Mathematical model of Boltzmann's sigmoidal equation applicable to the set-up of the RF-magnetron co-sputtering in thin films deposition of $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$

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Abstract. In this work, we present the stoichiometric behaviour of Ba^{2+} and Sr^{2+} when they are deposited to make a solid solution of barium strontium titanate. $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ (BST) thin films of nanometric order on a quartz substrate were obtained by means of *in-situ* RF-magnetron co-sputtering at 495°C temperature, applying a total power of 120 W divided into intervals of 15 W that was distributed between two magnetron sputtering cathodes containing targets of BaTiO_3 and SrTiO_3 , as follows: 0–120, 15–105, 30–90, 45–75, 60–60, 75–45, 90–30, 105–15 and 120–0 W. Boltzmann's sigmoidal modified equation (Boltzmann's profile) is proposed to explain the behaviour and the deposition ratio Ba/Sr of the BST as a function of the RF-magnetron power. The Boltzmann's profile proposal shows concordance with experimental data of deposits of BST on substrates of nichrome under the same experimental conditions, showing differences in the ratio Ba/Sr of the BST due to the influence of the substrate.

Keywords. Sputtering deposition; thin films; stoichiometric behaviour; barium strontium titanate; Boltzmann's equation.

1. Introduction

The solid solution of $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ (BST) is a ceramic material with the crystalline structure called perovskite. To deposit BST like a thin film of a nanometric order and with metallic contacts, a device is built, which operates as a capacitor [1,2] when it is applied a controlled electric current and a polarized sweep voltage, and BST has a property called resistive switching. This property allows the BST to be considered as a promising material for the application in memories of nonvolatile ReRAM type [1]. The controlled stoichiometric content is very important for any applications such as: (a) electro-optics devices with $\text{Ba}_{0.65}\text{Sr}_{0.35}\text{TiO}_3$ [3], (b) tunable devices $\text{Ba}_{0.45}\text{Sr}_{0.55}\text{TiO}_3$ [4] and (c) DRAM memories devices with $\text{Ba}_{0.50}\text{Sr}_{0.50}\text{TiO}_3$ [5]. It is relevant to investigate properties related to the resistive switching such as (a) barrier potential (E_g), (b) superficial resistivity and (c) stoichiometric behaviour of Ba^{2+} and Sr^{2+} in the solid solution of BST. On the other hand, the Boltzmann's sigmoidal equation has been used to model the behaviour of the transition phase for smart gels such as polymeric systems that exhibit a reversible transition phase when exposed to the environmental stimulus [6]. Also, Boltzmann's sigmoidal equation (through a semilog-based sigmoidal model) has

been used to define the relationship between kinetics reaction and its dynamic influence on viscosity in chemorheology of photopolymerizable acrylates process. The value of this sigmoidal model defines preparation and process conditions to be expected to control crosslinking so as to make the best use of dimensional stability or other thermophysical properties [7].

1.1 Boltzmann's sigmoidal equation

An analysis of the experimental data and mathematical models reported in the literature on transition phenomena revealed exhibit patterns of their physical and geometric behaviour. For instance, sigmoidal patterns and inflection points are observed in the same transitions. Moreover, if the transition changes from continuous to discontinuous at the inflection point, the inflection point may correspond to the critical stage. The sigmoidal mathematical model proposed by Boltzmann in 1879 was based on the sigmoidal logistic equation

$$y(x) = \left[\frac{1}{1 + e^x} \right] \quad (1)$$

Equation (1) has been used to describe behaviours exhibited when a certain factor triggers a transition (reversible or not) from a steady state to another one with very different magnitude. For example, in some bacterial growth, food permits exponential reproduction; when the food is sufficient to feed only a certain number of individuals, finally the play of stability and population occurs. This is an appropriate starting point for the prediction of transition phenomena. Thus, the following Boltzmann's sigmoidal equation, where the original function is modified, which contains the required geometric characteristics, is proposed:

$$y(x) = y_f - \left[\frac{y_f - y_i}{A + e^{(x-c)/\alpha}} \right], \quad (2)$$

where y_i and y_f are the equilibrium values of the dependent variable before and after the transition, respectively, c is an inflection point and α is a coefficient that describes the behaviour of the slope of the process during the transition and identifies the continuity or discontinuity of the process. If a unique value of the dependent variable is observed for each value of the independent variable, the function is continuous; on the other hand, if α is small and nearly zero, its value is critical and it is in agreement with the inflection point; because the transition can be faster, A is a parameter that adjusts the position of the critical value with respect to the geometric location of the transition. If $A = 1$, the value is located at the middle of the transition [6]. If $\alpha \rightarrow 0$, the derivative of equation (2) tends to infinity. If $x \rightarrow c$, a discontinuous transition is observed that can be expressed by the following equation:

$$y' = \left[\frac{(y_f - y_i) e^{(x-c)/\alpha}}{\alpha (A + e^{(x-c)/\alpha})^2} \right]. \quad (3)$$

The Boltzmann's sigmoidal equation can be used to describe changes in BST (parameter 'x') or stoichiometric content (mol%) in BST as a function of RF-magnetron power applied on targets BaTiO₃ and SrTiO₃ placed above magnetron cathodes. This can be performed by changing the parameters of equation (2) as follows: $y(x)$ by $x\%$ where $x\%$ is the stoichiometric content of Ba²⁺ at some point, y_i by x_1 where x_1 is the stoichiometric content of Ba²⁺ when RF-magnetron power is 120 W, y_f by x_2 where x_2 is the stoichiometric content of Ba²⁺ when RF-magnetron power is 0 W, x by w where w is a specific value of RF-magnetron power to obtain some specific value of $x\%$, c by w_0 where w_0 is the middle value indicated by $A = 1$, c by Δw where Δw is the RF-magnetron power gap around w_0 where the deposition ratio Ba/Sr changes its behaviour. The Boltzmann's sigmoidal equation, transformed for purposes of this paper, is called 'Boltzmann's profile'. The Boltzmann's profile is as follows:

$$x \text{ (wt\%)} = x_2 - \left[\frac{x_2 - x_1}{1 + e^{(w-w_0)/\Delta w}} \right] \quad (4)$$

Table 1. Conditions of RF-magnetron power over both magnetrons with targets of BaTiO₃ and SrTiO₃.

Sample	RF-magnetron power (W)	
	BaTiO ₃	SrTiO ₃
M1	0	120
M2	15	105
M3	30	90
M4	45	75
M5	60	60
M6	75	45
M7	90	30
M8	105	15
M9	120	0

1.2 Materials, methods and samples preparation

To prepare the BST films, the sputtering chamber was evacuated to a pressure of 1.2×10^{-3} or less; later a 'flushing' was performed with argon gas at a pressure of 3.9 Pa for 10 min. For the deposition, an Ar + O₂ gas mixture was introduced in the chamber at the ratio Ar/O₂ = 90/10 and a pressure of 6.6 Pa to ignite the plasma and do a pre-sputtering to the targets for a duration of 15 min. Finally, the working pressure was kept at 3.9 Pa to carry out the deposition. A stainless-steel porta-substrate at a distance of 8 cm from the magnetron in a 'off-axis' configuration was used. The quartz substrate was rotated at 100 rev min⁻¹ to make uniform films at *in-situ* temperature of 495°C. Samples were deposited using two magnetrons with targets of BaTiO₃ 0.125" thick with a purity of 99.95% and SrTiO₃ of 0.125" thickness and a purity of 99.9%, both of 2" diameter (SCI Engineered Materials, Inc). The total power applied was of 120 W, which was distributed between the two magnetrons as show in table 1.

1.3 Characterization techniques

The chemical composition was analysed using a scanning electron microscope (SEM) Jeol JSM-5300 equipped with a Kevex energy-dispersive spectrometer (EDS) model Delta 1. The transmission spectra of thin films were obtained on a Perkin-Elmer, Lambda 40 Spectrophotometer model. Samples were measured in the range of 250–800 nm, with a pitch of 0.1 nm and a passing speed of 240 nm min⁻¹. The thicknesses of the M1–M9 samples (see table 1) were measured by processing the transmission spectra, using a commercial program called SCOUT [8].

2. Results and discussion

The experimental data of atomic percentage of Ba²⁺ and Sr²⁺ of the film were obtained by means of the EDS technique, after calculating the stoichiometric content of Ba (x) and Sr ($1-x$), of the solid solution of BST. The following expressions were

Figure 1. Boltzmann's profile for stoichiometric behaviour of the deposition ratio Ba/Sr vs. RF-magnetron power on (a) quartz and (b) nichrome substrate.

obtained:

$$\frac{\text{Ba (at\%)}}{\text{Ba (at\%) + Sr (at\%)}} = x,$$

$$\frac{\text{Sr (at\%)}}{\text{Ba (at\%) + Sr (at\%)}} = 1 - x.$$

Ba (at%) is the atomic percentage of barium and Sr (at%) is the atomic percentage of strontium; the values of 'x' and '1 - x' are multiplied by 100 and plotted as shown in figure 1.

Experimental discrete points to plot Boltzmann's profile of figure 1a were obtained under the same deposition conditions (temperature and substrate rotation, reservoir pressure, ratio of Ar/O₂, total power applied and step power of 15 W in pairs in the range of 0–120 W); experimental discrete points used to plot the Boltzmann's profile of figure 1b were obtained from [1].

In figure 1a and b the horizontal axes ('bottom' and 'up') represent the magnitudes of the power (W) applied to target barium titanate (BaTiO₃) and strontium titanate (SrTiO₃), respectively. Vertical axes ('left' and 'right') represent the stoichiometric content expressed in Ba²⁺ (%) and Sr²⁺ (%), respectively, of the solid BST solution. For both figure 1a and b, the parameters that define the Boltzmann's profile are found in table 2; they are obtained from the best fit by setting $x_1 = 0$ W and $x_2 = 100$ W. The straight lines from w_0 towards points x_1 and x_2 represent the average deposition of Ba²⁺. The straight line slopes m_1, m_2 for figure 1 are $m_{1a} = 0.695$ and $m_{2a} = 1.040$ and figure 2, $m_{1b} = 1.01$ and $m_{2b} = 0.70$, for deposits on quartz and nichrome, respectively. These results indicate that the rate of change in deposition of Ba²⁺ into the solid BST solution is less when the film is grown on quartz compared with growth on nichrome. The perpendicular at each end of the line represents Δw , and generates intersections (w, x) with the Boltzmann's profile of x (wt%). These values were used to calculate the straight line slopes representing the value of average deposition ratio Ba/Sr in the transition zone containing w_0 ; straight line slope value for figure 1a is $m_{3a} = 1.53$ and figure 2, $m_{3b} = 1.46$.

To find the contribution of the substrate used in the behaviour of the deposition ratio Ba/Sr of the BST solution, the thickness of the samples M1 (deposition of SrTiO₃ exclusively) and M9 (deposition of only BaTiO₃) was measured. The thicknesses of the samples were obtained by processing the transmission spectra (not shown here) using the program SCOUT [8]. Table 3 shows the thickness, deposition time and calculated deposition rate (thickness/time).

The values of the deposition rate in table 3 show that with the same RF-magnetron power applied, the contribution to the film thickness of BaTiO₃ compared with SrTiO₃ is higher; the deposition ratio Ba/Sr = 3/1 nearly and may be due to the difference in ionic radius of Ba²⁺ (1.35 Å) and Sr²⁺ (1.13, 1.18 Å) [1,9–11]. Comparing the values of the straight line slopes m_{1a} and m_{1b} , m_{2a} and m_{2b} of figure 1a and b, it is concluded that the average deposition ratio Ba/Sr in the solid BST solution at the interface on quartz and nichrome determines this behaviour. So far, the results show that the behaviour of deposition ratio Ba/Sr in the thin film growth

Table 2. $x_1, x_2, w_0, \Delta w$ and R^2 from the fit for Boltzmann's profile, from the samples of BST-quartz and BST-nichrome, of equation (4).

BST deposition	x_2 (%)	x_1 (%)	w_0	Δw	R^2
BST-quartz	100	0	71.95 ± 1.44	16.02 ± 1.29	0.99137
BST-nichrome	100	0	49.46 ± 0.96	16.23 ± 0.86	0.99633

Figure 2. Profile of the derivate $x(w)$ as well as $x'(w) = dx/d$ (RF-magnetron power) at stoichiometric equilibrium point of (a) 71.95 W and (b) 49.46 W.

Table 3. Deposition speed of BaTiO₃ and SrTiO₃ on quartz substrate at 549°C with RF-magnetron power of 120 W.

Sample	Thickness	Deposition time	Deposition rate (nm min ⁻¹)
M1	108	61	1.93
M9	320.6	60	5.88

from solid solution of BST depends on the value of the RF-magnetron power and substrate. Derivative of equation (4) gives

$$x'(\text{wt}\%) = \frac{dx}{d(\text{RF-magnetron power})} = \frac{(x_2 - x_1)e^{(w-w_0)/dw}}{dw(A + e^{(w-w_0)/dw})^2}. \quad (5)$$

Figure 3. Boltzmann's profile for the experimental values of Ba²⁺ and Sr²⁺ in the solid solution of BST on (a) quartz and (b) nichrome substrate.

Figure 2a and b presents the rate of change of atomic percentage of Ba^{2+} in the solid BST solution; the peak of the curve corresponds to the value of the slope depending on w_0 , so that $m_q = 1.5562$ and $m_n = 1.5388$ for the deposition on quartz and nichrome, respectively, where the stoichiometric content of $\text{Ba/Sr} = 50\%/50\%$ ($\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$). From the closeness of the m_q and m_n values, besides the fact that w_0 at BST-quartz and BST-nichrome total approximately 120 W, it is concluded that the processes are reciprocal. Figure 3a presents Boltzmann's profile for stoichiometric content of Ba: x (wt%) and Sr: $(1 - x)$ (wt%) in the solid BST solution on quartz substrate as follows:

$$x \text{ (wt\%)} = 100 - \left[\frac{100}{1 + e^{(w-71.96/16.02)}} \right],$$

$$(1 - x) \text{ (wt\%)} = \left[\frac{100}{1 + e^{(w-48.06/16.02)}} \right],$$

$$x \text{ (wt\%)} = 100 - \left[\frac{100}{1 + e^{(w-49.47/16.23)}} \right],$$

$$(1 - x) \text{ (wt\%)} = \left[\frac{100}{1 + e^{(w-70.63/16.23)}} \right].$$

This set of equations of the Boltzmann's profile gives, then, in the RF-magnetron co-sputtering set-up, the obtained deposition ratio Ba/Sr, for stoichiometric concentrations of BST and the current deposition conditions. Therefore, the construction of Boltzmann's profile, based on the deposition conditions, the substrate temperature and RF-magnetron power value, helps in setting up the conditions for stoichiometric concentrations.

3. Conclusions

This mathematical model can be used to set up an RF-magnetron co-sputtering system for calculating the optimum

parameters of film deposition with controlled stoichiometric content (parameter ' x ') when used with complementary power RF-magnetron cathodes. The derivative of the sigmoidal Boltzmann model shows the influence of substrate at the point (magnitude of RF-magnetron power) where the ratio Ba/Sr becomes 50%/50% mol. Specifically, in the solid BST solution, controlled stoichiometry can be achieved by the use of Boltzmann's profile with RF-magnetron co-sputtering.

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