Mechanisms of nano-shorts in the electrical breakdown of ferroelectric thin films

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Micro-Raman, SEM and electron nano-probe techniques are used to show that bismuth titanate thin films undergoes a local phase transformation from layered-perovskite structure to pyrochlore-like structure during filamentary electrical breakdown, with the loss of Bi and oxygen. In PZT, dendrite-like structures (precursors of electrical shorts) of a few microns diameter, produced by bipolar voltage cycling (i.e. fatigue), exhibit almost pure regions of α-PbO, β-PbO and rutile-TiO_2. Note that β-PbO is not the stable ambient phase.

Key words: PZT, breakdown, fatigue, PbO and rutile

Introduction

Electrical breakdown including Time-Dependent Dielectric Breakdown (TDDB) is a very important reliability issue for ferroelectric Random Access Memory (FeRAM) applications. The factors that affect the breakdown field (E_B) include film thickness, temperature, field ramping rate, electrode materials, electrode area, doping, etc. The process of electrical shorting in ferroelectric perovskite oxides such as lead zirconate titanate (PZT) was first shown by Plumlee to arise from filamentary conduction pathways through the material, initiated at the anodes and/or cathodes[1]. This mechanism was modelled in detail by Duiker et al in terms of oxygen-deficient pathways[2]. However, nothing is known on the chemical kinetics or the local crystal structure of the breakdown paths.

Experimental and results:

The composition of sol-gel spin-coated PZT thin films used in present work is $PbZr_{0.52}Ti_{0.48}O_3$ (PZT52) with thickness 540 nm. The substrates used are Pt/Ti/SiO_2/Si. The Sm-substituted bismuth titanate films (BSmT) were fabricated by sol-gel spin-coating method on Pt/TiO_2/SiO_2/Si substrate, and were then annealed at 700 °C for 10 minutes in a flowing oxygen atmosphere.

Our PZT films were shorted by fatiguing them with extremely high bipolar field of 320 kV/cm until failure was achieved ($>10^9$ cycles) (RT 6000S). The result was a number of filamentary shorts, typically < 10 microns in diameter (Fig.1). The degraded spot indicated by an arrow in Fig.1 as a [2D] map has been viewed through an optical microscope and illuminated by a 632 nm wavelength He-Ne laser (LabRam300). Fig. 2 shows the 2D Raman mapping results on the degraded spot indicated in Fig. 1. The 3D pattern exhibits different Raman characteristics and intensity for the spectra collected from different area (inset in Fig. 2.). We assign the sharp peak at 145 cm^{-1} and the peak at 338 cm^{-1} (B_{1g} mode) to the α-PbO phase, according to our own standard Raman spectra on PbO powders (unpublished), Adams' work[3] and the work of Hedous *et al.*[4]. The peak at 285 cm^{-1} is attributed to β-PbO[3]. Note that β-PbO is not a stable phase at ambient temperature and pressure. Therefore, it may indicate a medium-T and medium-pressure process experienced by the film during bipolar cycling[5]. We confidently assign the peaks at 140 cm^{-1}, 441 cm^{-1} and 610 cm^{-1} to the rutile phase of TiO_2[6]. Other TiO_2 phases (i.e., brookite, anatase, etc.) have not been observed in our studies[7]. We tentatively assign the broad band from 700-900 cm^{-1} to a pyrochlore-like phase (or possibly Ti/Zr-O clusters indicated by a frequently-observed sharp peak at 824 cm^{-1}

), since this feature has also been observed during the annealing process of PZT thin films or powders[8, 9].

Because Sm-doped bismuth titanate is rather fatigue-free, it was not shorted by excessive fatigue, but instead by simply applying a field greater than the breakdown field (E_B about 50 MV/m). Raman scattering measurements were then carried out on the BSmT film interface after shorting and electrode removal. Only parts of the film interfaces are degraded, as evidenced by randomly distributed multiple dark spots. Raman spectra collected from breakdown regions and the unaffected regions are shown in Fig. 3. The undamaged regions show spectra, compared closely with the Aurivilius phase in Graves' work[10]. Raman data from the breakdown regions show compared features with the phase, which has been assigned to pyrochlore-like and amorphous bismuth titanate structures in Refs.[11-15].

In order to test this perovskite-pyrochlore hypothesis, elemental analysis has been conducted and summarized in Table I on different surface regions by assuming stoichiometric oxide conditions. Pyrochlore phases have formula $A_2B_2O_7$ with ionic ratio A/B ions of 1:1. The ionic ratio of (Bi^{3+}+Sm^{3+}) to Ti^{4+} is 4:3 (1.33) in the layered perovskite BSmT. From Table I, the A/B ratio is 1.37±0.02 for undamaged areas, and 1.21±0.02 for the breakdown region, compared with the ratio 1:1 expected for pyrochlore. This is reasonable, because the nano-probe samples a region somewhat larger than the diameter of the filamentary breakdown, so that a Bi/Ti ratio somewhere between 1.33 and 1.00 is expected.

Summary

BSmT thin films undergo an interfacial phase transformation from layered-perovskite structure to pyrochlore-like structure during electrical breakdown, depleted slightly in Bi and oxygen. In PZT, dendrite-like structures (precursors of electrical shorts) of a few microns diameter, produced by extremely fatigue, exhibit almost pure regions of α-PbO, β-PbO and rutile-TiO_2.

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Table I. SEM elemental analysis of shorted and untreated regions of the Sm-doped bismuth titanate film.

	Untreated Region			Degraded Region		
Element	k-ratio	ZAF	At%	k-ratio	ZAF	At%
Bi-M	0.5531	1.155	18.5 ± 0.2	0.5430	1.160	17.7 ± 0.2
Ti-K	0.1330	0.925	15.5 ± 0.3	0.1459	0.931	16.6 ± 0.3
Sm-L	0.0617	0.148	2.9 ± 0.3	0.0531	1.158	2.4 ± 0.2

Figure captions:

1. SEM micrographs of the electrode surface of the PZT films after serious fatigue ($>10^9$). The arrow indicates the degraded spot for 2D Raman mapping measurement.
2. Some selected characteristic Raman features indicating PbO, rutile-TiO_2 and a pyrochlore-like structure from 2D mapping data. Inset shows three dimension illustration of the 2D Raman mapping results on the degraded spot indicated in Fig. 1. The scale bar is in unit of micrometer.
3. Raman spectra of the BSmT film collected from degraded regions and normal regions. Inset shows the shorted electrode image after removal of the degraded Pt area.

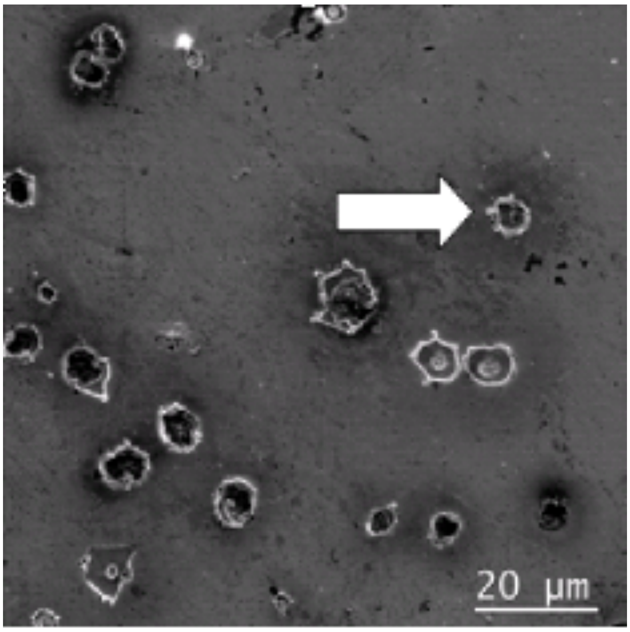

Fig. 1

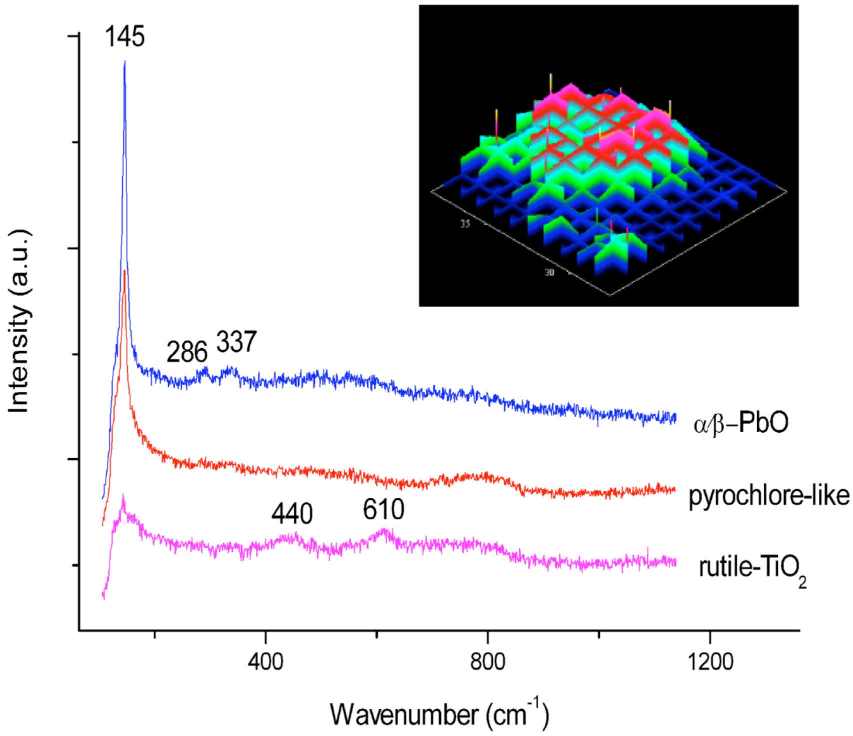
145
286
337
440
610
α/β–PbO
pyrochlore-like
rutile-TiO2
Intensity (a.u.)
400
800
1200
Wavenumber (cm-1)
35
30

Fig. 2

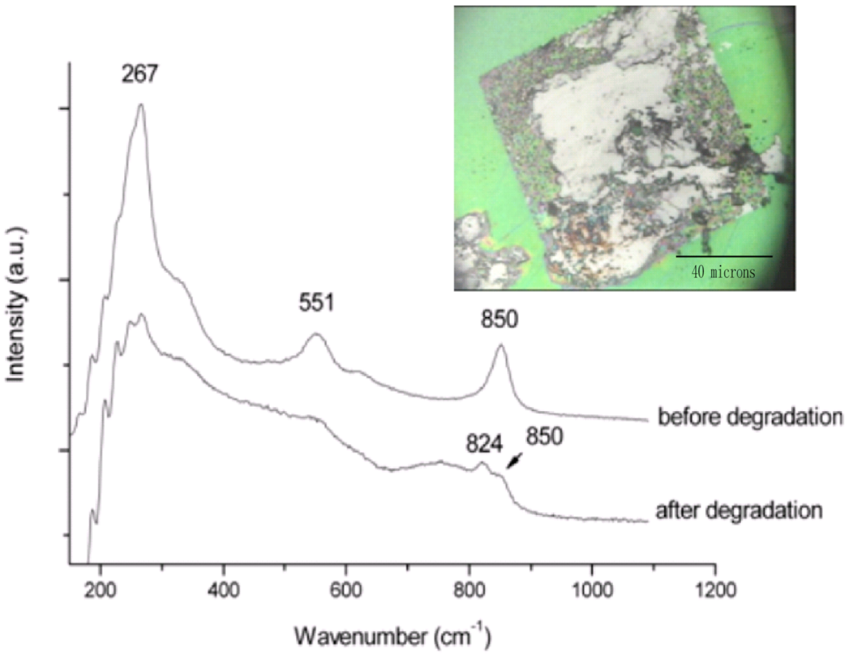
40 microns
267
551
850
824
850
before degradation
after degradation
Intensity (a.u.)
200
400
600
800
1000
1200
Wavenumber (cm^{-1})

Fig. 3