ANL/MSD/CP-9965

58307

(Ba, Sr) TiO3 Dielectrics: Relationship Between Bulk and Thin Film Properties

Angus I. Kingon, Stephen K. Streiffer*, Charles B. Parker, and Susanne Stemmer**

Department of Materials Science and Engineering, NCSU, Raleigh, NC 27695-7919
*Materials Science Division, Argonne National Laboratory, Argonne, IL 60439
**University of Illinois at Chicago, Chicago, IL 60607-7059

RECEIVED
MAR 07 2000
OSTI

Submitted to the US-Japan Seminar on Dielectric and Piezoelectric Ceramics, Okinawa, Japan, held on November 3-5, 1999.

The submitted manuscript has been created by the University of Chicago as Operator of Argonne National Laboratory ("Argonne") under Contract No. W-31-109-ENG-38 with the U.S. Department of Energy. The U.S. Government retains for itself, and others acting on its behalf, a paid-up, nonexclusive, irrevocable worldwide license in said article to reproduce, prepare derivative works, distribute copies to the public, and perform publicly and display publicly, by or on behalf of the Government.

This work was supported by the U.S. Department of Energy, Office of Science Division of Materials Sciences, under contract #W-31-109-ENG-38.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, make any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

$(Ba,Sr)TiO_3$ Dielectrics: Relationship between Bulk and Thin Film Properties

Angus I Kingon, Stephen K Streiffer*, Charles B Parker, and Susanne Stemmer**

Department of Materials Science and Engineering, NCSU, Raleigh. NC 27695-7919
Fax: (919) 515 3419, Email: angus_kingon@ncsu.edu
*Argonne National Laboratories, Materials Science Division, Argonne, Il 60439- 4838
Email: streiffer@anl.gov
**University of Illinois at Chicago, Chicago, Il 60607-7059
Email: stemmer@uic.edu

Thin films of complex perovskites have a number of potentially important applications. Of major scientific and practical concern is the scaling of properties as film dimensions are reduced. This paper describes a satisfactory relationship between bulk and thin film dielectric properties of $(Ba,Sr)TiO_3$. Relative contributions of strain, A:B cation stoichiometry, and interface are separated to explain temperature dependent dielectric behavior.

1. INTRODUCTION

$(Ba,Sr)TiO_3$ (BST) thin films represent an important dielectric system for application in high density DRAMs, as well as for backend capacitors integrated onto the Si chip. There has been significant development over the past six years, such that incorporation into 4Gb DRAM appears likely.[1]

One of the disappointments regarding BST films has been the very substantial lowering of the dielectric constants of thin films relative to their bulk analogues. An example of experimental thin film dielectric permittivity versus temperature data, in comparison with polycrystalline bulk data of the same Ba/Sr ratio is shown in Fig. 1. This behavior is of concern, as it may limit the extendability of BST through future generations. There has been scattered speculation regarding the origin of the lowered dielectric constant. The effect has been linked to film strain, intrinsic ferroelectric size effects through grain size or film thickness scaling, and extrinsic interface effects. No satisfactory description of the dielectric behavior of the perovskite films has been presented, nor have relative contributions of different phenomena to the dielectric function been discerned.

As a result, we have investigated the dielectric response of a series of {100} fiber-textured $(Ba_xSr_{1-x})Ti_{1+y}O_{3+z}$ samples deposited by liquid-source metal-organic chemical vapor deposition onto $Pt/SiO_2/Si$, as a function of the two most commonly varied microstructural parameters, *viz* film thickness and Ti nonstoichiometry (y). The thickness dependent data allows us to extrapolate to obtain the thickness independent dielectric susceptibility, and thus examine directly the effect of composition (ie y, the Ti non-stoichiometry) on the "bulk" film properties. Thereafter, we discuss the effect of biaxial strain originating from the thermal mismatch with the silicon substrate on the temperature-dependent dielectric susceptibility. The approach allows us to examine the relative contributions to the lowering of the dielectric permittivity.

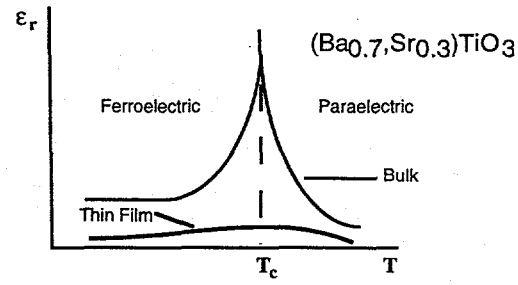

Figure 1: Typical permittivity versus temperature dependence for a BST thin film[2] compared to a bulk ceramic sample with the same Ba/Sr ratio[3].

2. EXPERIMENTAL

All films were BST with Ba/Sr=70/30 deposited by liquid source MOCVD under the auspices of the US DRAM Consortium. Experimental procedures have been described previously[4,5].

3. RESULTS AND DISCUSSION

3.1 Empirical Description of the Dielectric Data

It has been shown in earlier work that the field dependence of the dielectric response of these BST thin

films is well described by the familiar free energy expansion[6]:

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

where E_{app} is the apparent field applied to the dielectric in the thickness dierection, the α's are the empirical dielectric stiffnesses, and P refers to the polarization. It has also been demonstrated[6] that the dielectric stiffness α'_3 in the first order term carries almost all the temperature and thickness dependence. This term can therefore be decomposed into:

$$\alpha'_3 \approx \frac{\beta}{t} + \gamma(T) \qquad (2)$$

where β is the thickness dependant and γ the thickness independent portions of the dielectric stiffness.

The experimental dielectric data for several thicknesses and compositions have also been examined in Curie - Weiss form, with typical data for y=0.04 (ie 51%Ti) shown in Fig 2. Besides the thickness dependence, it can be seen that the films fit Curie-Weiss behavior above a temperature of about 380K. Below this temperature, for all film thicknesses and compositions, there is a deviation from the classical behavior. By utilizing only the data above this temperature, an effective Curie-Weiss constant (C') and extrapolated Curie temperature can be obtained. The Curie constant is almost thickness independent, but strongly stoichiometry dependent. The composition closest to stoichiometry is closest to the bulk value. We deduce that the apparent thickness dependence of the Curie-Weiss temperature (see Fig 2) is simply a manifestation of the shift of the curves along the temperature axis. This is possibly best deduced by rearranging equations (1), (2) and the Curie-Weiss expression, to yield[5]:

$$T_3(t) = \theta - \frac{2\varepsilon_0 C'\beta}{t} \qquad (3)$$

where T_3 is an extrapolated intercept (effective Curie temperature) for a given thickness.

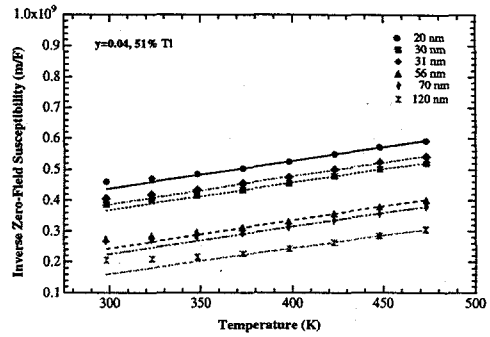

Fig 2: Inverse susceptibility versus temperature for BST films of different thickness, and one Ti stoichiometry.

3.2 Removing the Thickness Dependence: Ti Stoichiometry

The dielectric properties can be stripped of their thickness dependence by fitting the data to Equation (2), for all temperatures. This yields the dielectric stiffness or the susceptibility of the bulk of the films as a function of temperature, as well as the parameter β of Eqn 2. The data is plotted in Fig 3, for two different compositions. Notice again the deviation from Curie-Weiss behavior at about 380K, as well as the strong dependence upon the Ti content. Fig 4 shows the data plotted as relative dielectric constant for the "bulk" of the films at 300K as a function of Ti stoichiometry. (Also shown for comparison is the measured relative permittivities for the same films of 30nm thickness).

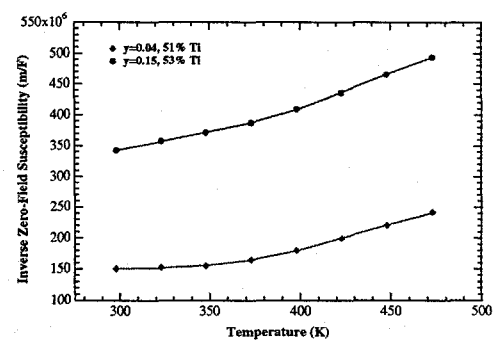

Fig 3: Inverse susceptibility versus temperature, stripped of film thickness dependence, ie described by 2γ(T) in Eqn 2.

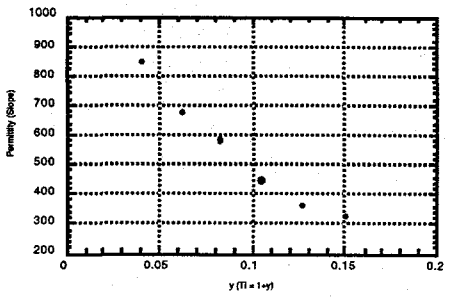

Fig 4: Effective relative permittivity values calculated from the experimental data, as a function of the Ti stoichiometry (y).

There is an important difference between the thin films and bulk BST which should be noted. The solid solubility limit for Ti over-stoichiometry of bulk BST is known to be small, ie less than y=0.001[7]. In contrast, the solubility limit for excess Ti in these thin films is dramatically larger, around y=0.1[8]. Excess Ti is accomodated in the grain interiors. At Ti excesses as large as y=0.15 (Ba+Sr/Ti=46.5/53.5), Ti can be observed at the grain boundaries, probably in the form of amorphous TiOx[8]. Other properties such as dielectric loss and degradation correlate strongly with the excess titanium.[9]

3.3 Temperature and Stress Dependent Landau-Ginzberg-Devonshire Description

We have recently undertaken an analysis of the effect of biaxial stress, due to the thermal mismatch of the BST film and silicon substrate, on the dielectric properties[2,5]. The approach extends the thermodynamic analysis undertaken by Pertsev and coworkers[10] and Desu et al[11]. The symmetry-breaking imposed by the biaxial strain implies that one must consider different orientations of the spontaneous polarization with respect to the plane as separate phases. The strain modifies the thermodynamic stability and thus the Curie-Weiss temperatures of these phases[10]. We have added the temperature dependence of the mismatch strain, allowing us to calculate the temperatures corresponding to the transition from the cubic prototype phase to the phases with the polarization in the plane θ_1, and normal to the plane θ_3, respectively. The apparent modifications to the bulk Curie constants can also be calculated. It is clear from the analysis (consistent with intuition) that the biaxial strain in this case increases the stability of the phase with in-plane polarization, and decreases the stability of the phase with polarization normal to the plane. In addition, as long as one includes the appropriate coupling terms between the in-plane and out-of-plane polarization, one can calculate the full temperature dependence of the dielectric stiffness (inverse susceptibility), above and below the the unstrained, bulk Curie-Weiss temperature. Similarly, the temperature-dependent values of the spontaneous polarizations can be calculated. The solid lines in Fig 3 are the calculated values of dielectric susceptibility (with the thickness dependence stripped out). The values of strain which were utilized were those experimentally measured by x-ray diffraction. The agreement to the experimental is excellent. The agreement has been shown to extend to far lower temperatures[5].

The analysis has several important implications, which are worth emphasizing. Firstly, it provides strong evidence for the role of stress in modifying the temperature dependent permittivity. The calculated results also emulate the shape or rounding of the inverse susceptibility versus temperature curve. In addition, the analysis predicts a phase transition from the prototype phase to a ferroelectric phase with in-plane polarization at θ_1, or 390K. This corresponds to the measured deviation from Curie-Weiss behavior observed in all samples. It should be noted that not hysteresis was observed in the P-E loops at temperatures between θ_1 and θ_3. However, this is expected, as the polarization is confined to the film plane, and would therefore not be observable in the capacitor configuration utilized.

3.4 Origins of the Thickness Dependence

The thickness dependence is treated empirically in this work. It has several possible origins which will yield the observed series or interfacial capacitance. These include:

- extrinsic interface effects, particularly atmospheric contamination
- compositional changes in the BST adjacent to the interface, driven by film nucleation effects or by segregation under thermodynamic equilibrium
- microstructural changes adjacent to the growth interface
- incomplete polarization screening by the metal electrodes, or built-in fields due to Fermi level pinning and charge transfer
- suppression of the soft mode near the interface, ie the so-called "dead layer" theory[12]

We have recently presented a discussion of these various possibilities[5], concluding that the last mechanism has attractive features for description of the available data. Other mechanisms are not excluded, however. This topic will be discussed in greater detail at the Workshop.

4. CONCLUSIONS AND IMPLICATIONS

We find that the overall behavior of these samples is adequately described by mean-field, Landau-Ginzburg-Devonshire theory as for bulk ferroelectrics. We have quantified the impact of three separable factors for these films that greatly alter the permittivity as a function of temperature, compared to that found for bulk ceramic samples at the same Ba/Sr ratio of 70/30: i) Ti nonstoichiometry; ii) the apparent "interface" effect which results in a reduction of the dielectric constant with decreasing thickness; and iii) plane equibiaxial stress resulting from thermal expansion mismatch with the Si substrate. When properly considered, these three factors yield a satisfactory description of the relationship between the temperature-dependent dielectric properties of the thin films and the bulk. The results form a strong basis for making decisions regarding BST capacitor development.

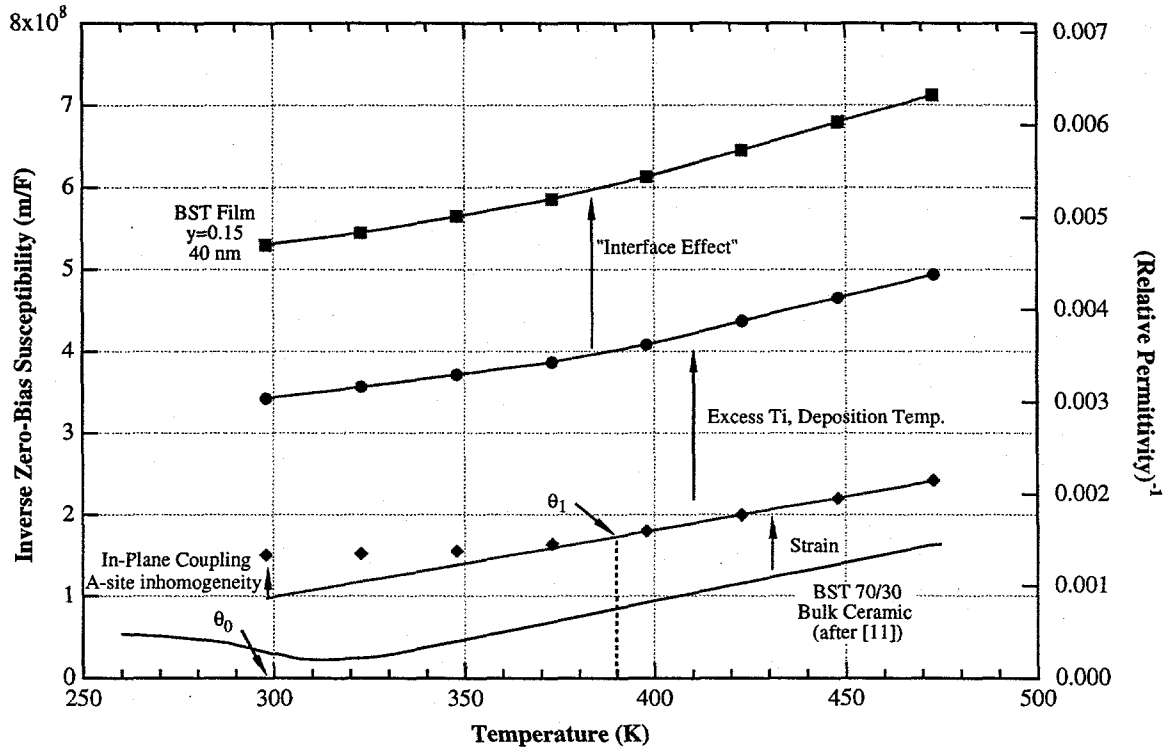

Fig 5: Summary showing the relative contributions to the dielectric behavior of BST films, with the data referring to a typical film with y=0.15 (Ba+Sr/Ti=46.5/53.5) and thickness of 40nm. θ_1 is the predicted Curie-Weiss temperature for a transition from a paraelectric phase to a ferroelectric phase with the polarization in the plane of the film.

REFERENCES

[1] A.I. Kingon, S.K. Streiffer, C. Basceri, and S.R. Summerfelt, MRS Bull. **21**, 46 (1996)

[2] Streiffer S K, Basceri C, Parker C B, Lash S E, Christman J, Maiwa H, and Kingon A I, Proc. of the International Symposium on the Applications of Ferroelectrics, IEEE, 31, 1999.

[3] A.D. Hilton and B.W. Rickers, J. Phys. D: Appl. Phys. **29**, 1321 (1996).

[4] P.C. van Buskirk, J.F. Roeder, C. Basceri, S.E. Lash, C.B. Parker, S.K. Streiffer, and A.I. Kingon, J. Korean Phys. Soc. **32**, S1591 (1998).

[5] S.K. Streiffer, C. Basceri, C.B. Parker, S.E. Lash and A.I. Kingon, to be published in J. Appl. Phys., October 15, 1999.

[6] Cem Basceri, S.K. Streiffer, Angus I. Kingon, and R. Waser, J. Appl. Phys. **82**, 2497 (1997).

[7] R.K. Sharma, N.-H. Chan, and D.M. Smyth, J. Am. Ceram. Soc. **64**, 448, (1981).

[8] S. Stemmer, S.K. Streiffer, N.D. Browning, and A.I. Kingon, Appl. Phys. Lett. **74**, 2432 (1999).

[9] C. Basceri, Ph.D. Thesis, North Carolina State University, 1997.

[10] N.A. Pertsev, A.G. Zembilgotov, and A.K. Tagantsev, Phys. Rev. Lett. **80**, 1988 (1998).

[11] S.B. Desu, V. P. Dudkevich, P.V. Dudkevich, I.N. Zakharchenko, and G.L. Kushlyan, Mat. Res. Soc. Symp. Proc. **401**, 195 (1996).

[12] C Zhou and D.M. Newns, J. Appl. Phys. **82**, 3081 (1997).