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## LETTER TO THE EDITOR

## Intrinsic dielectric response in ferroelectric nano-capacitors

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### Abstract

Measurements on 'free-standing' single-crystal barium titanate capacitors with thickness down to 75 nm show a dielectric response typical of large single crystals, rather than conventional thin films. There is a notable absence of any broadening or temperature shift of the dielectric peak or loss tangent. Peak dielectric constants of  $\sim 25\,000$  are observed, and Curie–Weiss analysis demonstrates first order transformation behaviour. This is in dramatic contrast to results on conventionally deposited thin film capacitor heterostructures, which show large dielectric peak broadening and temperature shifts (e.g. Parker *et al* 2002 *Appl. Phys. Lett.* **81** 340), as well as an apparent change in the nature of the paraelectric–ferroelectric transition from first to second order. Our data are compatible with a recent model by Bratkovsky and Levanyuk (2004 *Preprint cond-mat/0402100*), which attributes dielectric peak broadening to gradient terms that will exist in any thin film capacitor heterostructure. The observed recovery of first order transformation behaviour is consistent with the absence of significant substrate clamping in our experiment, as modelled by Pertsev *et al* (1998 *Phys. Rev. Lett.* **80** 1988), and illustrates that the second order behaviour seen in conventionally deposited thin films cannot be attributed to the effects of reduced dimensionality in the system, nor to the influence of an intrinsic universal interfacial capacitance associated with the electrode–ferroelectric interface.

The charge storage characteristics of ferroelectric perovskite oxides have made them one of the key materials in the development of novel random access memory (RAM) technology. However, a lack of understanding of the origins of changes in functional properties between thin film and bulk remains an unresolved concern.

Observations on ferroelectric thin films consistently show that a significant broadening of the Curie anomaly (peak in dielectric constant with respect to temperature) occurs as films

are made thinner [1–4]. Typically, parameters expressing peak ‘diffuseness’ are many orders of magnitude greater for films  $\sim 100$  nm or thinner than for bulk [2, 3]. In addition, the broadening of the dielectric peak is associated with an apparent change in the nature of the paraelectric–ferroelectric phase transition from first to second order [4–6]. Until now, the origins of these changes in functional behaviour have not been clear, but several pertinent ideas exist in literature:

- (i) It is known [7–10] that two-dimensional (2D) effects broaden out first order discontinuities at phase transition temperatures and make systems appear second order. While  $\sim 100$  nm films are clearly not 2D, ferroelectrics are dominated by long-range Coulombic forces, and it is difficult to be certain about the thickness at which effects due to the reduction of system dimensionality may become evident; while some understanding of the thickness limits on the existence of static properties such as polarization and ferroelectricity have recently been established [6, 11], this has not been extended to an understanding of the thickness at which dimensionality-induced changes in intrinsic functional *dynamics* might be observed.
- (ii) Since the earliest work on thin film ferroelectrics, the influence of a parasitic ‘interfacial capacitance’ has been identified [12]. This manifests itself as a small capacitive component that acts electrically in series with the rest of the film, suppressing the dielectric constant in the system as a whole. Since series addition of dielectric response follows  $1/C_T = \sum_i 1/C_i$ , the influence of the interfacial capacitance is greatest at the Curie anomaly, and less influential far from the anomaly, automatically generating a peak-smearing effect. The potential origins of the interfacial capacitance fall into two broad classes—those related to unavoidable physics of the ferroelectric–electrode boundary [13–22] and those induced through specific processing of the heteroepitaxial system [23–28] (for example, chemically or microstructurally distinct interfacial regions, or the influence of grain boundaries).
- (iii) The strain state of a ferroelectric thin film can be affected by the lower electrode, or the substrate onto which it is grown. Landau–Ginzburg–Devonshire considerations, assuming homogeneous strain alone [29, 30], have shown that this can also result in the paraelectric–ferroelectric phase transition changing from first to second order. In addition, there is a growing body of evidence to suggest that minimizing mismatch strain can recover ‘bulk-like’ properties to some degree [31, 32].
- (iv) It has been widely recognized (for example, in yttrium barium copper oxide [33]) that the presence of a surface in an otherwise centric material is formally equivalent to a field. Recently, this symmetry argument has been developed into a detailed theory for ferroelectric thin films by Bratkovsky and Levanyuk [34]: assuming an arbitrary gradient in a scalar quantity across the film (such as defect concentration, chemical concentration, density or temperature) they calculate the broadening effect this has on the dielectric response near the Curie temperature ( $T_C$ ); a rather complete washing-out of the dielectric peak is predicted. We note that the disorder models of Harris [35] and Stinchcombe [36] may also be relevant in the context of such phase transition broadening (second order or tricritical).

The Bratkovsky and Levanyuk model is particularly timely, for although phenomenological treatments involving gradient terms have been investigated before [37, 38], recent experiments by Ma and Cross [39] have highlighted the likelihood that strain gradient terms could dominate ferroelectric thin film functional response—a view reinforced by Catalan *et al* [40], who predicted that strain gradients should smear out the dielectric response around  $T_C$ .

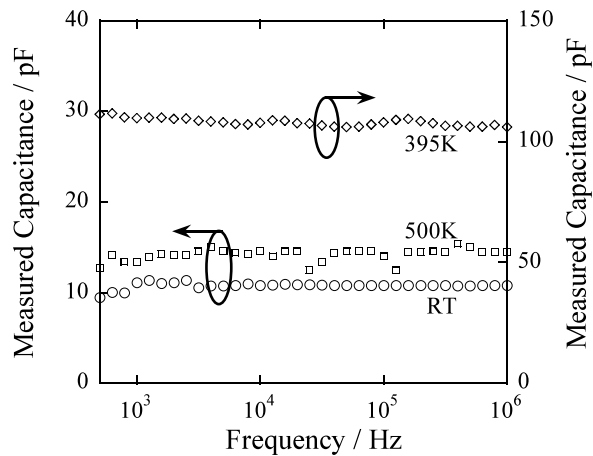
Oxygen vacancy gradients ( $\nabla c$ ) could also play a role. Reference to Scott and Dawber [41] suggests that in materials such as barium titanate a bulk diffusion-limited depth dependence

over the outermost 10 nm with a peak value of  $8 \times 10^{21} \text{ cm}^{-3}$ , and ' $c = \exp(z^{-6/5})$ ' grain-boundary limited dependence at depths 10–30 nm or deeper, exist near to ferroelectric surfaces. One could fit the Bratkovsky–Levanyuk model with two separate step-like dependences of  $\nabla c$ . However, vacancy concentration gradients may simply represent a special case of strain gradients, as vacancies produce significant inhomogeneous strain. Balzar *et al* [42] supports this view.

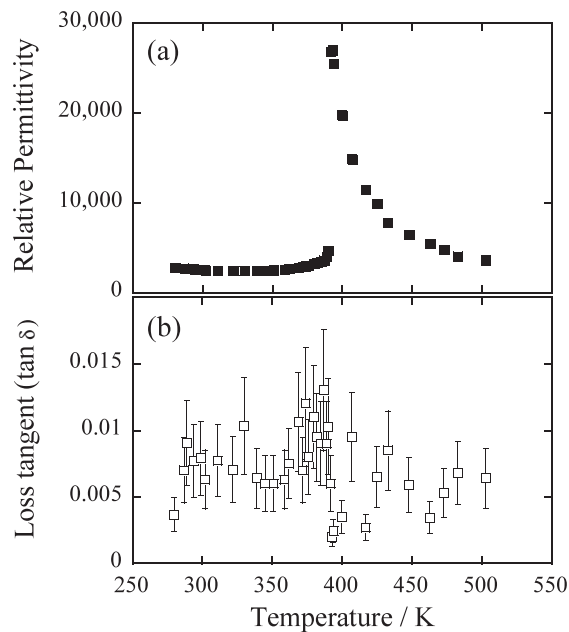
In the present study, by examining the functional properties of single crystal lamellae cut using a focused ion-beam microscope (FIB), we largely eliminate the interfacial strain, scalar concentration gradients and microstructural variability associated with conventional thin film deposition. Functional characterization shows that, in heteroepitaxial systems investigated to date, dielectric broadening and apparent second order phase transition behaviour must be due to such extrinsic factors; they are neither the result of reduced dimensionality, nor unavoidable intrinsic interfacial capacitance associated with the electrode–ferroelectric interface.

Commercially obtained polished single crystal square plates of  $\text{BaTiO}_3$  were used as starting materials. These crystals were placed in an FEI200TEM FIB, such that the incident primary gallium (Ga)-beam was parallel to the top polished surface, and perpendicular to one of the sides of the plates. Milling steps were then performed, to create a thin lamella parallel to the top polished surface, connected to the rest of the  $\text{BaTiO}_3$  single crystal along three of its four sides. A series of such lamellae of varying thickness was produced from the same single crystal, before furnace-annealing in air at 700 °C for 1 h. Gold was then evaporated onto the crystal from two directions, such that both sides of the dielectric lamella were fully coated. The coated crystal was again placed in the FIB, but with the polished crystal surface perpendicular to the Ga-beam. Rectangular electrodes ( $5 \mu\text{m} \times 7 \mu\text{m}$ ) on the top surface of the lamellae were isolated by milling through to the dielectric; further milling defined gold strips that connected the lamellae electrodes to contact pads. A micromanipulator was then used to make electrical contact. More details of the fabrication procedure, and a demonstration that the thermal anneal fully recovered any damage caused through Ga-ion implantation, can be found elsewhere [43]. The capacitance and loss tangent were measured using an HP4284A LCR meter and HP4192A impedance analyser with applied test voltages of 100 mV. Temperature variable measurements used a heating rate of  $\sim 1 \text{ K min}^{-1}$ , with the temperature monitored using a K-type thermocouple, mounted on the surface of a dummy  $\text{BaTiO}_3$  crystal of identical dimensions to that containing the test capacitors.

Figure 1 illustrates the frequency dependence of the measured capacitance from a thin single crystal lamella, at several temperatures. In all cases, the spectral profile is reasonably flat, with no indication of space charge activity. The figure also illustrates the large variation in measured capacitance with temperature. This is further elaborated upon in figure 2, where the dielectric constant and loss behaviour from the thinnest of the lamellae examined (75 nm) is plotted at 10 kHz against temperature. As can be seen, the dielectric constant goes through a distinct sharp anomaly at the Curie temperature, mirroring the response that is typically seen in bulk single crystal material. The temperature of the Curie anomaly was found to be  $\sim 395 \pm 5 \text{ K}$  for all the lamellae examined (between  $\sim 450$  and  $\sim 75 \text{ nm}$  in thickness). Such observations are completely different from any published data on conventionally grown heteroepitaxial capacitor structures across the same thickness range. Also worthy of note are the absolute magnitudes of the dielectric constant, and the low loss tangents, again strongly reminiscent of bulk single crystal behaviour. Figure 3 is a Curie–Weiss plot for the dielectric constant data, illustrating that the thin lamellae adhere well to Curie–Weiss behaviour above the dielectric peak, with  $T_0$  below the apparent  $T_C$ —a sufficient condition for the description of first order transformation behaviour [44]. We note that it is not possible to discriminate between first and second order transitions via the ratio of slopes above and below  $T_C$ : in some

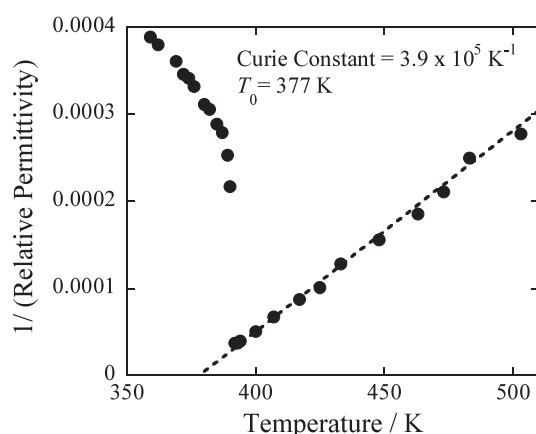


**Figure 1.** The frequency dependence of the capacitance measured at three different temperatures for thin BaTiO<sub>3</sub> lamellae. All lamellae investigated showed the distinct lack of spectral dependence illustrated here. Strong temperature dependence is, however, evident.



**Figure 2.** The calculated relative permittivity (a) and measured loss tangent (b) as a function of temperature (on heating) at 10 kHz for a 75 nm-thick single crystal BaTiO<sub>3</sub> capacitor. The absolute magnitude of the dielectric constant, its demonstration of a sharp Curie anomaly, and the occurrence of the anomaly around 395 K demonstrate that the thin lamella behaves like a bulk single crystal, and not as a conventionally grown thin film.

early textbooks it was claimed that such a ratio must be exactly 2:1 for second order transitions and a much larger ratio for first order. This, however, is erroneous and follows from naive free energy expansions that ignore polarization–strain coupling. A comprehensive explanation is given by Errandonea [45] (see also [44]).



**Figure 3.** Above the observed Curie anomaly, the dielectric response of the thin lamellae showed Curie–Weiss response, with  $T_0$  below  $T_C$ .

Overall, the dielectric response (in terms of absolute magnitude of dielectric constant, variation with temperature and with frequency, apparent first order transformation behaviour) is that expected from bulk single crystal, with none of the changes in behaviour seen in conventionally grown systems, universally accepted as ‘size effects’. While this is striking, recent work on carefully grown thin film systems have hinted towards the result: Dittman *et al* [31] have shown that truly epitaxial growth can significantly sharpen the form of the peak in dielectric constant against temperature, and raise the peak dielectric constant closer to single crystal values than had previously been thought possible. Takashima *et al* [32] made similar observations in SrTiO<sub>3</sub> thin films. No one, however, has shown that full recovery of bulk-like functional behaviour can occur for ferroelectrics in the sub-100 nm thickness regime, as has been illustrated here. This result therefore acts as a paradigm for those involved in the thin film ferroelectric growth community, and for those seeking to use ferroelectric thin films in microelectronic applications.

In conclusion, the focused ion beam microscope has been used to fabricate thin lamellae of single crystal BaTiO<sub>3</sub>, with gold evaporated on the lamellar walls to form parallel-plate capacitor structures. Functional characterization of these capacitors demonstrated that the smearing of the peak in dielectric constant, and the apparent change in the nature of the phase transition from first to second order, are neither related to the fundamentals of reduced dimensionality nor to any unavoidable intrinsic interfacial capacitance associated with the electrode–ferroelectric interface. Rather, the influence of homogeneous strain through strain coupling to a substrate, or gradient terms associated with chemical, defect or strain gradients, are the primary suspects.

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## References

- [1] Shaw T M, Suo Z, Huang M, Liniger E, Laibowitz R B and Baniecki J D 1999 *Appl. Phys. Lett.* **75** 2129
- [2] Parker C B, Maria J-P and Kingon A I 2002 *Appl. Phys. Lett.* **81** 340
- [3] Lookman A, Bowman R M, Gregg J M, Kut J, Rios S, Dawber M, Ruediger A and Scott J F 2004 *J. Appl. Phys.* **96** 555–62

- [4] Sinnamon L J, Bowman R M and Gregg J M 2002 *Appl. Phys. Lett.* **81** 889
- [5] Basceri C, Streiffner S K, Kingon A I and Waser R 1997 *J. Appl. Phys.* **82** 2497
- [6] Streiffner S K, Eastman J A, Fong D D, Thompson C, Munkholm A, Ramana Murty M V, Auciello O, Bai G R and Stephenson G B 2002 *Phys. Rev. Lett.* **89** 067601
- [7] Aizenman M and Wehr J 1989 *Phys. Rev. Lett.* **62** 2503
- [8] Cardy J and Jacobsen J L 1997 *Phys. Rev. Lett.* **79** 4063
- [9] Chatelain C and Berche B 1998 *Phys. Rev. Lett.* **80** 1670
- [10] Imry Y and Ma S-K 1975 *Phys. Rev. Lett.* **35** 1399
- [11] Junquera J and Ghosez P 2003 *Nature* **422** 506
- [12] Mead C A 1961 *Phys. Rev. Lett.* **6** 545
- [13] Zhou C and Newsom D M 1997 *J. Appl. Phys.* **82** 3081
- [14] Natori K, Otani D and Sano N 1998 *Appl. Phys. Lett.* **73** 632
- [15] Wurfel P and Batra I P 1973 *Phys. Rev. B* **8** 5126
- [16] Wang Y G, Zhong W L and Zhang P L 1995 *Phys. Rev. B* **51** 5311
- [17] Vendik O G, Zubko S P and Ter-Martirosyan L T 1998 *Appl. Phys. Lett.* **73** 37
- [18] Vendik O G and Ter-Martirosyan L T 1994 *Phys. Solid State* **36** 1778
- [19] Vendik O G and Zubko S P 2000 *J. Appl. Phys.* **88** 5343
- [20] Hwang C S, Lee B T, Kang C S, Lee K H, Cho H, Hideki H, Kim W D, Lee S I and Lee M Y 1999 *J. Appl. Phys.* **85** 287
- [21] Scott J F 1999 *Ferroelectrics* **232** 25
- [22] Robertson J and Chen C W 1999 *Appl. Phys. Lett.* **74** 1168
- [23] Paek S, Won J, Lee K, Choi J and Park C 1996 *Japan. J. Appl. Phys.* **35** 5757
- [24] Craciun V and Singh R K 2000 *Appl. Phys. Lett.* **76** 1932
- [25] Horikawa T, Mikami N, Makita T and Tanimura J 1993 *Japan. J. Appl. Phys.* **32** 4126
- [26] Lee W-J, Kim H-G and Yoon S-G 1996 *J. Appl. Phys.* **80** 5891
- [27] Zhu J, Zhang X, Zhu Y and Desu S B 1998 *J. Appl. Phys.* **83** 1610
- [28] Sinnamon L J, Saad M M, Bowman R M and Gregg J M 2002 *Appl. Phys. Lett.* **81** 703
- [29] Pertsev N A, Zembilgotov A G and Tagantsev A K 1998 *Phys. Rev. Lett.* **80** 1988
- [30] Ban Z-G and Alpay S P 2002 *J. Appl. Phys.* **91** 9288
- [31] Dittmann R, Plonka R, Vasco E, Pertsev N A, He J Q, Jia C L, Hoffmann-Eifert S and Waser R 2003 *Appl. Phys. Lett.* **83** 5011
- [32] Takashima H, Wang R, Kasai N, Shoji A and Itoh M 2003 *Appl. Phys. Lett.* **83** 2883
- [33] Scott J F 1990 *Appl. Phys. Lett.* **56** 1914
- [34] Bratkovsky A M and Levanyuk A P 2004 *Preprint cond-mat/0402100*
- [35] Harris A 1974 *J. Phys. C: Solid State Phys.* **7** 1671
- [36] Stinchcombe R B 2002 *J. Phys.: Condens. Matter* **14** 1473
- [37] Kogan Sh M 1964 *Sov. Phys.—Solid State* **5** 2069
- [38] Tagantsev K 1986 *Phys. Rev. B* **34** 5883
- Tagantsev A K 1991 *Phase Transit.* **35** 119
- [39] Ma W and Cross L E 2001 *Appl. Phys. Lett.* **79** 4420
- Ma W and Cross L E 2002 *Appl. Phys. Lett.* **81** 3440
- Ma W and Cross L E 2003 *Appl. Phys. Lett.* **82** 3293
- [40] Catalan G, Sinnamon L J and Gregg J M 2004 *J. Phys.: Condens. Matter* **16** 2253
- [41] Scott J F and Dawber M 1998 *J. Physique Coll. IV* **11** 19
- [42] Balzar D, Ramakrishnan P A, Spagnol P, Mani S, Hermann A M and Matin M A 2002 *Japan. J. Appl. Phys.* **41** 6628
- [43] Saad M M, Bowman R M and Gregg J M 2004 *Appl. Phys. Lett.* **84** 1159
- [44] Scott J F 2000 *Ferroelectric Memories* (Berlin: Springer)
- [45] Errandonea G 1980 *Phys. Rev. B* **21** 5221