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Crystal growth of BT-based ferroelectric films for nonvolatile memories

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Abstract Issues of ferroelectric high-density memories (> 64 Mb) indispensable for upcoming ubiquitous era have been on the cell integration less than 0.1 um^2 and reliabilities. Thus nanoscale control of microstructures of ferroelectric films with large switching polarization has been one of the issues to obtain the uniform electrical properties for realization of high-density memories. In this study the grain orientations and distributions of BT-based films by spin-on coatings were examined by FEG-SEM/EBSD. Ferroelectric domain characteristics by PFM were also performed to study the dependence of reliabilities on the grain orientations and distributions. It is believed that understandings of the nucleation and growth mechanisms of the a- or b-axis oriented films during the thermal processes such as RTA and furnace annealing affecting on grain orientation and uniformity could be possible based on our experimental results.

Key words Ferroelectric, BLT, Orientation, Nanoscale, Nucleation

1. Introduction

The remarkable growth of wireless communication systems such as mobile telephony, internet appliances, and personal digital assistants has been forecasted in upcoming ubiquitous era. The device performance such as low power consumption, fast operation, and small volume has been required for these systems. These requirements have accelerated the development of nonvolatile emerging memories such as ferroelectric random access memories (FeRAM), magnetic random access memories (MRAM), and phase change memories (PCM). Among them, FeRAMs, which were already commercialized in low-density level, have been one of promising candidates for the new systems, due to their superior low-voltage and high-endurance operations to nonvolatile flash memories, and also their fast operation matched for static random access memories. However, one of crucial issues for realization of the commercial high-density FeRAMs (> 64 Mb) has been on the uniform formation of capacitors to minimize the property variance in memory cells (< 0.1 um^2 size). Therefore it is important to control the grain distributions of ferroelectric films in nanoscale range. In this paper, the grain orientations and size distributions of BLT films by spin-on coatings were examined by an electron backscatter diffraction (EBSD) technique using SEM with a field emission electron gun. Ferroelectric domain characteristics by a piezo-response force microscope (PFM) were also performed to study the nanoscale dependence of the electrical properties on grain orientation and distribution. It is expected that capacitor processes affecting distributions of grain size and orientation such as rapid thermal annealing (RTA) and furnace annealing could be optimized for commercial FeRAMs based on this study.

2. Experimental Details

$(Bi_{4-x}M_x)Ti_3O_{12}$ (BLT) films doped with La of 0.85 atomic percent and 90nm thickness were grown by the spin-on coating technique using metal organic decomposition (MOD) sources, on thermally oxidized Si wafers with bottom Pt electrodes [1-6]. A baking treatment at 270°C was followed by rapid annealing treatments at 750°C and O_2 ambient for 30 sec, and furnace annealing at 650°C and O_2 ambient for 1 hr. Top Pt electrodes by sputtering were formed using the shadow mask of 100 μm diameter.

Electrical measurements were carried out for single capacitors with the storage area of 3×10^{-4} cm^2 using a Radiant Technologies RT66A tester. The electron backscatter diffraction (EBSD) patterns were measured by the automated system (TSL, Inc.) attached in FEG-SEM (Hitachi, scanning electron microscope using a field emission gun) to study the distribution dependence of grain size and orientation of polycrystalline films. Ferro-

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electric domain image measurements were performed by the piezoelectric scanning probe microscope of PSIA, XE-100. A lock-in amplifier (SRS, model SR830) was employed to measure oscillation changes of a Si_3N_4 cantilever on the bare surface of BLT films induced by the ac amplitude of 2 V and 17 kHz using a conductive cantilever tip (Micromash, CSC12, spring constant 1.5 N/m, coated with Ti and Pt layers).

3. Results and Discussion

The grain orientations and distributions of ferroelectric films in the nanoscale range were examined by the EBSD technique [7-11], in which Kikuchi patterns are collected from a detector attached to the FEG-SEM. In this measurement the electron beam is scanned on a particular area of interest in the samples. Electron beams backscatterd on the surface of samples give rise to a digital image of Kikuchi bands, which are directly related to the crystalline information in the scanned regions and presented to a computer for crystallographic indexing. A quality factor image, which is measured using the step size of 50 nm and defining the sharpness of the diffraction pattern, is represented in Fig. 1(a). This image includes qualitatively the crystalline information between polycrystalline grains. The brighter the quality image, the higher the reliability of the measured image. Thus, the darker regions may include some measurement errors due to the smaller grains than the electron beam size of 50 nm. Indexing results of the Kikuchi patterns provide the useful information of crystallographic orientations on the surfaces of BLT films. Distributions of the grain orientations are imaged by different colors based on a theoretical calculation of the measured diffraction patterns. This analysis technique includes the processing of statistical data of grain size and orientations. The analysis results of grain orientations for the normal direction to films are represented in Fig 1(b), using an orientation indicator [Fig. 1(c)] by the standard projection in which colors describe crystal directions consisting of angle space between crystalline axes. A- or b-axis oriented grains are distributed in all over the BLT film surface as imaged in Fig. 1(b) by red or green colors. The size of a- or b-axis oriented grains are relatively small, compared to c-axis oriented grains, which are imaged in Fig. 1(b) by blue color as indicated by 1, 2, and 3 numbers in Fig. 1(b), and which are also localized in larger area than other grains.

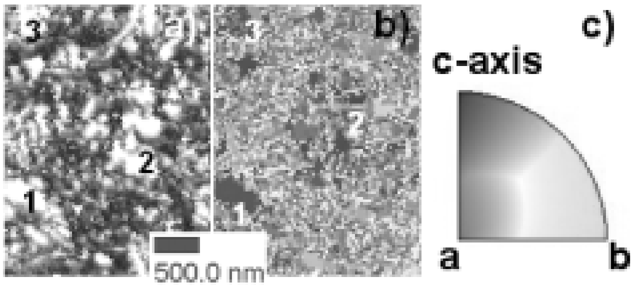

Fig. 1. a) An imaging quality map and (b) nanoscale orientation image for normal direction of the films by EBSD technique using an orientation indicator (c) in the standard projection consisting of axis and angle space for BT-based films.

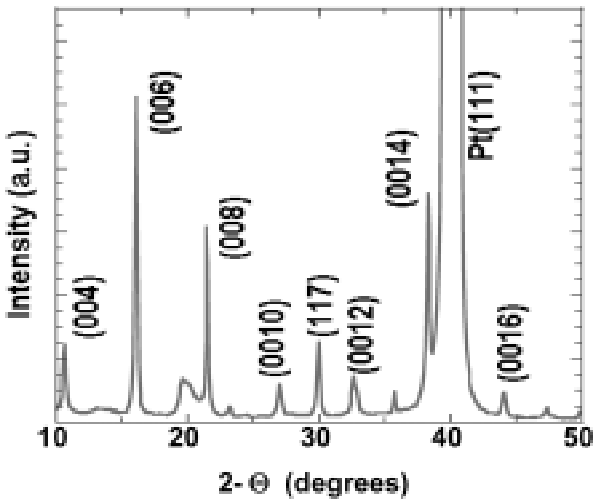

Fig. 2. X-ray diffraction θ-2θ scan for polycrystalline BLT films on Si wafer using Pt electrode.

θ-2θ x-ray scans were performed to compare the nanoscopic orientations of Fig. 1 with macroscopic polycrystalline orientations (Fig. 2) of BLT films on Pt electrodes. The very strong (00*l*) type and relatively strong (117) peaks were observed. This macroscopic XRD measurement qualitatively corresponds to the measurement results of the nanoscale grain orientations in the Fig. 1. Hysteresis loop measurements were performed to confirm the existence of ferroelectric phases in the films. The remnant polarization of around 12 μC/cm^2 at the applied voltage of 5 V is observed as shown in Fig. 3. Ferroelectric domain characteristics were performed by phase measurements of PFM [12-19] to study the dependence of electrical properties on grain orientations and distributions. Nanoscopic ferroelectric domain switching using an applied voltage through a conductive cantilever tip with nano-size is significantly dependent on the grain orientations. Ferroelectric domains of c-axis orientated grains, which are indicated by 1, 2, and 3 numbers in Fig. 4(a) and (b), respectively, show no changes in the phase image as shown in Fig. 4(b),

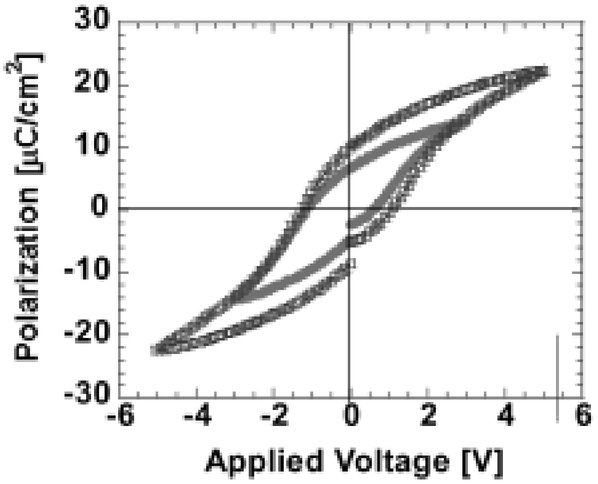

Fig. 3. A hysteresis loop for a polycrystalline BLT capacitor on Si wafer using Pt electrode.

even after applied voltage of 10 V. However, the ferroelectric domains in the other regions except for c-axis oriented grains are almost all switched toward one polarization direction after applied voltage of 10 V. Comparison of the PFM (Fig. 4) and EBSD measurements (Fig. 1) supports strongly the results of grain orientation dependence of ferroelectric domain characteristics. It is estimated that the c-axis oriented grains with plate-like shape in the local large area have almost linear dielectric properties. Thus it is possible to expect that there are no changes in the polarization state right after removing the applied voltage as shown in Fig. 4(b). On the other hand, the smaller grains of ellipsoidal shape [Fig. 4(a)] with some orientations between a- or b-axis and c-axis have strong ferroelectric properties, and thus the phase contrast in Fig. 4 are aligned in one direction due to their strong remnant polarization even after removing the applied voltages. These results correspond to the previous reports for the crystallographic orientation dependence of polarization properties of the single crystal Bismuth Tantalate ($Bi_4Ti_4O_{12}$) [20]. Consequently, the crystalline orientations of BLT films are successfully characterized by the EBSD technique. It turns out that the morphology of grains is different from the orientations of grains normal to the films. Capacitor processes causing variations of grain size and orientation such as rapid thermal annealing (RTA) and furnace annealing should be optimized for the realization of high-density memories. Basic understandings of the nucleation and growth of the a- or b-axis oriented films during the processes have been under investigation in our group based on these experimental results.

4. Summary

The grain orientation and size distributions of BT-based films by spin-on coatings were examined by an EBSD technique. Ferroelectric domain characteristics by PFM were also performed to study the dependence of electrical properties on grain orientations and distributions. It is demonstrated that EBSD technique is successful for characterizations of film orientations. C-axis oriented grains with plate-like morphology show almost linear dielectric behavior. A- or b-axis oriented grains (< ~0.1 µm) with superior ferroelectric properties show ellipsoidal morphology. Suppression of the plate-like structure is important for realization of high-density BLT-based memories.

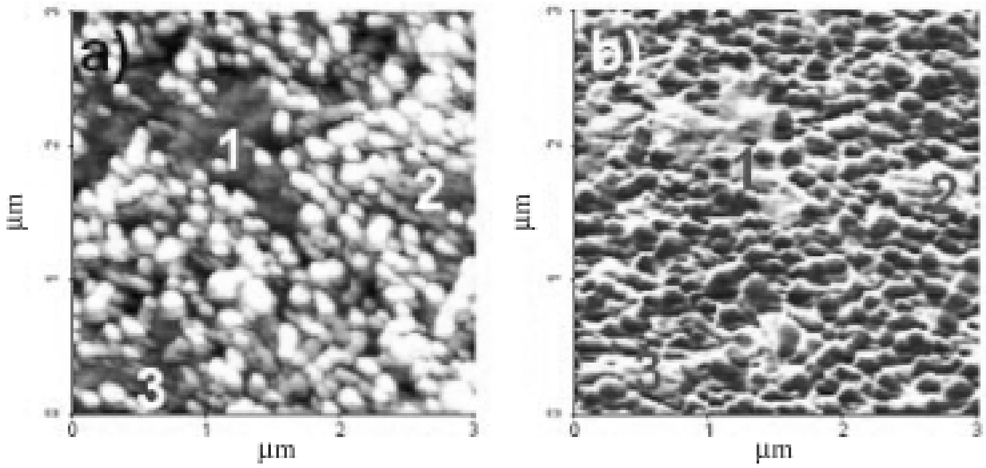

Fig. 4. a) A topographical surface image and b) ferroelectric domain image by phase measurements of a piezoelectric scanning probe microscope, after applied the tip bias of 10 voltages through the cantilever tip for a BLT film on Pt bottom electrode.

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