measurement of its composition is important for production
control. The X-ray fluorescence (XRF) analysis of the chemical composition of thin films has
been reported by several researchers[1][2][3]. The XRF intensity of elements is given by

\[ I_Z = k_Z C_Z \rho t \]  

where \( I_Z \) [sec⁻¹] is the XRF intensity of the element \( z \), \( k_Z \) [g⁻¹·cm²·sec⁻¹] is the sensitivity factor for
the element \( z \), \( C_Z \) [g·g⁻¹] is the concentration of the element \( z \), \( \rho \) [g·cm⁻³] is the density of the film,
and \( t \) [cm] is the thickness of the film. Absorption of X-ray is neglected since the film is very
thin. The existence of oxygen is also ignored in order to simplify the analysis. The equation can
be converted into

\[ \frac{I_Z}{I_{Sr}} = \frac{k_Z C_Z}{k_{Sr} C_{Sr}} \]  

(Z = Ba, Ti)  \hspace{1cm} (2)

to render it independent of the density and the thickness. The ratio of sensitivity factors is
determined by measuring a reference sample;

\[ \frac{k_Z}{k_{Sr}} = \frac{I_{Z,R} C_{z,R}}{I_{Sr,R} C_{Sr,R}} \]  

(Z = Ba, Ti)  \hspace{1cm} (3)

where \( I_{Z,R} \) is the XRF intensity of the element \( Z \) in the reference sample and \( C_{Z,R} \) is the
concentration of the element \( z \) in the reference sample. The composition of an unknown sample
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is determined using the following equations;
\[
\frac{C_{Sr}}{C_Z} \frac{k_{Sr} I_{Sr}}{k_Z I_Z} \quad (Z = \text{Ba, Ti}) \quad (4)
\]
\[
C_{\text{Ba}} + C_{\text{Sr}} + C_{\text{Ti}} = 1 \quad (5)
\]

For DRAM applications, an electrode material that exhibits good electric properties in combination with BST is sought. Hieda et. al recently suggested the use of SRO[4]. However, the chemical analysis of BST deposited on SRO is very difficult using XRF because the Sr radiation produced by SRO is much greater than that from BST. To overcome this difficulty, grazing incidence is used to analyze the upper BST layer without irradiating the lower SRO layer. The intensity of Sr XRF from SRO is calculated using the Ru XRF intensity and eliminated. A higher angle of incidence is used to analyze the lower SRO layer. The intensity of Sr XRF from the upper BST layer is calculated using Ba and Ti XRF intensity and eliminated. Monochromatic X-rays are used to provide the same penetration depth for all elements. Energy dispersive X-ray spectroscopy system (EDXRS) is used to measure the XRF radiation. Overlapping peaks of Ba and Ti XRF were deconvoluted by a least square fitting method.

**GRAZING INCIDENCE X-RAY FLUORESCENCE**

When a very low angle of incidence is used, the XRF from the lower SRO layer is very weak since the irradiating X-rays are absorbed mostly in the upper BST layer. Fig. 1 shows an XRF spectrum obtained using a 0.1-degree incidence angle. The Ru XRF peak in this spectrum is much smaller than that in Fig. 2, which shows a spectrum using a 2-degree incidence angle. The XRF intensity of element Z in the case of grazing incidence is
\[
I_{\text{BST},Z} = k_Z C_{\text{BST},Z} \rho_{\text{BST}} d_Z \quad (6)
\]
where \(d_Z [\text{cm}]\) is the effective penetration depth of the irradiating X-rays for the element Z. The effective penetration depth is dependent on the composition of the film and the wavelength of the irradiating X-rays as well as the atomic number Z. As shown in Fig. 3, the effective penetration depth for Sr is greater than that for the other elements, since the energy of the Sr-K absorption edge is higher and the effective excitation energy for the Sr-K is also higher. To simplify the calculation, we used a monochromator to select the Ag-K\(\alpha\) line as shown in Fig. 4. With monochromatic excitation, all elements have the same value of \(d_Z\) and Eq. 6 is converted into
\[
I_{\text{BST},Z} = k_Z C_{\text{BST},Z} \rho_{\text{BST}} d \quad (7)
\]
Therefore, the composition of the film is calculated in the same way as for normal XRF and using the following equations;
\[
\frac{C_{BST, Sr}}{C_{BST, Z}} = \frac{k_Z I_{BST, Sr}}{k_{Sr} I_{BST, Z}} \quad (Z = Ba, Ti) \quad (8)
\]
\[
C_{BST, Ba} + C_{BST, Sr} + C_{BST, Ti} = 1 \quad (9)
\]

**ELIMINATION OF XRF FROM SRO LAYER**

As shown in Fig. 1, the Ru XRF peak from the lower layer is weak but detectable. The detected XRF intensities of the elements are:

\[
I_{Det, Ba} = I_{BST, Ba} \quad (10)
\]
\[
I_{Det, Sr} = I_{BST, Sr} + I_{SRO, Sr} \quad (11)
\]
\[
I_{Det, Ti} = I_{BST, Ti} \quad (12)
\]
\[
I_{Det, Sr} = I_{BST, Sr} \quad (13)
\]

Sr-K XRF intensity from the SRO layer is calculated using the Sr-K / Ru-K XRF intensity ratio measured using a SRO single layer sample. The difference in composition between the unknown sample and the reference sample is negligible in practice since the XRF intensity from SRO is less than 1\% of that from BST.

\[
I_{SRO, Sr} = I_{SRO, Ru} \frac{I_{SRO, Sr, R}}{I_{SRO, Ru, R}}
\]
\[
= I_{SRO, Ru} \frac{k_{Sr} C_{SRO, Sr, R}}{k_{Ru} C_{SRO, Ru, R}} \quad (14)
\]

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**Figure 1** XRF Spectrum of BST/SRO using a 0.1-degree incidence angle

**Figure 2** XRF Spectrum of BST/SRO using a 2-degree incidence angle
DETERMINATION OF THE CHEMICAL COMPOSITION OF THE SRO LAYER

At a higher angle of incidence, irradiated X-rays are mostly transmitted through both the upper BST and the lower SRO layers. The XRF intensities are:

\[ I_{Det,Z} = I_{BST,Z} + I_{SRO,Z} \quad (Z = \text{Ba, Sr, Ti, Ru}) \]  
\[ I_{BST,Z} = k_Z Z_{BST,Z} P_{BST} I_{BST} \quad (Z = \text{Ba, Sr, Ti}) \]  
\[ I_{SRO,Z} = k_Z Z_{SRO,Z} P_{SRO} I_{SRO} \quad (Z = \text{Sr, Ru}) \]

These are converted into following equations.

\[ I_{SRO,Sr} = I_{Det,Sr} - I_{BST,Sr} \]
\[ = I_{Det,Sr} - \frac{I_{Det,Ba} + I_{Det, Ti}}{k_{Ba} Z_{BST,Ba} + k_{Ti} Z_{BST, Ti} + k_{Sr} Z_{BST, Sr}} \]  
\[ I_{SRO,Ru} = I_{Det,Ru} \]

For the elimination of Sr-K XRF from the BST layer, the composition of the BST layer was determined using a lower angle of incidence is used.

DECONVOLUTION OF Ba-L AND Ti-K

Despite the fact that we operated the X-ray tube at relatively high power 1.5kW, number of photon irradiated onto the sample was not very large. One reason was that the monochromator cuts other X-rays than Ag-K\(\alpha\). The other reason was long excitation path caused by the combination of grazing incidence angle and large sample diameter. We used EDXRS since XRF intensity is insufficient for the use of wavelength dispersive X-ray spectroscopy (WDXRS). Ba-L lines and Ti-K lines are very close in energy and overlapping peaks are observed when EDXRS
is used. Fig. 5 shows overlapping Ba-Lα and Ti-Kα peaks. The precision of the least square fitting of these α peaks alone is insufficient because the actual spectrum has a statistical error in each channel. For precise deconvolution, least square fitting is performed under the conditions shown in Table 1. Since monochromatic excitation is used, line ratios (Kα - Kβ and Lα - Lβ - Lγ) can be fixed.

![Figure 5. Overlapping of Ba-Lα and Ti-Kα](image1)

![Figure 6. Overlapping of Ba-L and Ti-K](image2)

<table>
<thead>
<tr>
<th>Table 1. Fitting Parameters</th>
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<tbody>
<tr>
<td>Parameter(s)</td>
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<tr>
<td>Energy / ch</td>
</tr>
<tr>
<td>Peak Energy</td>
</tr>
<tr>
<td>Peak width</td>
</tr>
<tr>
<td>Peak Height Ratio</td>
</tr>
<tr>
<td>(Kα - Kβ, Lα - Lβ - Lγ)</td>
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<tr>
<td>Peak Height (Kα, Lα)</td>
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Fit : Determined by least square fitting as fitting parameters

![Figure 7. XRI Pattern of BST / SRO](image3)

<table>
<thead>
<tr>
<th>Table 2. Comparison of Conventional XRF and Combined XRI / GIXRF apparatus</th>
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<tr>
<td>Density Effect</td>
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<tr>
<td>Density Measurement</td>
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<tr>
<td>Reference Sample</td>
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<tr>
<td>Daily Calibration</td>
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<td>Common Element in Interface Layer</td>
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THICKNESS DETERMINATION AND COMBINED APPARATUS

The X-ray Interference Method (XRI) based on X-ray Reflectivity Measurement (XRR) is one method for determining the absolute thickness of a film. Thickness gauges employing this method have been used in semiconductor fabricators[5]. The combination of GIXRF and XRI can be used as an alternative method to a conventional XRF spectrometer for studying wafers[6]. Fig. 7 shows the XI pattern of a BST / SRO stacked film. The thickness of both BST and SRO can be calculated by analyzing this pattern. The features of the combined apparatus are compared with those of a conventional XRF in Table 2.

CONCLUSION

The Composition of BST deposited on SRO was determined using GIXRF. The slight influence of Sr-K XRF from SRO was eliminated using the Ru-K XRF intensity and the normal composition of SRO. The composition of SRO deposited under BST was also determined using higher-incidence-angle XRF. The effect of Sr-K XRF from BST was eliminated using Ti-K and Ba-L XRF intensities and the measured composition of BST. The thickness of both BST and SRO was determined using XRI.

REFERENCES