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Effect of microstructure on lifetime performance of barium titanate ceramics under DC electric field loading

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Abstract

Bulk barium titanate ($BaTiO_3$) ceramic specimens with various amounts of abnormal grains are prepared. A direct current (DC) electric field of 6 MV m^{-1} is applied to the specimens and their lifetimes are evaluated. Comparing to the specimens with only small normal grains, the time to failure of the specimens with coarse abnormal grains is significantly shorter. It is found that the $BaTiO_3$ specimens would fail within 200 h when abnormal grains are present in the microstructure. However, the lifetimes of the specimens containing abnormal grains vary significantly from one to another. The Weibull statistics is adopted to estimate the extent of data scatter. The statistical analysis indicates that the amount of abnormal grains has little influence on the lifetime performance of bulk $BaTiO_3$ ceramics under large DC electric fields. In most of the failed $BaTiO_3$ specimens, regardless of their lifetimes, large through-thickness round holes with recrystallization features are present. A mixed failure mode consisting of avalanche and thermal breakdowns is observed for the failed specimens.

Keywords: $BaTiO_3$; Microstructure-final; DC electric field; Dielectric breakdown

1. Introduction

With relatively high dielectric constants, barium titanate ($BaTiO_3$)-based oxides have been widely adopted as the dielectric materials for ceramic capacitors.[1] The application of $BaTiO_3$ thin films as the tunnel barriers for ferroelectric random access memories (FERAMs) has also been proposed recently.[2] Due to the increasing demand on device miniaturization, the required thickness of the dielectric layers in electronic components is continuously decreasing. For example, the dielectric layer thickness in multilayer ceramic capacitors (MLCCs) has now been reduced down to 1 μm and the typical tunnel barrier thickness in FERAMs is as small as 2–3 nm.[2,3] One of the biggest effects from the ongoing trend of device miniaturization is the increase in electric field strength experienced by the dielectric layer, resulting in its premature failure. A considerable literature currently exists concerning the reliability and fatigue behaviors of ferroelectric ceramics under alternating current (AC) electric fields.[4–12] Additionally, a recent study by the authors shows that the lifetime performance of $BaTiO_3$ ceramics under AC electric fields depends strongly on the amount of coarse abnormal grains present within the microstructure.[13] In contrast, the effect of material makeup, such as the microstructure, on the failure behaviors of ferroelectric ceramics under high direct current (DC) electric fields has received little attention. This insufficiency shall be addressed in the present study. Considering nowadays that most portable electronic and communication devices are operated under DC voltage, the reliability of the dielectric layers within the devices under sufficiently large DC electric fields is becoming an important issue.

The microstructure of $BaTiO_3$ is sensitive to its composition, especially to the Ba/Ti ratio and the amount of impurity.[14] A slightly lower than 1, Ba/Ti ratio will induce the formation of a liquid phase above the eutectic temperature (1312 °C) of $BaTiO_3$–$Ba_6Ti_{17}O_{40}$.[14,15] The presence of the liquid phase could trigger the growth of abnormal grains during sintering. A bimodal grain size distribution is thus commonly observed in the Ti-rich $BaTiO_3$ specimens. Internal stresses within the microstructure are commonly induced when cooling through the Curie temperature. Depending on the grain size, the resultant residual stresses could initiate spontaneous cracking.[16] Based on thermal expansion analyses, the presence of abnormal grains

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within the sintered bulk $BaTiO_3$ ceramics has been related to the formation of microstructural defects and microcracks.[17] Considering the complexity of the grain growth behavior in $BaTiO_3$ and its importance as a dielectric material within commercial electronic devices, an examination of the relationship between the microstructural features of $BaTiO_3$ and its reliability under DC electric field loading is indeed necessary.

There are two major types of lifetime failures in the dielectric materials: (1) dielectric breakdown that takes place at low temperatures under a very high electric field and (2) resistance degradation at elevated temperatures caused by the electromigrations of oxygen vacancies and the resultant electron-hole pairs. For this particular study, the former type of failure (i.e., dielectric breakdown) is of interest. In the present study, bulk $BaTiO_3$ ceramic specimens with various amounts of abnormal grains are prepared and their failure time under high DC electric fields at room temperature are determined. The failure criteria for the specimens are decided based on standards commonly adopted in highly accelerated life tests (HALT), which are frequently employed to examine the reliability of dielectric materials.[18,19]

2. Experimental procedure

A commercial $BaTiO_3$ powder (NEB, Ferro Co., USA) with a reported Ba/Ti ratio of 1.000 ± 0.002 was used as the raw material. The powder was ball-milled in ethanol with zirconia balls for 4 h, followed by drying at 100 °C for 24 h. The resulting powder mix was sieved (150 mesh) and pressed into sample discs of diameter 10 mm at 30 MPa. The discs were then pre-heated at 600 °C for 1 h with both the heating and cooling rates of 1 °C/min to remove any organic residues. After pre-heating, the sample discs were sintered at 1320–1410 °C for various dwell times (5 min to 2 h) in a covered alumina crucible with both the heating and cooling rates of 5 °C/min. Notice that different sintering parameters were designed to produce $BaTiO_3$ specimens of different microstructural features.

Crystalline phases of the sintered $BaTiO_3$ specimens were confirmed using X-ray diffractometry (XRD; MXP18, MAC Science Co., USA) with Cu $K\alpha$ radiation. Densities of the sintered specimens were determined by the Archimedes' method. Polishing and etching steps were carried out on the specimens for the observation of microstructures. Surfaces of the specimens were ground with SiC papers and polished with alumina slurry. The microstructural features at the polished surfaces were revealed by thermal etching at temperatures 100–150 °C below the sintering temperatures and then examined using scanning electron microscopy (SEM; XL30, Philips Co., The Netherlands). The sizes of the grains were verified by sketching the grain boundaries from the SEM micrographs, and the area of each grain was determined by an image analysis technique.[20] By assuming each grain had a spherical shape, the grain diameter could be approximated from the grain area. In order to estimate the grain size distribution for each sintering condition, more than 800 normal and/or 600 abnormal grains were counted.

DC electric field loading experiments on the sintered $BaTiO_3$ specimens were carried out in a silicon oil bath at room temperature. Periodic checks were made on the specimen and oil temperature using remote infrared sensing; it was found that the oil temperature in the vicinity of the specimen remained stable and close to the laboratory (room) temperature throughout the tests. The applied static electric field was in the thickness direction of the specimens and of magnitude 6 MV m^{-1} unless otherwise stated. Silver-based pastes were fired onto the circular faces of the specimens to form the top and bottom electrodes. The diameter of the circular electrodes was 6 mm and the thickness of the specimens was about 500 μm. The electrical loading was supplied by a high voltage amplifier (GPT-615, Gwinstek Co., Taiwan). The DC loading experiments were terminated when the insulation resistivity of the specimens decreased to below 10^6 Ω-cm (i.e., considered failed) or when the loading time exceeded 720,000 s (200 h). The dielectric properties and elastic moduli of the specimens before and after the loading experiments were determined by a LCR meter (2330A, NF Electronic Instrument, Japan) operated at 1 kHz and the ultrasonic technique, respectively. The surfaces and cross-sections of the failed $BaTiO_3$ specimens were examined under SEM.

3. Measurements

The XRD analyses indicate a single phase perovskite structure for all sintered $BaTiO_3$ specimens. Fig. 1 shows the typical micrographs of the $BaTiO_3$ specimens prepared under different sintering conditions. The microstructural properties of the specimens are listed in Table 1. Fig. 1a shows that there are no abnormal grains present in the specimen sintered at 1320 °C for 5 min. When the sintering dwell time is lengthened to 2 h, apart from an increase in density, abnormal grains start to appear in the microstructure with a volume fraction of about 0.38 (see Fig. 1b). A mixture of normal and abnormal grains is also evident in the microstructure of the specimen sintered at 1360 °C for 2 h, within the abnormal grains have a volume fraction of about 0.80 (see Fig. 1c). In contrast, for the specimen sintered at 1410 °C for 2 h, only coarse abnormal grains are observed in the microstructure (see Fig. 1d). The grain size distribution curves for the prepared $BaTiO_3$ specimens are shown in Fig. 2. A bimodal grain size distribution is clearly evident for the specimens sintered at 1320 °C for 2 h and 1360 °C for 2 h. The size variation of the coarse abnormal grains (i.e., the right-hand side peak of the size distribution curve) is substantial. Take the specimen sintered at 1410 °C for 2 h as an example, the size of the coarse abnormal grains varies from 60 to 600 μm. Dielectric measurements listed in Table 1 indicate that the dielectric constant and dissipation factor of the sintered $BaTiO_3$ specimens exhibit a strong dependence on the amount of coarse abnormal grains and the specimen density, respectively. The dielectric constant decreases with increasing amount of abnormal grains, while the specimen density is a good indication of the level of porosity in the microstructure.

The time to failure of the $BaTiO_3$ specimen sintered at 1320 °C for 5 min and loaded under various DC electric field strengths is shown in Table 2. When the applied DC electric field