Research Article

Stoichiometry Calculation in $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ Solid Solution Thin Films, Prepared by RF Cosputtering, Using X-Ray Diffraction Peak Positions and Boltzmann Sigmoidal Modelling

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A novel procedure based on the use of the Boltzmann equation to model the $x$ parameter, the film deposition rate, and the optical band gap of $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ thin films is proposed. The $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ films were prepared by RF cosputtering from $\text{BaTiO}_3$ and $\text{SrTiO}_3$ targets changing the power applied to each magnetron to obtain different Ba/Sr contents. The method to calculate $x$ consisted of fitting the angular shift of (110), (111), and (211) diffraction peaks observed as the density of substitutional Ba$^{2+}$ increases in the solid solution when the applied RF power increases, followed by a scale transformation from applied power to $x$ parameter using the Boltzmann equation. The Ba/Sr ratio was obtained from X-ray energy dispersive spectroscopy; the comparison with the X-ray diffraction derived composition shows a remarkable coincidence while the discrepancies offer a valuable diagnosis on the sputtering flux and phase composition. The proposed method allows a quick setup of the RF cosputtering system to control film composition providing a versatile tool to optimization of the process.

1. Introduction

The $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ solid solution (BST-SS) is a ceramic material with a great potential to be used in dynamic random access memories (DRAM) and integrated optic devices. It is known that ferroelectric and optical properties of BST-SS are stoichiometry dependent, for example, the electrical resistance, hysteresis cycle, and resistive switching [1], extinction coefficient and refraction index [2], the relative dielectric constant, breakdown strength, and energy density of multifunctional fibers [3], and the remanent polarization [4]. BST-SS usually crystallizes in a cubic lattice changing its lattice parameter between $a$ (Å) = 4.0577 and $a$ (Å) = 3.936 associated with the extreme compositions: $\text{BaTiO}_3$ (BTO) and $\text{SrTiO}_3$ (STO) [ICCD, PDF International cards 00-075-0215 (BTO); 00-040-1500 (STO)]. The progressive Sr
substitution in the Ba$_x$Sr$_{1-x}$TiO$_3$ solid solution leads to a lattice contraction, reflected in the shift of Bragg angles, as reported in BST materials prepared by diverse techniques such as arc discharge [5], sol-gel [6–8] pulsed laser deposition [7], hydrothermal reaction [9], and chemical synthesis [10]. As much as both titanates are miscible in each other, the peak shift is linear and continuous between the extreme compositions; that is, it follows Vegard's law. However, the presence of the metastable tetragonal phase is possible due to the presence of oxygen vacancies [11, 12]. On the other hand, reactive sputtering modelling has been widely studied since the early work of Berg et al. [13]. Berg's and other models such as that developed by Strijckmans and Depla [14] take into account the nonlinearity inherent to the sputter deposition process involving reactive species. A general conclusion extracted from the models is that the hysteresis due to the change in the target (poisoned target) cannot be eliminated by the power fed to the RF system because the thickness of the compound film varies in proportion to the power and also depends on the reactive gas flux. The underlying mechanisms of the sputtering process using ceramic targets have been described since the early 1980s [15]. An accepted description of the process for ceramic targets is that the species are evaporated as individual atoms with different sputtering yields [16] causing an initial enrichment with the species of smaller yield, although a stationary point on the target composition compared with the sputtering flux is eventually reached. Usually oxygen is added to increase the control of the stoichiometry [11], although there is not yet an established procedure to control the sputtering process. Figure 1 depicts a scheme of the Boltzmann sigmoidal equation, where before and after of the exponential growth there are two zones of stabilization distinguished by a central turning point, A1, A2, and \((X0, (A1 + A2)/2)\), respectively. This function has also been used to describe other phenomena such as phase transition in smart gels [17], the relationship between reaction kinetics and its dynamic influence on viscosity in the chemorheology behavior of photopolymerizable acrylates [18], and the stem and rosebud growth in roses [19], among others.

Boltzmann’s sigmoidal equation can be written as (1) when it is increasing and as (2) when it is decreasing.

\[
y(x) = y_f - \frac{y_f - y_i}{A + e^{(x-c)/\alpha}}
\]

\[
y(x) = y_i - \frac{y_f - y_i}{A + e^{(x-c)/\alpha}}
\]

where \(y_f\) and \(y_i\) are final values of the dependent variable, \(x\) the independent variable, \(c\) is the value of \(x\) at the inflection point, and \(\alpha\) is a coefficient that describes the behavior of the slope of the process during the transition.

In the present contribution, a further development of the proposed Boltzmann modelling for BST-SS cosputtered films is presented in order to predict film properties such as film thickness and optical band gap, using as initial input the information extracted from X-ray diffractograms. The Boltzmann model is followed closely when the lattice parameter is plotted as a function of applied power.

### 2. Experimental Details

BST-SS films were prepared by RF magnetron sputtering in a system equipped with two magnetrons: BaTiO$_3$ (99.95%, SCI Engineered Materials Inc.) and SrTiO$_3$ (99.9%, SCI Engineered Materials Inc.). Targets were 2\(\text{in.}\) in diameter and 0.125\(\text{in.}\) thick. Before film deposition, the sputtering chamber was evacuated to a base pressure around 1.2 \(\times 10^{-3}\) Pa; then, an Ar flushing was done filling the chamber to a pressure of 3.9 Pa during 10 minutes. For the film deposition, an Ar + O$_2$ gas mixture was introduced into the chamber with an Ar/O$_2$ = 90/10 ratio at an initial pressure of 6.6 Pa to ignite the plasma and perform a target presputtering during 15 minutes. Thereafter, the working pressure was set at 3.9 Pa to carry out the deposition. Quartz substrates 1 \(\times 1\) cm$^2$ were successively rinsed with trichloroethylene, acetone, and ethanol before film deposit. A stainless-steel substrate holder was fixed at a distance of 8 cm from the magnetron in off-axis configuration. The substrate holder was rotated at 100 rpm for ensuring film uniformity; the substrate temperature was set at 549°C. The total applied RF-magnetron power was 120 watts, distributed between the two magnetrons as shown in Table 1, in order to produce Ba$_x$Sr$_{1-x}$TiO$_3$ films with different compositions. The sputter deposition time for all of samples was 68 minutes.

Chemical composition was obtained by energy dispersive X-ray spectroscopy (EDS) employing a Jeol JSM-5300 electron microscope equipped with a KeveX Delta 1 spectrometer. The optical transmission spectra of the films were obtained in a Perkin-Elmer, Lambda 40 Spectrophotometer in the range of 250 to 800 nm. Film thicknesses were calculated from the transmittance spectra using the SCOUT software [20]. The X-ray diffractograms were acquired in a Phillips X'Pert diffractometer using CuK$\alpha$ = 1.54060 \(\text{Å}\), in a 2 theta range 20–95’ with a step size of 0.02’ and step time 1 s in the grazing incidence geometry with an incidence angle 0.5’.

![Graph of a typical Boltzmann curve described by (1).](image-url)
planes. Observed shift of (111) and (211) plane of the cubic phase reflections at higher diffraction angles is identified. As STO sputtering power increases a shift of the BST-SS tetragonal phase [8, 18, 23] was also observed. Figure 3 presents the X-ray diffractograms of the BST-SS films described in Table 1. Diffraction peaks corresponding to (100), (111), (210), (220), and (222) planes of the cubic BTO and STO phases were identified [21]. Diffraction peaks from (032) and (031) of the orthorhombic phase Ba0.91Sr0.09TiO3 (marked with *) [22], planes of (221) and (321), planes of the BTO tetragonal phase, and those of (211), (221), (310), (311), and (321) planes (marked with ***) of the BST-SS tetragonal phase [8, 18, 23] were also identified. As STO sputtering power increases a shift of the BTO cubic phase reflections at higher diffraction angles is observed, indicating a lattice contraction due to the higher Sr composition in the films. Figure 3 depicts the values of the diffraction angles for the (110) plane of the measured films versus applied power, fitted employing the Boltzmann sigmoidal equation. A similar analysis was carried out for the shift observed for the positions associated with (III) and (211) planes.

### Table 1: RF power applied to BaTiO3 and SrTiO3 targets.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BaTiO3 (W)</th>
<th>SrTiO3 (W)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B0S120</td>
<td>0</td>
<td>120</td>
</tr>
<tr>
<td>B15S05</td>
<td>15</td>
<td>105</td>
</tr>
<tr>
<td>B30S90</td>
<td>30</td>
<td>90</td>
</tr>
<tr>
<td>B45S75</td>
<td>45</td>
<td>75</td>
</tr>
<tr>
<td>B60S60</td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td>B75S45</td>
<td>75</td>
<td>55</td>
</tr>
<tr>
<td>B90S30</td>
<td>90</td>
<td>30</td>
</tr>
<tr>
<td>B105S15</td>
<td>105</td>
<td>15</td>
</tr>
<tr>
<td>B120S0</td>
<td>120</td>
<td>0</td>
</tr>
</tbody>
</table>

The variables in (2) were assigned as follows: $y_{x3}$ is $Ad(p)$ representing the diffraction angle for the (110) plane; $y_{x}$ is $Ad_{1}$ corresponding to the diffraction angle when the STO magnetron power is 120 W, $y_{x}$ is $Ad_{2}$, the diffraction angle with a BTO magnetron power $= 120$ W, $x$ is $P$, which represents the magnetron power values; $c$ is $P_{0}$, the middle value indicated to be $A = 1$, and $x$ is $\Delta P$ which is the slope around $P_{0}$; thus (2) is rewritten as follows:

$$Ad(p) = Ad_{1} - \left[\frac{Ad_{1} - Ad_{2}}{1 + e^{(P - P_{0})/\Delta P}}\right].$$

(3)

The fitting values for $Ad_{1}$, $Ad_{2}$, $P_{0}$, $\Delta P$, and $R^{2}$ for (110), (III), and (211) planes of the cubic phase are presented in Table 2. Composition values $x$ were obtained by considering that that peak shift follows Vegard’s law with the extreme values corresponding to those of SrTiO3 $(x = 0)$ and BaTiO3 $(x = 1)$. Figure 4 compares the XR–XRD–derived stoichiometry evolution curve versus the magnetron power with the experimental composition measured by EDS, correspondingly fitted with Boltzmann’s equation (Table 3). The Ba content was converted to $x$ with the following expression:

$$\%at \text{ Ba} = x.$$

(4)

Although the curves show a very close behavior, there is a separation in the middle part of the curve, that is, from BTO power $= 30$ W and from STO power $= 15$ W and a remarkable discontinuity between BTO magnetron power from 45 to 60 W. The inset in Figure 4 depicts the difference between the composition obtained from XRD ($X_{XRD}$) and that obtained from EDX measurements ($X_{EDS}$). To evaluate the discrepancy, in the inset the difference versus the power is plotted. The difference curve displays a bimodal increase when the power in each magnetron increases with a minimum value.
Nonstable sputtered flux is expected because of the atomic masses in power in STO target, an instability in the composition of the target, that is, the BTO target, begins to increase, decreasing composition and Ba/Sr sputtering yields. When the power in volume zones in the film attributed to the variations in flux curves can be due to Ba-rich and Sr-rich composition X-ray diffractograms in Figure 2.

The inset in Figure 5(a) presents the thickness of the studied samples as a function of the Ba composition obtained from XRD. The thickness reduction of the film B15S105 compared with that of pure SrTiO3 (B0S120) can be explained due to the mass difference, the sputtering yield, and scattering events. As the cosputtering process starts Ti ions would suffer additional scattering events due to the presence of Ba atoms affecting the film deposition rate. Also it is known that the sputtering yield of SrTiO3 is smaller than that of BaTiO3 [24]. It is worth emphasizing that, in this work, due to the employed deposition characteristics, the variation in the lattice parameter is due to the substitutional incorporation of Ba as its ionic radius is greater than that of Sr [1, 7]. The effect of differences in the thermal expansion coefficient (TEC) between substrate and BST-SS films is very important for epitaxial growth giving place to values of critical film thickness from 1 to ten nanometers [25]. Reported values of the TEC of BST-SS are close to those of SrTiO3 and BaTiO3, plasma process [5]. Composition also may be affected by changes in target erosion and total gas pressure during the sputtering process [13]. Additional discrepancies may be due to stress originated by the difference in size of Ba and Sr cations and to the different phases present in addition to the main one, interplanar spacing from XRD data is sensitive to these EDS measurements.

The values for the Boltzmann fit of the EDS curve are presented in Table 3 and compared with those from the XRD curves for (110), (111), and (211) diffraction planes. The values in (1), for the $x_1$ and $x_2$ parameters, were set at 0 and 1, respectively.

Figures 5(a) and 5(b) present the lattice parameter $a$ (Å) calculated from diffraction peaks associated with (110), (111), and (211) planes of the prepared films versus the $x$ parameters derived from XRD and EDS, respectively. Points were fitted with a straight line corresponding to Vegard’s Law:

\[ a(\text{Å}) = A + Bx, \]  

where $x$ is the molar fraction in Ba$_{x}$Sr$_{1-x}$TiO$_3$ and “a” is the lattice parameter calculated from the XRD peaks (110), (111), and (211), respectively. Table 4 presents the $A$, $B$, and $R^2$ values, which indicate a linear relation of the composition of the cubic BST-SS with Vegard’s law as observed in Figure 5(a).

The inset in Figure 5(a) presents the thickness of the studied samples as a function of the Ba composition obtained from XRD. The thickness reduction of the film B15S105 compared with that of pure SrTiO3 (B0S120) can be explained due to the mass difference, the sputtering yield, and scattering events. As the cosputtering process starts Ti ions would suffer additional scattering events due to the presence of Ba atoms affecting the film deposition rate. Also it is known that the sputtering yield of SrTiO3 is smaller than that of BaTiO3 [24]. It is worth emphasizing that, in this work, due to the employed deposition characteristics, the variation in the lattice parameter is due to the substitutional incorporation of Ba as its ionic radius is greater than that of Sr [1, 7]. The effect of differences in the thermal expansion coefficient (TEC) between substrate and BST-SS films is very important for epitaxial growth giving place to values of critical film thickness from 1 to ten nanometers [25]. Reported values of the TEC of BST-SS are close to those of SrTiO3 and BaTiO3,
scatter of data is expected due to the limitations of the EDS technique, mainly its lack of sensitivity to distinguish between the contribution from different crystallographic phases. Although Rietveld phase refinement is beyond the scope of the present contribution, it is a future task to elucidate the contribution of each phase in the cubic BST-SS.

The lattice parameter as a function of the RF-power is shown in Figure 6. The dependence follows a Boltzmann profile; a nonlinear behavior for a unique composition of Ba/Sr has been reported as a function of oxygen partial pressure and total gas pressure of the RF-magnetron sputtering process [11, 12].

The transmittance spectra of the deposited films are presented Figure 7(a) and analyzed according to Tauc model in Figure 7(b). In the transparent region (above the absorption edge) in the transmittance spectra, the number of interference maxima-minima are reduced as the BTO sputtering power increases indicating a reduction in the film thickness, as will be discussed below. Correspondingly, the absorption edge shifts towards higher wavelength as is clearly observed in Figure 7(b).

By extrapolating the linear portion of the plot to $(\alpha h v)^2 = 0$, the band gap ($E_g$) values were calculated and presented in Figure 7(c) as a function of the composition parameter $x$. For the sake of fitting, both axes are inverted. The sigmoidal dependence of the band gap with composition is evident. The tendency in the band gap values for BST-SS agrees with those reported in literature [2, 6, 30, 31].

Figure 8 presents the evolution of deposition rate, calculated from the film thickness and the sputter time, with respect to (a) the RF-magnetron power and (b) the $x$ parameter in the $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ solid solution. In Figure 8(a) a small decrement in the deposition rate is observed when the BTO target is turned on at the minimum power employed.
Correspondingly, when compared with the $x$ parameter, the deposition rate increases exponentially as follows:

$$Y = 1.807 + 0.033e^{x/22}.$$  

(7)

In Figure 8(a) the relationship between deposition rate Ba/Sr and 120 W in both targets is approximately 3/1.

The calculations of the area under the Boltzmann curve fitted to DRX and EDS in Figure 4 show a relationship between Ba/Sr roughly 3/2 and 1/1 respectively; these results indicate a better relationship between the DRX Boltzmann fit and deposition rate compared with the relationship between EDS Boltzmann fit and deposition rate due to reasons previously explained. Therefore, the growing of $X$-parameter

(105/15 power ratio STO/BTO). Thereafter the sputtering rate shows an exponential increase in the BTO magnetron power, fitted with the following expression:

$$Y = -0.037 + 1.582e^{P_{BTO}(W)/97}.$$  

(6)

Correspondingly, when compared with the $x$ parameter, the deposition rate increases exponentially as follows:

$$Y = 1.807 + 0.033e^{x/22}.$$  

(7)
is directly related to the increment in the magnitude of power on BTO. These facts allow us to conclude that the calculations of $x$-parameter based on DRX measurements are more accurate than those of EDS technique.

4. Conclusions

$\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ (BST) films were grown on quartz substrates at 549°C by RF magnetron cosputtering from BTO and STO targets, using a total power of 120 W distributed between the two magnetrons. The films present a mixture of the cubic, orthorhombic, and tetragonal phases of BST. The Boltzmann fitting to the shift of diffraction peaks from the (110), (111), and (211) BST cubic phase planes as function of the applied RF-magnetron power allowed proposing a direct methodology to obtain the composition in $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ cubic solid solution. The $x$ parameter calculated with the Boltzmann expression was compared with the $x$ parameter obtained from the EDS measurements, and a close agreement was found. The lattice parameter variation versus power and the optical band gap versus the $x$ parameter were adjusted with similar Boltzmann expressions. The film deposition rate as a function of power and $x$ parameter follows an exponential growth behavior. The proposed method for estimation of the $x$ parameter from simple X-ray diffraction analysis has been found useful for presetting the initial sputtering conditions to adjust $x$, film thicknesses, and optical band gap allowing a direct production of BST films with the adequate properties required for technological applications.

Disclosure

M. Meléndez-Lira is on sabbatical leave from Departamento de Fisica at Cinvestav-IPN.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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[21] International Centre for Diffraction Data (ICDD), "PDF cards 00-040-1500 (STO); 00-075-0215 (BTO); 00-034-0411 (BST-SS with x=0.6)," (1982, 1997).


