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Crystallization of $Bi_{4-x}La_xTi_3O_{12}$ films prepared by the sol-gel technique on IrO_2/Ir multi-layered electrode

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We have studied $Bi_{4-x}La_xTi_3O_{12}$ ($x = 0.75$)(BLT) films grown on IrO_2/Ir multi-layered structure electrode. IrO_2/Ir electrodes were prepared by RF sputtering method and BLT films were prepared by the sol-gel technique. It is demonstrated that c-axis oriented BLT films with low leakage current density can be obtained at 750°C by flashing annealing process. It is also found that the electrical properties are improved by inserting Pt between BLT and IrO_2/Ir electrodes. Remanent polarization of 14 $\mu C/cm^2$, coercive field of 120 kV/cm were obtained.

Key words: bismuth lanthanum titanate, iridium oxide, thin film, ferroelectrics, barrier metal

1. Introduction

Iridium oxide, IrO_2, is applicable to electrode for high density integrated ferroelectric random access memory (FeRAM), and has been extensively studied as a bottom electrode for ferroelectric PZT films. Recently, $Bi_{4-x}La_xTi_3O_{12}$ (BLT) has attracted much attention because BLT is fatigue free, low temperature crystallization is possible, good squareness of hysteresis curve can be obtained and does not contain Pb[1]. However, there has been a few reports on the BLT films on IrO_2 electrodes[2, 3].

In this paper, we study BLT thin films on IrO_2 and IrO_2/Ir multi-layered electrodes. We used three kinds of electrodes, IrO_2 (100 nm) single-layer, $[IrO_2/Ir]_2/IrO_2$ multi-layered electrodes and $Pt/[IrO_2/Ir]_2/IrO_2$. The substrates are SiO_2/Si for all electrodes. The thickness of both IrO_2 and Ir layers in multi-layer electrodes is 50nm. Moon et al reported multi-layer structure iridium electrode as a diffusion barrier[4]. They use Ir metal deposition followed by rapid thermal oxidization. In this work we fabricated IrO_2/Ir multilayer electrodes with in-situ oxidization process by RF sputtering.

2. Experimental

Iridium oxide electrodes were obtained by RF magnetron sputtering method. The substrate temperature was 480 °C, flow ratio of oxygen to argon was 50%, and the total pressure was 0.6 Pa. Sputtering power was 100 W. The multi-layered electrodes were obtained by alternative deposition of IrO_2 and Ir.

BLT (180 nm) thin films were prepared by the sol-gel method. Sol-gel precursor solution (Mitsubishi Materials Corp.) was spin-coated on the

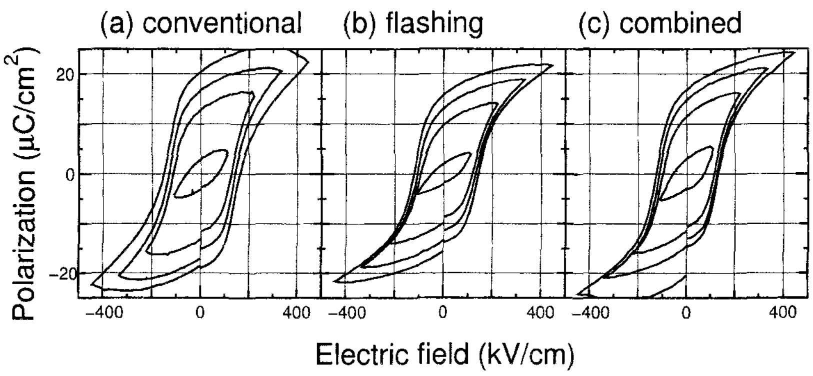

Fig. 1 P-E characteristics of BLT films fabricated with three kind of consolidation conditions. (a) conventional method; 400°C, 10min. (b) flashing method; 600 °C, 30 s. (c) combined method; 600 °C, 30 s and 400 °C, 10 min. After the consolidations, the samples were annealed at 750 °C.

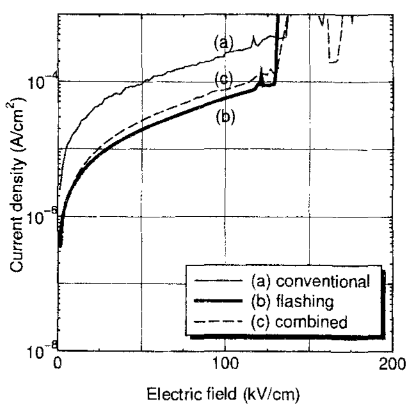

Fig. 2 Current density of BLT films prepared with three kind of consolidations as a function of electric field; (a) conventional method, (b) flashing method, (c) combined method. After the consolidation, the samples were annealed at 750 °C

Table I BLT preparation process;(a)conventional, (b) flashing, (c) combined.

process	dry	consolidation	crystallization
a	180°C	400°C, 10min	600~750°C
b		600°C, 30sec	
c		600°C, 30sec + 400°C, 10min	

substrates and dried at 180 °C on a hot-plate. Dried samples were consolidated by different conditions shown in Table I. The "Conventional process" means that dried sample is consolidated at 400 °C on the hot-plate for 10min in O_2. In the "flashing process", samples were annealed at 600 °C for 30 s in O_2 using rapid thermal annealing (RTA). In the "combined method", samples were first annealed 600 °C for 30 s. followed by 400°C annealing for 10 min in O_2.

After the consolidation, the samples were crystallized at 600~700 °C in O_2. Pt top electrodes were deposited by the electron beam evaporation method. Samples were then post-annealed at 600 °C for 10 min in O_2 to recover the process

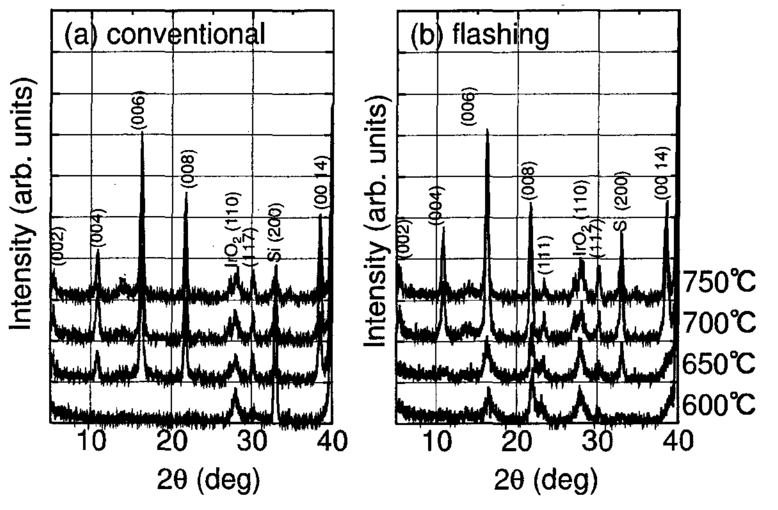

Fig. 3 XRD patterns of BLT films prepared on Ir multi-layered electrode, by (a) conventional consolidation and (b) flashing consolidation.

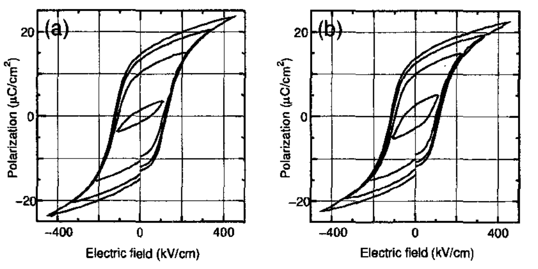

Fig. 4 P-E hysteresis loops of BLT films on $Pt/[IrO_2/Ir]_2/IrO_2$ multilayered electrode consolidated with (a) conventional and (b) the "flashing" methods. The crystallization temperature is 750 °C.

damage.

The structure of the films was analyzed with x-ray diffraction (XRD). The electrical properties of the films ware measured at room temperature using an RT66A test system.

3. Results and Discussion

The P-E hysteresis curves of the BLT films annealed at 750 °C are shown in Fig.1. The P-E curves of BLT films prepared by the conventional method are shaped round due to the large leakage current. This is consistent with the current-voltage characteristics shown in Fig.2. On the other hand, relatively good P-E hysteresis loops can be obtained for the BLT films prepared by the "flashing" and the "combined method" especially when the samples were annealed at 750 °C. Figure 2 shows current density of the BLT films prepared at 750 °C as a function of electric field. As shown in Fig.2, the leakage current density of these samples were one order of magnitude lower than that of the BLT films prepared by the conventional method.

We then fabricated BLT films using the flashing consolidation on Ir/IrO_2 multi-layered electrodes.

Figure 3 shows XRD patterns of BLT films prepared by the "flushing" consolidation on

$[IrO_2/Ir]_2/IrO_2$ electrodes and the "conventional". Although the amount of thermal budget for the "flashing" consolidated sample is much less than the sample prepared by the "conventional" consolidation, crystallization of the BLT films with the "flashing". consolidations is as good as that of the BLT films prepared by the conventional process. It is interesting to note that broad peaks were obtained for the BLT films prepared by the "flashing" annealed even at 600°C. This may be due to the effect of flashing consolidation that forms nucleus to layer by layer. Figure 4 shows P-E hysteresis curves of BLT films prepared by (a) conventional and (b) flashing consolidation on multi-layered electrode ($Pt/[IrO_2/Ir]_2/IrO_2$). The crystallization was carried out at 750 °C. The Pt layer was inserted because it was found that Pt insertion improved the electrical properties. The leakage current density is in the order of 10^{-7} A/cm^2 for the electric field up to 100 kV/cm. Good P-E hysteresis can be obtained with a remanent polarization of 14 μC/cm^2 and a coercive electric field of 120 kV/cm. These characteristics are as good as these of BLT films prepared on standard Pt/Ti electrode. This means that the $Pt/[IrO_2/Ir]_2/IrO_2$ multi-layered electrode is applicable to the FeRAMs and Metal-Ferroelectric-Metal-Insulator-Semiconductor(MFMIS) transistors.

4. Conclusions

We have demonstrated the effect of consolidation methods for BLT films prepared on iridium oxide and $Pt/[IrO_2/Ir]_2/IrO_2$ multi-layered electrode. The flashing method was effective to lowering the leakage current of BLT films on iridium oxide electrode. Good P-E hysteresis loops were obtained for BLT films prepared by the "flashing"

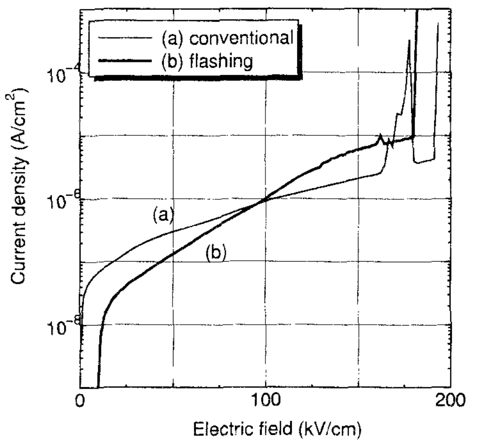

Fig. 5 Current density of BLT films on $Pt/[IrO_2/Ir]_2/IrO_2$ multilayered electrode consolidated with (a) conventional and (b) the "flashing" methods. The crystallization temperature is 750 °C.

consolidation on $Pt/[IrO_2/Ir]_2/IrO_2$ electrodes. A remanent polarization of 14 μC/cm^2 and a coercive field of 120 kV/cm were obtained.

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