Ferroelectric properties of FIB-prepared single crystal BaTiO$_3$ nanocapacitors

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ABSTRACT

Parallel-plate capacitors with dielectric thickness varying between ~500 nm and <100 nm have been fabricated from BaTiO$_3$ bulk single crystals using focused ion beam (FIB) milling. Electrical measurements suggest that the dielectric response is the same as found in bulk. This contrasts with most experimental observations made in the last 40 years, performed on conventionally deposited thin film capacitor heterostructures of similar dimensions. The implication is that all the functional degradation seen to date, on reducing dielectric thickness, is due to extrinsic sources, and not to either intrinsic size effects or fundamental physics associated with the ferroelectric-electrode boundary. This paper describes two specific approaches to FIB fabrication of the single crystal *thin film* capacitor structures, and presents details of their structural and functional characterization.

Keywords: ferroelectric, nanocapacitor, BaTiO$_3$, focused ion beam, dielectric constant, loss tangent.

1   INTRODUCTION

Unfortunately for ferroelectric memories (FRAMs), the continual effort to reduce the size of electronic devices has major ramifications, as size reduction appears to be associated with severe degradation in dynamic functional properties in the ferroelectric material itself [1,2]. In particular, the dielectric constant suffers a dramatic collapse by orders of magnitude in moving from bulk to thin film geometries [3,4] and the coercive field increases considerably [5]. However, to date it is unclear to what extent property degradation is due to intrinsic issues [6,7] of reduced size (i.e., critical volumes, interface physics etc) and to what extent it is due to extrinsic issues [7-10] associated with fabrication methodology (i.e., substrate strain, vacancy defects, grain boundary etc).

In this study, an attempt is being made to examine the functional properties of extremely thin BaTiO$_3$ lamellae cut from bulk single crystals using FIB milling. The experiment has been undertaken in order to observe functional behaviour in the absence of many of the factors which are not well controlled in conventional fabrication of thin film capacitor heterostructures (or are unavoidable), but which have been suspected as contributing to functional degradation. For example: (i) microstructure-related regions of reduced permittivity [11]; (ii) strain clamping of ferroelectric to substrate [12]; (iii) gradient terms in the ferroelectric induced through defect concentration gradients [10] or interfacial strain relaxation [13].

The idea in examining single crystal *thin film* capacitors is to observe scaling effects on ferroelectric dynamic functional behaviour in the cleanest possible test-system, providing a paradigm for the best possible film properties obtainable which will be of use to those involved in the thin film growth community and to those seeking to use ferroelectric thin films in microelectronic applications.

2   EXPERIMENTAL

Commercial BaTiO$_3$ single crystals were used as a starting material. In order to fabricate BaTiO$_3$ single crystal nanocapacitors by an FEI200TEM FIB microscope, two methods were employed. Firstly, the BaTiO$_3$ single crystal lamellae were milled at the edges of the BaTiO$_3$ bulk single crystal. After a thermal anneal, gold was evaporated onto the crystal from two directions, such that both sides of the dielectric lamellae 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 x 7 μm^2) 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. Details about the fabrication of the edge-prepared lamellae and specific issues associated with Ga-removal were presented elsewhere [14]. Figure 1 shows an example of an edge-prepared BaTiO$_3$ capacitor. In the second fabrication process, the single crystal lamellae were prepared as previously, given a similar thermal anneal, but were then covered with Pt sputtered from an angle of 20° to the lamellar milled surfaces. Then the lamellae were cut free from the parent single crystal (again using FIB) and lifted out, using a micromanipulator and fine glass rod, onto a

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commercial Pt/Ti/SiO$_2$/Si wafer and coated with Au by thermal evaporation. The isolation of the capacitor top electrode was done by FIB. An example is shown in figure 2. Electrical measurements performed on such free-standing capacitors were performed by either micromanipulator contact (as before, but without separate contact pads), or through use of an atomic force microscope with conducting tips.
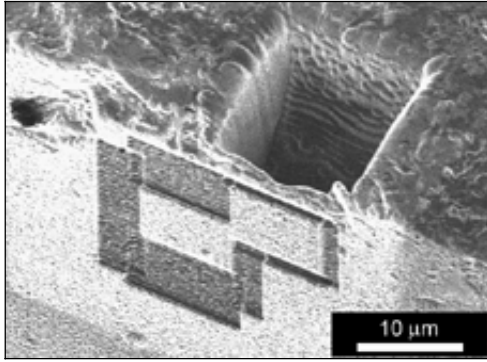

Figure 1: FIB image of an edge-prepared BaTiO$_3$ capacitor.
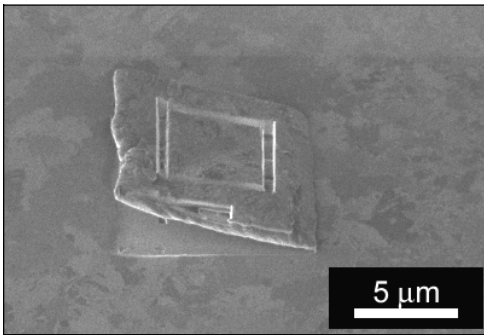

Figure 2: FIB image of a lifted out BaTiO$_3$ capacitor standing free on a substrate.

The capacitance and loss tangent were measured using an HP4284A LCR meter and an HP4192A impedance analyzer with applied voltages of 100 mV.

3   RESULTS AND DISCUSSION

Figure 3 illustrates the temperature dependence of the dielectric constant found in lamellar single crystal capacitors prepared using the first of the methodologies described above. As can be seen, the response is similar to bulk single crystals, rather than conventional thin films. An important feature is that no broadening or temperature shift of the dielectric peak or loss tangent is present. Peak dielectric constant is about 25,000. The dielectric constant goes through a very sharp peak at the Curie temperature, mirroring the response that is typically seen in bulk single crystals. The temperature of the Curie anomaly was found

to be about 395 ± 5 K for all the different capacitor thicknesses ranging from ~450 nm down to ~75 nm.

Figure 4 illustrates the first order transition behaviour in the Curie-Weiss analysis with $T_0 < T_c$ measured on a thin edge-prepared BaTiO$_3$ nanocapacitor. More details on the electrical measurements performed on edge-prepared BaTiO$_3$ single crystal nanocapacitors and a summary of the current literature pertinent to thin film effects on the nature of the permittivity anomaly observed around the Curie temperature can be found in ref [15].
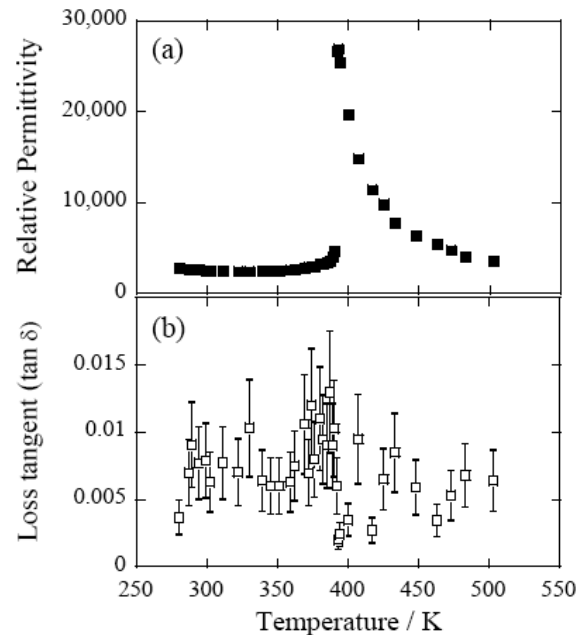

Figure 3: (a) Dielectric constant and (b) loss tangent of an edge-prepared BaTiO$_3$ capacitor with thickness of about 75 nm plotted at 10 kHz.
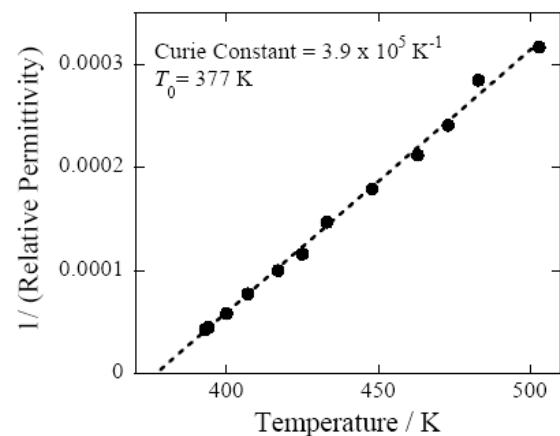

Figure 4: Curie-Weiss plot for the dielectric response.

In addition, I-V measurements were performed on these capacitors, an example of which is shown in figure 5. It is important to note that the data appears to separate into three regimes: a space charge limited current regime above

200 MV/m, an intermediate linear regime, and a non-ohmic regime with trap discontinuities at very low voltages. These features differ from thin films. Details about this work can be found in Ref. [16].

Overall, comparing the functional response in conventionally fabricated thin film heteroepitaxial capacitor systems with those made from single crystals presented in this paper, we observe that the dielectric broadening, apparent second order phase transition behaviour and collapse in dielectric constant present in conventional thin films are likely to be associated with extrinsic factors. They appear not be the result of size effects, nor due to fundamental factors associated with electrode-ferroelectric interface. Rather, they may be due to homogeneous strain associated to coupling to a substrate, grain boundaries and microstructural effects, or due to gradient terms related to chemical defects, oxygen vacancies or strain gradient flexoelectricity present in epitaxial thin films [10-13].
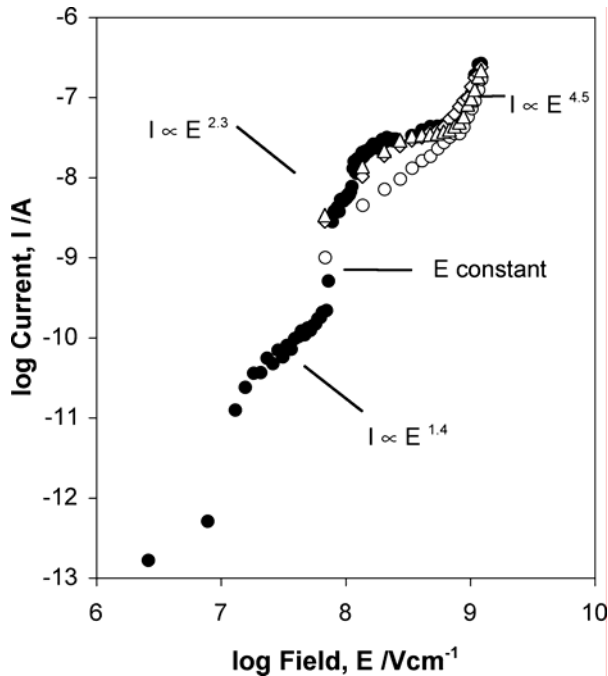
Figure 5: Three cycles I(V) graphs of a BaTiO$_3$ capacitor with a thickness of about 75 nm (Notation: circles – 1st cycle, triangles – 2nd cycle, diamante – 3rd cycle, and filled circles – lower fields).

Some concern was felt that data obtained from FIBed lamellae, that were in close proximity to bulk single crystal material, could include contributions from stray capacitance that had not been accounted for in our interpretation of data presented above. Hence the drive to investigate BaTiO$_3$ nanocapacitors that had been lifted away from the parent single crystal and placed on a different substrate.

Before detailed functional analysis of these stand-alone capacitors has been performed, ongoing efforts have concentrated on studying Ga-removal from the two sides milled BaTiO$_3$ lamellae before covering them with electrode and lifting them out. There is a notable difference in the amount of Ga ions impregnating the surface layers of the BaTiO$_3$ in milling not one, but two sides of the lamellae (in comparison with the first fabrication route where only one side is milled away). The considerable amount of Ga - induced wall damage and Ga implantation was overcome initially by annealing at 700°C for 1h. However, our recent work has shown that although Ga may be effectively expelled from the BaTiO$_3$ crystals, it appears to form oxide particles attached onto the BaTiO$_3$ lamellae. This had not been previously noted.
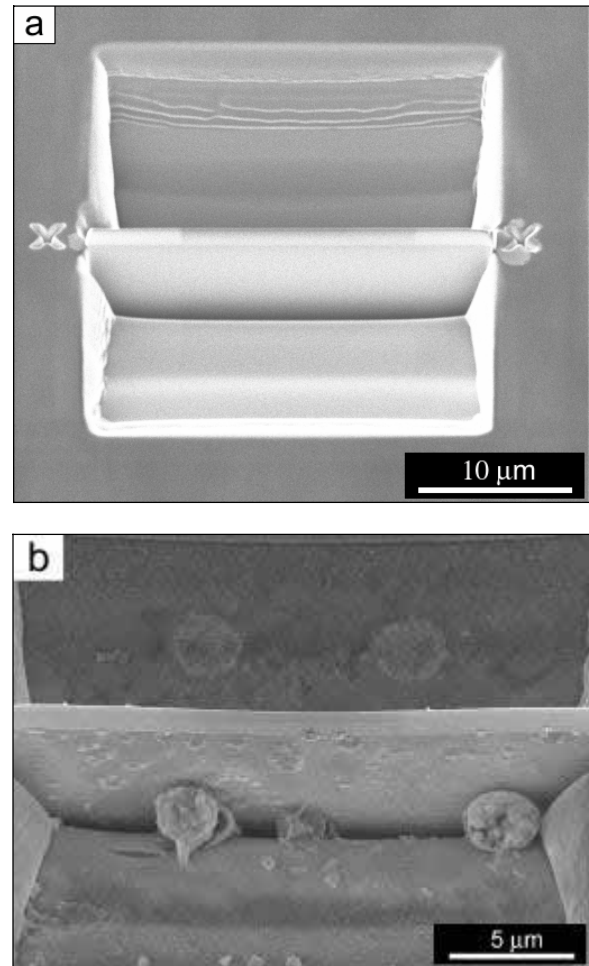
Figure 6: (a) FIB image of a BaTiO$_3$ lamella before annealing, and (b) SEM image of the same lamella after annealing at 700 °C for 1 h.

Figure 6 shows a FIB-milled BaTiO$_3$ lamella before and after annealing at 700 °C for 1h. The lamella is tilted 30 degrees for a better view. An important feature is the formation of large particles on the sides of lamella. Energy Dispersive X-ray (EDX) microanalysis identified the presence of Ga in large proportion up to 53 % in the large particles and about 10 % along the lamella wall. Moreover, higher temperature (up to 800 °C) or longer annealing time

(up to 3 hours) did not show any differences in the $BaTiO_3$ lamellae morphology. In conclusion, annealing treatment performed at higher temperatures or for longer time did not result in successful Ga-removal. Presently, chemical routes are in progress in order to remove the Ga contamination, followed by annealing treatment to recrystallize the possible amorphous layers on the lamella walls. This chemical method includes using different acids (i.e., HCl, HNO_3, KOH, or ultimately HF). Details will be presented in a future article.

4   CONCLUSION

$BaTiO_3$ single crystal nanocapacitors with thickness ranging from 500-450 nm to 70-50 nm have been successfully prepared by FIB milling. Two routes have been considered. One was fabricating edge-prepared $BaTiO_3$ nanocapacitors, the other was lifting out $BaTiO_3$ nanocapacitors. Dielectric measurements and I(V) measurements performed on edge-prepared $BaTiO_3$ nanocapacitors with different thickness suggest that the reduction in dimensionality did not affect the dielectric properties, suggesting that so-called size effects on dynamic functional behaviour seen in conventionally deposited thin film systems are not the result of intrinsic size-related behaviour, nor due to unavoidable ferroelectric-electrode boundary physics. Checking of such a conclusion is underway through the investigation of genuinely *stand-alone* single crystal nanocapacitors size effects as results of intrinsic contributions.

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