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Comparative Study of Reliability Issues in La-doped Bismuth Titante Thin films According to the Bottom Electrode Materials

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We have investigated the effects of bottom electrode materials on fatigue and hydrogen-induced degradation in La-doped bismuth titanate ($Bi_{3.25}La_{0.75}Ti_3O_{12}$; BLT) thin films. BLT thin films were deposited on $SrRuO_3$ (SRO) and platinum (Pt) electrodes by pulsed laser deposition. BLT films on both electrodes showed good crystallized structures and ferroelectric properties after post-deposition annealing. Also, it was observed that there is almost no fatigue degradation in both cases. However, substantially different hydrogen-induced degradation behavior was observed in the case of BLT-based capacitors according to the bottom electrode materials. When Pt was used as a bottom electrode, the hydrogen-induced degradation was found to be very severe, resulting in polarization failure even at 300°C. In contrast, BLT films on SRO electrodes were highly immune to hydrogen-induced degradation.

Keywords: ferroelectric materials, fatigue, hydrogen-induced degradation, conductive oxide electrode, La-doped bismuth titanate

1. INTRODUCTION

Ferroelectric random access memories (FRAM) have been extensively studied for non-volatile memory applications.[1,2] One of the most important requirements for memory devices is degradation-free characteristics. Fatigue, retention (imprint), and hydrogen-induced degradation are the major degradation phenomena in ferroelectric materials.[3-8] Considerable efforts have been directed toward improving ferroelectric performances by using various ferroelectric materials and numerous different approaches, i.e., grain boundary control, epitaxial growth, using conductive oxide electrodes, etc. have also been reported.[3-10] Among many kinds of ferroelectric materials, La-doped bismuth titanate (BLT) has been studied extensively since negligible fatigue has been observed even when using conventional Pt electrodes.[1] However, other degradation behaviors, for example, data retention and hydrogen-induced degradation, have been reported to be severe when a Pt electrode is used, even in the case of BLT thin films.

In this paper, we report on the fatigue and hydrogen-induced degradation of BLT thin films in conjunction with the use of different bottom electrodes, especially pure metal and conductive metal-oxide electrodes, in order to verify the effects of using oxide electrode materials on the improvement of ferroelectric properties in the case of BLT thin films.

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2. EXPERIMENTS

We previously reported on the synthesis of ferroelectric $Bi_{3.25}La_{0.75}Ti_3O_{12}$ (BLT) capacitors with different bottom electrode materials, i.e., $SrRuO_3$ (SRO) and Pt electrodes.[8] Briefly, thermally oxidized Si substrates (SiO_2/Si) were used for the preparation of BLT-based capacitors. Pulsed laser deposition (PLD) was employed to deposit SRO bottom electrodes and Pt/Ti multilayer was deposited by sputtering. BLT films were deposited on SRO/SiO_2/Si and Pt/Ti/SiO_2/Si at 400°C under an oxygen pressure of 300 mTorr by PLD. Following the BLT deposition, the films were cooled under an oxygen pressure of 300 Torr. After the deposition, the films were postannealed at 700°C for 1 h in oxygen. The nominal BLT thickness was 400 nm. A Pt top electrode with an area of 2.5×10^{-6}-4×10^{-6} cm^2 was deposited by sputtering at room temperature and defined by a standard lift-off process.[8] Figure 1 shows the schematic illustration of ferroelectric capacitor structures based on BLT thin films with different bottom electrode materials, i.e. Pt and SRO. The crystal structures of the films were investigated using X-ray diffraction (XRD). The polarization properties were examined using a Radiant RT66A tester (Radiant Technologies) under virtual ground mode at room temperature. We have measured the dielectric and electrical characteristics

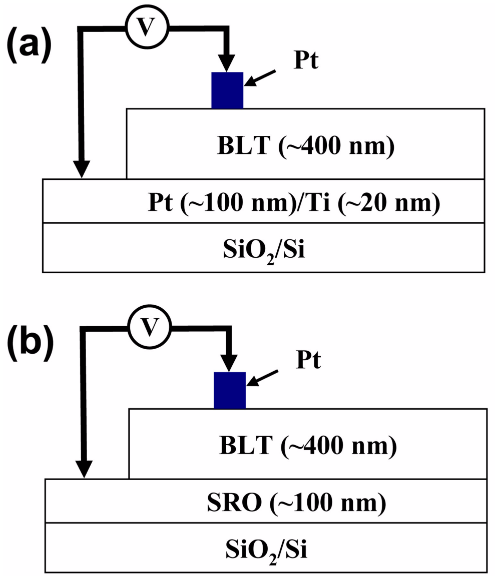

Fig. 1. Schematic illustration of ferroelectric capacitor structures based on BLT thin films with different bottom electrode materials, i.e. (a) Pt and (b) SRO.

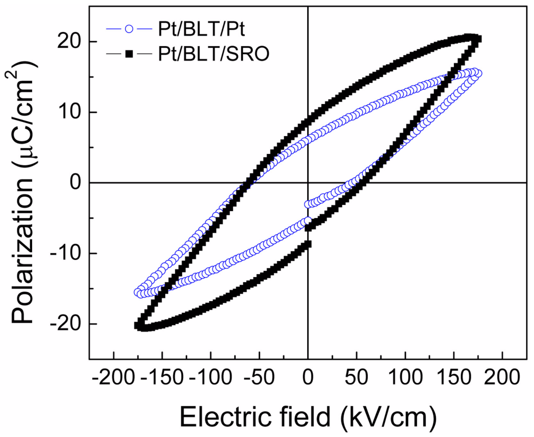

Fig. 2. Ferroelectric hysteresis of BLT thin films according to different bottom electrode materials.

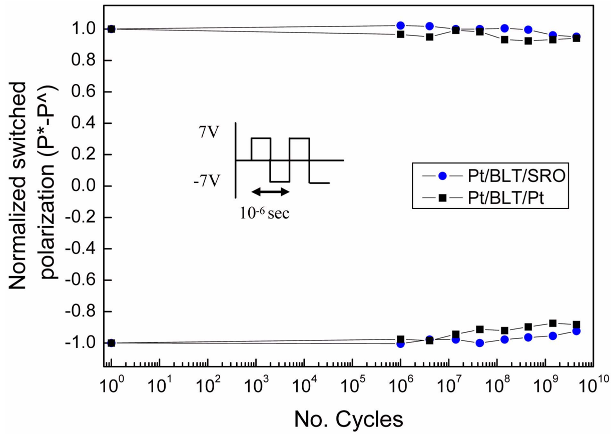

Fig. 3. Fatigue characteristics of BLT thin films deposited on Pt and SRO electrodes. Inset shows the bias pulses applied to the ferroelectric capacitors to measure the fatigue characteristics.

before and after annealing in forming gas (6% hydrogen/94% Argon, 99.99% purity; FGA). FGA was conducted at 200, 250, and 300°C for 30 min.

3. RESULTS AND DISCUSSION

We previously investigated the x-ray diffraction patterns (θ-2θ scans) of BLT thin films on Pt and SRO bottom electrodes, respectively. Both BLT films on Pt and SRO show (117)-preferred orientation.[8] As the (117) orientation is at approximately 50° with respect to the [100] direction, where the spontaneous polarization vector of BLT lies along this direction.[11,12] It is also noted that BLT on Pt mainly showed *c*-axis diffraction peaks along with (117) diffraction; in contrast, BLT on SRO shows many other diffraction peaks as well. This implies that BLT on SRO can potentially show better ferroelectric properties than BLT on Pt, since it is well known that *c*-axis oriented BLT films have a much smaller polarization component along the film normal. This has been confirmed from the polarization vs. electric field (*P*-*E*) measurement, as shown in Fig. 2. BLT films both on Pt and SRO showed good ferroelectric properties. However, the remanent polarization values were higher when BLT was deposited on SRO electrodes. This is due to the formation of a non-*c*-axis oriented film when BLT was deposited on SRO electrodes.

One of the most important issues in ferroelectric memory devices is the fatigue characteristics. Fatigue of ferroelectric thin films is characterized by the loss of switchable polarization with repeated switching cycles. This loss of switchable polarization limits the lifetime of ferroelectric memory devices. In this case, the loss of switchable polarization reduces the ability to differentiate the two remanent polarization states (i.e., the logic states), until they eventually become indistinguishable.[13] We have investigated the fatigue behavior of ferroelectric capacitors composed of Pt top electrode/BLT films/SRO or Pt bottom electrodes, as shown in Fig. 3. Both capacitors showed good fatigue-resistance behaviors according to the number cycles. There was almost no appreciable degradation up to 4.4×10^9 cycles at a 1 MHz square wave form at ±7 V in polarization values. From the results, it was found that BLT films are highly immune to fatigue degradation regardless of electrode materials.

Figure 4 shows the change of *P*-*E* curves according to the FGA temperatures. Figure 4(a) shows the hydrogen-induced degradation of BLT films on Pt electrodes. BLT films can maintain ferroelectric properties up to 200°C. However, beyond this temperature, severe degradation was observed, and at 300°C the films were completely degraded, resulting in no ferroelectric properties. Otherwise, when BLT films

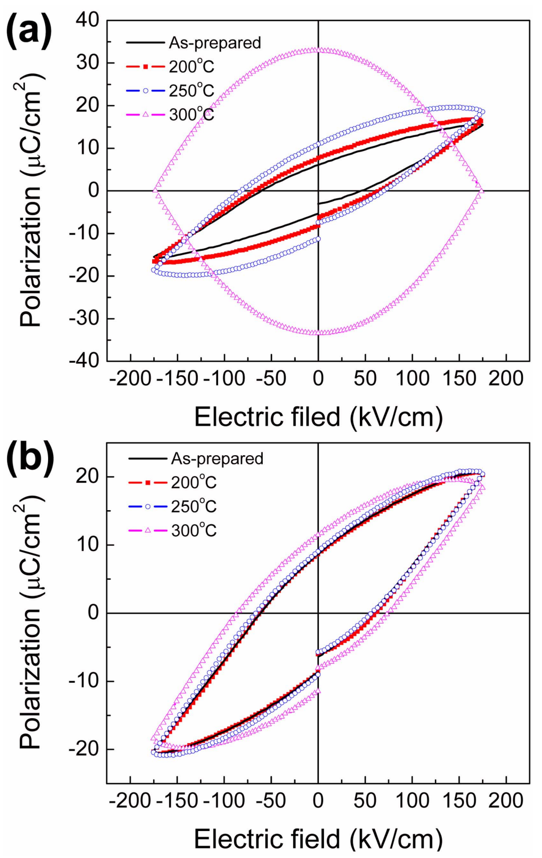

Fig. 4. Hydrogen-induced degradation of BLT films deposited on (a) Pt and (b) SRO electrodes according to the FGA temperatures.

were deposited on SRO electrodes, there was almost no degradation up to 250°C and a slight degradation was observed when the device was annealed at 300°C in hydrogen-contained ambient. It is noted, however, that even at 300°C the film maintains ferroelectric properties according to the applied electric field.

Several mechanisms have been reported for hydrogen-induced degradation in ferroelectric thin films. One is related to the catalytic nature of the top electrodes, which results in dissociation of molecular hydrogen to atomic hydrogen.[14] Most previous studies discussed the formation of polar hydroxyl bonds during annealing under the hydrogen-containing ambient.[15] There have also been several reports on the effects of grain boundaries on hydrogen-induced degradation. The grain boundary is the dominant pathway for diffusion of atomic hydrogen into the thin films.[6,7,16]

In the present work, we compared the effects of bottom electrode materials on the degree of hydrogen-induced degradation in BLT thin films. Pt is a widely used electrode material for ferroelectric capacitors. However, it is also a good catalyst to dissociate molecular hydrogen to atomic hydrogen. The major problem is that there is no additional oxygen source while there are many pathways during the process for the loss of oxygen in the ferroelectric materials. In contrast, conductive oxide electrodes are good electrode materials and they also act as oxygen sources. Thus, conductive oxide electrodes have potential to be adopted in ferroelectric memory devices, since less degradation is shown when they are used.

4. CONCLUSIONS

We systematically investigated the effects of bottom electrode materials (Pt and SRO) on fatigue and hydrogen induced-degradation in BLT thin films. BLT thin films on both electrodes showed good ferroelectric properties and fatigue characteristics. It was observed that there is no appreciable loss of switchable polarization with repeated switching cycles in both cases. However, substantially different hydrogen-induced degradation properties have been obtained in BLT thin films according to the bottom electrode materials. When a Pt electrode was used as a bottom electrode, BLT thin films were completely degraded at 300°C FGA temperature. However, BLT thin films on SRO electrodes showed robust properties with respect to hydrogen-induced degradation at the same temperature. From the results conductive oxide electrodes are expected to be excellent candidates for electrode materials in ferroelectric memory devices.

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