

**The Influence of Strain on the Dielectric Behavior of (Ba, Sr) $Ti_{1+x}O_3$ Thin Films
Grown by LS-MOCVD on Pt/SiO₂/Si***

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The Influence of Strain on the Dielectric Behavior of $(\text{Ba,Sr})\text{Ti}_{1+x}\text{O}_3$ Thin Films Grown by LS-MOCVD on Pt/SiO₂/Si

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Abstract – The strain state and its coupling to dielectric behavior have been investigated for {100} BST thin films deposited on Pt/SiO₂/Si at 640°C. It is estimated from x-ray diffraction that the in-plane biaxial strain is approximately 0.7%. We postulate that this is of sufficient magnitude to confine any spontaneous polarization to the plane of the film. The thickness-corrected dielectric behavior perpendicular to the substrate for these samples shows evidence of coupling to such an in-plane phase transition at approximately 390K, as manifested by deviation from Curie-Weiss-like behavior at this temperature.

INTRODUCTION

Thin film $(\text{Ba}_x\text{Sr}_{1-x})\text{Ti}_{1+y}\text{O}_{3+z}$ (BST) is currently a leading candidate for use as a high-permittivity dielectric in a variety of applications, as a replacement for silicon oxide and nitride dielectrics. When used as an integrated layer on Si, the BST is generally under a large, plane biaxial tensile stress because of thermal expansion mismatch with the underlying substrate. It is expected that there will be substantial coupling of this stress to the dielectric properties of the film through the electrostrictive effect. In this paper, we estimate the magnitude of this stress, and investigate its impact on the permittivity measured in the film thickness direction.

EXPERIMENTAL PROCEDURES

Details of sample preparation and measurement techniques have been given elsewhere [1], [2]. Briefly, {100}-textured BST films were deposited at approximately 640°C onto Pt-coated Si wafers by liquid-delivery-source chemical vapor deposition, to thicknesses ranging from 20 nm to 160 nm at 640°C. The Ba to Sr ratio was chosen to be 70/30, while samples for dielectric measurement were grown at a

(Ba+Sr)/Ti ratio of 46.5/53.5 ($y=0.15$). Electron beam evaporation was used to deposit the Pt bottom electrodes at 315°C directly onto SiO₂/Si [3]. Pt top electrodes were evaporated at 315°C onto the BST through a shadow mask so as to define capacitors for electrical testing. After top electrode deposition, the samples were annealed at 550°C for 30 minutes in air so as to obtain symmetric, low leakage currents under both positive and negative polarities and to achieve the lowest dielectric loss.

We have previously reported on the dielectric response of a BST thickness series of a single composition of $x=0.7$ and $y=0.15$ [1]. Dielectric behavior was investigated as a function of temperature through measurement of sample capacitance and loss tangent as a function of temperature. Capacitance-voltage analyses were performed at a frequency of 1 kHz using an HP4192A impedance analyzer and probe station equipped with a resistively heated sample chuck. A measurement frequency of 1 kHz was chosen because it was well away from artifacts caused by the test fixture residual impedance, but was not so low as to cause loss of measurement resolution on the impedance analyzer. We have previously established that the permittivity and loss tangent of these specific samples are almost independent of frequency, so choice of 1 kHz was not critical. The ac oscillation level for the measurements presented here was 0.1 V, because this yielded the greatest signal to noise ratio without suppressing the permittivity peak near zero bias.

X-ray measurements were made on films 120nm thick and of various at.%Ti. The methodology of the experiments follows the d vs. $\sin^2(\psi)$ method [4] and is as follows. Off-specular scans were performed, sampling BST reciprocal lattice vectors as a function of angle with respect to the plane stress axes, from the film normal ($\psi = 0^\circ$) to close to parallel to the sample surface ($\psi = 90^\circ$). A stiffness tensor was assumed for the BST, and the value of $\sin^2(\psi_0)$ where $d = d_0$, the unstressed lattice parameter, was extracted based on the assumed stiffness tensor. Principal strain values were then calculated from this d_0 and the measured lattice spacings as a function of inclination; these strains were then converted to stress using the assumed stiffness tensor. The in-plane stress values were compared to

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wafer curvature stress measurements [5], a new stiffness tensor chosen, and the procedure iterated until a satisfactory match was achieved. By this method, the proper stiffness tensor was constructed, and in-plane biaxial strains and unstressed lattice parameters estimated.

RESULTS AND DISCUSSION

Strain Measurements

The results of x-ray diffraction measurements are shown in Table I. The calculated stress values are large, and agree reasonably closely with values from curvature measurements for a film of the same thickness. The calculated strains are consistent with estimates based on thermal expansion mismatch between the BST and Si, for cooling from 640°C, $x_1 = \Delta\alpha(T - T_{dep})$. Excess Ti does increase the unstressed lattice parameter, d_0 , over the bulk value, so it is reasonable to conclude that some excess Ti is accommodated in the BST lattice. However, there is no clear trend with increasing %Ti; more data is needed to determine the effect of excess Ti on strain.

Table I: Strain and unstressed lattice parameter as a function of %Ti.

	Strain in-plane	Stress (MPa)	d_0 (Å)
51.0 %Ti	0.00734	2200	3.9887
51.5 %Ti	0.00727	2200	3.9888
52.5 %Ti	0.00759	2300	3.9915
53.0 %Ti	0.00718	2200	3.9895
Bulk 70/30	—	—	3.9750

Dielectric Behavior

The relationship governing the field dependence of the real part of the dielectric response of these BST thin films as a function of temperature T and thickness t has been identified to obey the equation [1],[6]:

$$E_{app} = 2\alpha'_3 P_3 + 4\alpha'_{33} P_3^3 \quad (1)$$

$$= 2\left(\frac{\beta}{t} + \gamma(T)\right) P_3 + 4\alpha'_{33} P_3^3$$

which relates the macroscopic quantities E_{app} , the apparent applied field in the film thickness direction, to P_3 , the polarization, along this same axis. This equation is consistent with expectations of ferroelectric behavior in BST as described by phenomenological Landau-Ginsburg-Devonshire theory. It was also found empirically that the measured dielectric stiffness α'_3 , which is in turn directly related to the zero-field reciprocal susceptibility, may be decomposed into a term β that governs the thickness dependence and is temperature independent, and a term γ that is thickness

independent and that controls the temperature dependence of the dielectric behavior.

Well above the bulk Curie-Weiss temperature θ_0 of approximately 300K, these samples were found to obey the Curie-Weiss law. As θ_0 is approached from above, the permittivities were found to depart from the Curie-Weiss law; however, contrary to behavior expected for e.g. a high quality, compositionally pure single crystal or ceramic specimen, inverse permittivity did not approach zero and then begin to increase again as temperature was decreased. This behavior is most easily demonstrated in plots of inverse permittivity versus temperature for samples of different thickness, Figure 1 ($y=0.15$), as lack of sharp minimum in inverse permittivity. Furthermore, ferroelectric behavior in the thickness direction appeared to be absent as evidenced by lack of hysteresis in forward and reverse capacitance-voltage sweeps taken at room temperature and below.

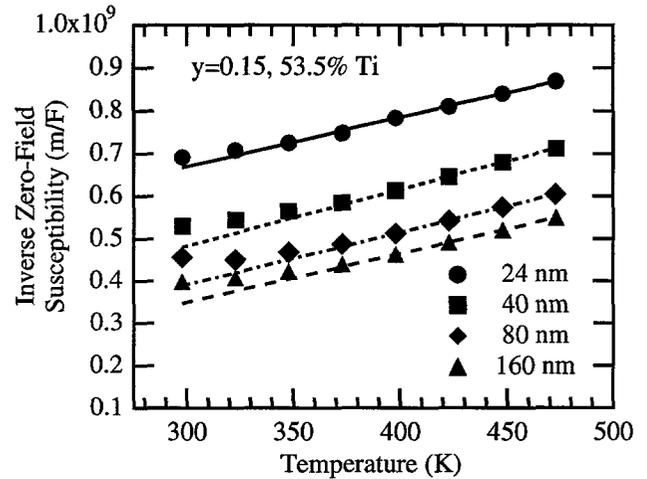


Fig. 1: Inverse zero-bias susceptibility for films of various thickness, showing deviation from Curie-Weiss behavior at $T \sim 390$ K.

Thus for all thicknesses, a linear region for α'_3 of the form

$$\alpha'_3 = \frac{T - T_3}{2\epsilon_0 C'} , T \gg T_3, \theta_0 \quad (2)$$

is observed, where C' is the measured Curie constant (in units of K), T_3 is an extrapolated intercept for a given sample, and ϵ_0 is the permittivity of free space. Thus, in the absence of any thickness dependence of the permittivity, we may express the behavior for a given Ti composition in the Curie-Weiss regime as:

$$\chi(T) = \frac{T - \theta}{2\epsilon_0 C'} , T \gg \theta_0 \quad (3)$$

where θ is an effective Curie-Weiss temperature for that composition. In this context, we may rearrange Equations 1 and 2 to show that

$$T_3(t) = \theta - \frac{2\varepsilon_0 C' \beta}{t} \quad (4)$$

i.e. that the thickness dependence can also be quantified as an apparent thickness dependent shift imposed on the effective ferroelectric Curie-Weiss temperature θ . It is important to emphasize, however, that this is not in the general sense a correct interpretation, in that the various curves all depart from Curie-Weiss behavior at approximately the same temperature, as is apparent from Figure 1. This implies that the change in dielectric behavior with film thickness may not be a true thickness-dependent shift in transition temperature, i.e. is not a modification of the bulk free energy as a function of film thickness as manifested by a shift in the curves along the temperature axis. Rather these samples appear to primarily display a thickness dependent reduction in macroscopic polarizability (i.e. a shift upwards along the inverse susceptibility axis), although there is some decrease in the apparent diffuseness of the phase transition as film thickness is increased.

No systematic variation in C' is found as a function of film thickness. C'_{ave} for these samples was found to be 9.45×10^4 K, which is somewhat larger than found for other specimens deposited previously [1].

Next, the thickness dependence of the dielectric properties may be stripped by extrapolating the data from the various samples, so as to construct inverse permittivity - temperature curves for infinitely thick material as is shown in Figure 2. In effect, this procedure yields $\gamma(T)$. Such a curve may then be used to calculate an effective Curie-Weiss temperatures, θ , as given in Equation 3. This is determined to be 40 K for

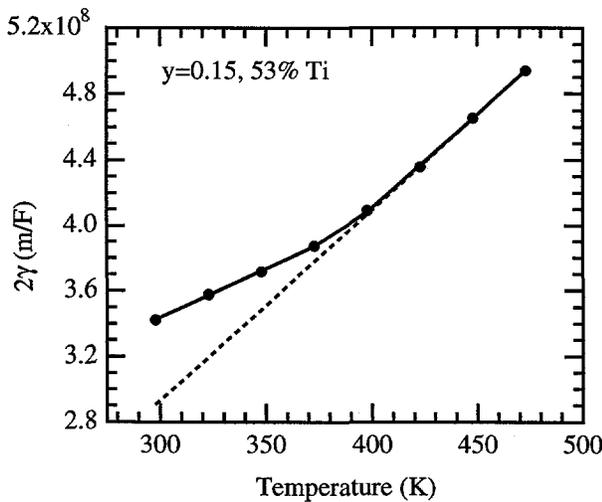


Fig.2: Dielectric behavior (points) stripped of the thickness effect, as described by Eqn. 3, showing deviation from Curie-Weiss behavior (dashed line). The solid line is a fit to the dielectric response, which includes the effect of a possible in-plane ferroelectric phase transition.

this composition. This is clearly well below the nominal bulk value, although again it is not evident how much of this is a true temperature shift and how much of this is simply a permittivity suppression.

The plane biaxial tensile stress at room temperature is sufficiently large such that any spontaneous polarization in the BST is expected to be confined to the plane of the film [7],[8], such that no switching can occur between remnant polarization states with distinguishable components in the film normal direction, for any field less than the breakdown field, applied normal to the film. If any possible domain patterning is neglected, the equibiaxial deformation of the film in the plane of the substrate is best accommodated by a spontaneous polarization along the in-plane, pseudocubic BST $\langle 110 \rangle$, with $P_1=P_2$.

Specifically, equibiaxial tensile stress decreases the temperature at which the paraelectric phase would transform to a phase with the polarization out of the plane of the film, while equibiaxial tensile stress increases the temperature θ_1 at which the paraelectric phase would transform to a phase with the polarization in the plane of the film. Calculation of these temperature shifts may be easily performed based on the free energy functional for plane stress boundary conditions as given by [7]:

$$\theta_3 = \frac{\theta - 4\varepsilon_0 C(\Delta\alpha_{Therm})T' \frac{Q_{12}}{s_{11} + s_{12}}}{1 - 4\varepsilon_0 C(\Delta\alpha_{Therm}) \frac{Q_{12}}{s_{11} + s_{12}}} \quad (5)$$

$$\theta_1 = \frac{\theta - 2\varepsilon_0 C(\Delta\alpha_{Therm})T' \frac{Q_{11} + Q_{12}}{s_{11} + s_{12}}}{1 - 2\varepsilon_0 C(\Delta\alpha_{Therm}) \frac{Q_{11} + Q_{12}}{s_{11} + s_{12}}} \quad (6)$$

Here, the Q 's are elements of the electrostrictive tensor under constant stress, s 's are elements of the elastic compliance tensor, $\Delta\alpha_{Therm}$ is the difference in thermal expansion coefficient α between film and substrate ($\alpha_s - \alpha_f$), and T' is an effective zero-stress temperature, such that the biaxial strain x is given by $x = (T - T') \Delta\alpha_{Therm}$.

In the experiments represented in Figures 1 and 2, we are sensing the polarizability of the out-of-plane direction. Therefore, above the transformation temperature θ_1 at which a spontaneous polarization would appear in the in-plane direction, the inverse susceptibility in the out-of-plane direction follows a Curie-Weiss curve shifted to the left, corresponding to Equation (5). However, below θ_1 , the in-plane spontaneous polarization becomes linked to the out-of-plane behavior through additional coupling terms, again renormalizing the dielectric response (in m/F):

$$\gamma = \frac{T - \theta_3}{2\varepsilon_0 C'} + 2 \left(\alpha_{12} + \frac{Q_{11}Q_{12} + Q_{12}^2}{s_{11} + s_{12}} \right) (P_1(T))^2 + (2\alpha_{112} + \alpha_{123})(P_1(T))^4 \quad (7)$$

In contrast to Equation 3, this is valid for all temperatures where γ is positive. Note that the temperature dependence of the equibiaxial strain arising from thermal expansion mismatch renormalizes the slope of the Curie-Weiss-like behavior above any phase transitions, i.e. the apparent Curie constant C' is modified from its bulk value, in addition to the above-described temperature shift in the dielectric behavior. Calculation of the spontaneous polarization $P_1(T)$ below θ_1 is a straightforward exercise starting from the free energy functional given by [7], but will not be discussed here. Additionally, were the spontaneous polarization to take an in-plane direction other than $\langle 110 \rangle$ (for instance in-plane $\langle 100 \rangle$ accompanied by domain patterning to accommodate the biaxial nature of the substrate constraint), the specific assignment of the coefficients in the prefactors for P_1^2 and P_1^4 in Equation (7) would be altered. However, this would not change the general form of the coupling nor the temperature dependence of P_1 . Thus, the conclusions discussed here hold without specific knowledge of the nature of the inferred in-plane polarization.

This model of the free energy of a film under plane equibiaxial stress has been fit to the thickness-corrected dielectric data, as shown by the solid line in Figure 2. The excellent correspondence between model and data strongly implies that the observed rounding of the out-of-plane dielectric behavior near the bulk phase transition temperature may result from a transformation to a ferroelectric phase with polarization in the plane of the film, at a temperature of approximately 390K. More work is necessary however to determine if quantitative agreement exists with the model under consideration here, because of the large number of poorly known coefficients that are required for evaluation of the dielectric behavior. However, neglecting Ti compositions effects which are clearly significant, reasonable assumptions for the coefficients in Equations (5) and (6), based on weighted averages of those of pure BaTiO₃ and SrTiO₃ [9] and the measured strain of approximately 0.7%, yield calculated temperatures in reasonably good agreement with the values for θ_1 and θ_3 as determined from the data in Figure 2.

CONCLUSIONS

The equibiaxial strain in the plane of the substrate for $\{100\}$ BST thin films deposited on Pt/SiO₂/Si at 640°C is estimated from x-ray diffraction measurements to be approximately 0.7%. We postulate that this is of

sufficient magnitude, based on the work of [7] and [8], to confine any spontaneous polarization to the plane of the film. The thickness-corrected dielectric behavior perpendicular to the substrate for these samples shows evidence of coupling to such an in-plane phase transition at approximately 390K, as manifested by deviation from Curie-Weiss-like behavior at this temperature.

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