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MOD PREPARATION AND CHARACTERIZATION OF BLT THIN FILM

K. TANAKA, K. UCHIYAMA [a], M. AZUMA, Y. SHIMADA,
T. OTSUKI [b], V. JOSHI and C. A. Paz de ARAUJO [c]

a. Panasonic Semiconductor Development Company,
5055 Mark Dabling Blvd. Colorado Springs, CO 80918 USA,
b. Semiconductor Company, Matsushita Electric Industrial Co., Ltd.,
1-1 Saiwai-cho, Takatsuki, Osaka 569-1193 Japan and
c. Symetrix Corporation, 5055 Mark Dabling Blvd. Colorado Springs,
CO 80918 USA

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The bismuth layered perovskite structured ferroelectrics (BLSF) are well known for their good ferroelectric characteristics. Recently, $SrBi_2Ta_2O_9$ (SBT) and $SrBi_2Ta_{2-x}Nb_xO_9$ (SBTN) have shown attractive properties for ferroelectric random access memories because of their high endurance characteristic. In addition to SBT and SBTN, their lies a possibility of many different BLSF materials waiting to be explored. One such material is lanthanum substituted bismuth titanate $Bi_{4-x}La_xTi_3O_{12}$ (BLT) that has received some attention lately. The BLT thin films were prepared by conventional metal organic decomposition technique on the platinum electrode for evaluating ferroelectric characteristics of BLT and possibility of low temperature crystallization. It was found that BLT can be crystallized at 550C with random orientation and very good ferroelectric properties were observed: the remnant polarization (2Pr) was over 20μC/cm^2 with low leakage current. Furthermore, the BLT capacitor did not show any significant fatigue up to 3.2×10^{10} cycles even at 85C.

Keywords: lanthanum substituted bismuth titanate, $Bi_{4-x}La_xTi_3O_{12}$, metal organic decomposition, low temperature crystallization

INTRODUCTION

The bismuth layered perovskite structured ferroelectrics (BLSF) are well known for their good ferroelectric characteristics and are formed by layering of oxygen octahedra between bismuth oxide layers. Especially, $SrBi_2Ta_2O_9$ (SBT) and $SrBi_2Ta_{2-x}Nb_xO_9$ (SBTN), which have double layers of Ta-O octahedra, are attractive materials for ferroelectric random access memories (FeRAMs) because of their high endurance characteristic and low operating voltage. [1]

On the other hand, SBT system required anneal temperatures up to 750C for the crystallization and this high processing temperature was an obstacle in integration with silicon devices. In a recent study, the modification and improvement of the conventional metal organic decomposition (MOD) technique has achieved 650C SBT crystallization with good ferroelectric characteristics that can be applied to high density FeRAM devices. [2]

In addition to SBT and SBTN, their lies a possibility of many different BLSF materials waiting to be explored. One such material is lanthanum substituted bismuth titanate $Bi_{4-x}La_xTi_3O_{12}$ (BLT) that has received some attention lately. The BLT system consists of bismuth oxide layers and triple perovskite like layers in which Bi ions are substituted with La ions. [3]

It has been reported that this material is suitable for nonvolatile memory application as it exhibits a high polarization charge ($24\mu C/cm^2$), good endurance (3×10^{10} cycles), and can be crystallized at low temperatures using the pulsed laser deposition (PLD) technique. [4]

The PLD technique has not been proven for high volume manufacturing. Also, there are few studies using conventional MOD technique for BLT ferroelectric system. [5-8] It is not clear whether BLT can be crystallized at lower temperatures than SBT system, i.e. below 650C. In addition, understanding of BLT's ferroelectric characteristics is not clear, strong *c*-axis orientation, especially the fatigue characteristic at high temperature that has been considered inferiors to SBT's endurance characteristic.

In this work, we report the possibility of low temperature crystallization of BLT thin films on platinum electrode using conventional MOD technique and the evaluation of initial ferroelectric characteristics, such as values of remanent polarization, leakage current, and fatigue characteristic at 85C.

EXPERIMENTAL

The BLT thin films were prepared by conventional MOD technique using rapid thermal annealing (RTA) and furnace annealing. This MOD technique is suitable for high volume manufacturing of FeRAM devices. The starting chemical used in this experiment is a MOD solution that involves all of the metals for BLT fabrication in one solution. This chemical was spin-coated on to the platinum bottom electrode and drying treatments were performed. Finally, the deposited film was annealed using RTA and furnace. The annealing temperature was between 550C and 650C.

For the electrical characterization of the BLT thin film, platinum thin film was sputtered on to BLT thin film as a top electrode. The capacitor size is $6940\mu m^2$.

The crystallinity of BLT thin films were first characterized by the X-ray diffraction (XRD) method using 2-axis diffractometer with Cu $K\alpha$ radiation. The BLT thin film was measured using the 2θ-θ scan and glancing-incident-angle scan methods. The 2θ-θ scan measurement was performed to check the orientation of the film and the glancing-incident-angle XRD measurements were performed to eliminate strong diffraction from substrate and platinum bottom electrode.

The ferroelectric characteristics were measured using the Sawyer-Tower method with temperature controlled wafer stage.

RESULTS AND DISUCCUSION

Figure 1 shows the XRD intensity profiles of BLT films annealed at different temperature from 550C to 650C. The main peaks are indexed.

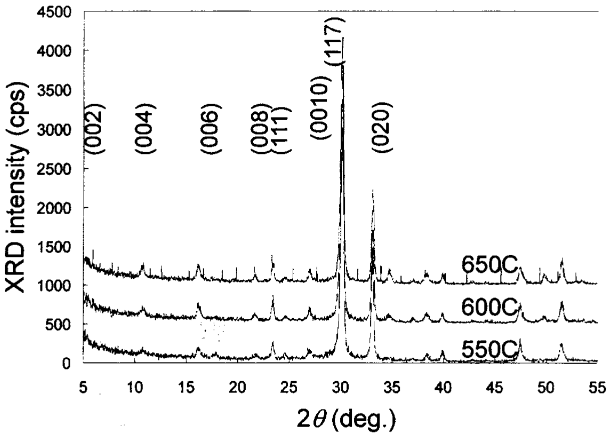

FIGURE 1 The glancing-incidence XRD intensity profiles of BLT films annealed at different temperature from 550C to 650C. The main peaks are indexed.

As shown in Fig. 1, there are no other peaks observed which can not be identified with BLT annealed at 650C. The obtained BLT film shows weak and broad (0 0 *l*) peaks and sharp (1 1 7) peak with high intensity. When compared to the theoretical peak intensity, this BLT film can be regarded as having no preferred orientation but almost random orientation.

There is no significant difference in peak profile as well as peak intensity between anneal temperatures from 550C to 650C. No additional peak is observed even at 550C anneal.

The BLT thin film on the platinum electrode can be crystallized using the conventional MOD technique even at 550C from XRD analysis.

Figure 2 shows the typical *P-E* hysteresis loops of 650C annealed BLT thin films at various applied field. The thickness of BLT thin film is 120nm. As shown in Fig. 2, the *P-E* hystersis loop above 250kV/cm is well saturated and square shaped with large remanent polarization (2*Pr*) and coercive field (2*Ec*). The 2*Pr* of BLT is about twice as large as that of SBT, on the other hand the 2*Ec* is also almost twice as large as that of SBT.

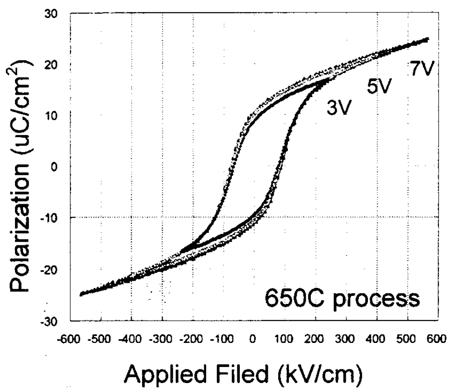

FIGURE 2 *P-E* hysteresis loops of 650C annealed BLT thin films (thickness: 120nm) at various applied field.

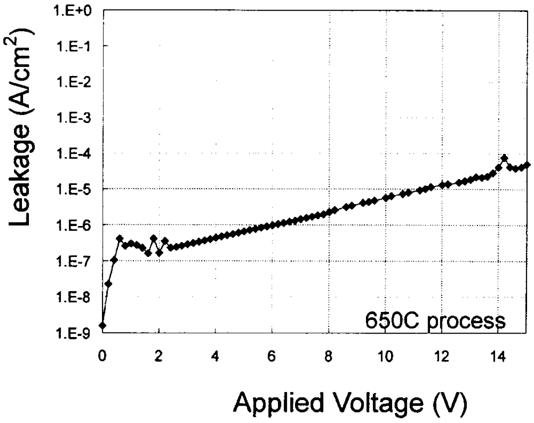

FIGURE 3 The remanent polarization $2Pr$ of 650C annealed BLT thin film as a function of applied voltage.

The applied voltage dependence of $2Pr$ is shown in Fig. 3. The BLT thin film is annealed at 650C and its thickness is 120nm. The $2Pr$ saturates above 300kV/cm, and its value is over 20μC/cm^2 and reaches 22μC/cm^2 at 580kV/cm, although the saturation of $2Pr$ in low applied field is worse than that of SBT, due to the high $2Ec$.

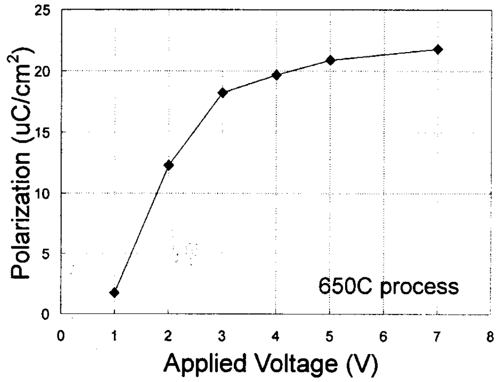

FIGURE 4 Leakage characteristic of 650C annealed BLT thin film.

There is no big difference of the *P-E* hystersis loop and 2*Pr* between annealing temperatures from 550C to 650C.

The leakage characteristic of 650C annealed BLT thin film is shown in Fig.4. There is a bump due to the polarization reversed current in the low applied voltage region. The BLT thin film does not show the destructive dielectric breakdown up to 1250kV/cm and its leakage current is below 10^{-6}A/cm^2 up to 333kV/cm and is kept low even up to 1250kV/cm.

Figure 5 shows fatigue characteristic of 650C annealed BLT thin film. The stress cycling field is 250kV/cm and its frequency is 1M Hz and the measure cycling field is 250kV/cm and its frequency is 1k Hz. The BLT thin film is kept at 85C during the stress and measure cycle. The BLT capacitor does not show any significant fatigue up to 3.2×10^{10} cycles even at 85C. After 1×10^{10} cycles, 2*Pr* keeps 97% of initial value, and after 3.2×10^{10} cycles 2*Pr* keeps 94% of initial value at 85C. No significant change in the shape of *P-E* hysteresis loop and of leakage current was observed after being subjected to 3.2×10^{10} cycles at 85C.

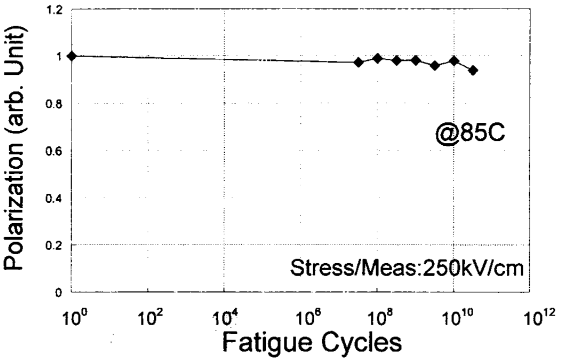

FIGURE 5 Normalized remanent polarization of 650C annealed BLT thin film at 85C.

CONCLUSION

The BLT thin films were successfully deposited using the conventional MOD technique even at 550C anneal temperature. The XRD analysis shows almost random orientation on the platinum electrode. The BLT thin film annealed at 650C showed a large 2*Pr*, over 20μC/cm^2; twice as large as that of SBT, with low leakage current. On the other hand 2*Ec* of BLT thin film was twice as large as that of SBT. The BLT capacitor did not show any significant fatigue up to 3.2×10^{10} cycles even at 85C.

The BLT can be crystallized at low temperature with good ferroelectric characteristics. The BLT can be regard as the one of good ferroelectric materials for realization of high density FeRAMs.

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