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Oriented growth of $Bi_{3.25}La_{0.75}Ti_3O_{12}$ thin films on RuO_2/SiO_2/Si substrates by using the polymeric precursor method: Structural, microstructural and electrical properties

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Abstract *c*-axis oriented $Bi_{3.25}La_{0.75}Ti_3O_{12}$ (BLT) thin films were grown on a RuO_2 top electrode deposited on a (100) SiO_2/Si substrate by the polymeric precursor method. X-ray diffraction and atomic force microscope investigations indicate that the films exhibit a dense, well crystallized microstructure having random orientations with a rather smooth surface morphology. The electrical properties of preferred oriented $Bi_{3.25}La_{0.75}Ti_3O_{12}$ (BLT) thin films deposited on RuO_2 bottom electrode leaded to a large remnant polarization (P_r) of 17.2 μC/cm^2 and (V_c) of 1.8 V, fatigue free characteristics up to 10^{10} switching cycles and a current density of 2.2 μA/cm^2 at 5 V. We found that the polarization loss is insignificant with nine write/read voltages at a waiting time of 10,000 s. Independently of the applied electric field the retained switchable polarization approached a nearly steady-state value after a retention time of 10 s.

Keywords Thin films · Atomic force microscopy · Dielectric properties · Fatigue

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1 Introduction

Among many valuable applications of ferroelectric thin films are nonvolatile memories and multifunctional components in microelectronic and optoelectronic devices. Recently, lanthanum-substituted bismuth titanate (BLT) has received much attention because of its improved fatigue behavior over the classical $Pb(Zr,Ti)O_3$ (PZT) capacitors [1]. As a fatigue-free material, BLT is of particular interest because it can be crystallized at relatively low processing temperatures below 650 °C, making it more compatible with Si based IC technology. Although a layer of metallic Pt is used for electrode in these devices, it has weak adhesion to a Si wafer and tends to cause ferroelectric fatigue due to the oxygen deficiency of the perovskite material. Moreover, it is very difficult to obtain epitaxial ferroelectric thin films deposited on metal structures with good adhesion. Recently, conductive oxides with perovskite-type structure have attracted much attention as candidates for electrodes in thin films, which are used for applications in ferroelectric memories [2]. These electrodes are required to integrate ferroelectric thin films into devices as alternative electrodes. However, these electrodes often lead to undesirably large leakage current. RuO_2 is a perovskite-type metallic oxide with a high electronic conductivity (at room temperature: 35 μcm) that declines with increasing temperature [3]. Together with the high thermal stability and the high chemical corrosion resistance [4], these properties are of particular interest in device applications, such as wiring in integrated circuits, thin- and thick-film resistors in integrated circuits [5], and for ultra-thin coatings to block diffusion between Al and Si in contact metallization for use in very large scale an electrode material for a high-energy-density-storage electrochemical capacitor [6, 7]. The purpose of this study is to use RuO_2 as the metal oxide bottom

electrode and at the same time to provide a template to grow better quality BLT films with preferred orientation. Our results demonstrate promising properties better than reported data. This happens mostly due to the occurrence of a lattice mismatch and to the appreciable difference in thermal expansion coefficients between the ferroelectric thin film and the metal electrode [8].

Among several method used to deposit thin films, solution deposition is a process that improves the stoichiometric control of complex mixed oxides and is compatible with many semiconductor manufacturing technologies. In previous works, our group have reported the preparation of thin films by the polymeric precursor method [9]. The overall process consists of preparing a coating solution based on metallic citrate polymerization. The precursor film is deposited by dip or spin coating and then treated to eliminate the organic material and synthesize the desired phase. The polymeric precursor method presents many advantages, such as the possibility to work in aqueous solutions with the high stoichiometry control. Moreover, it is a low-temperature process and a cost-effective method (inexpensive precursors and equipments). For obtaining good crystallized films, heat treatment at high temperatures for a long time is necessary, normally 2 h. These long heat treatments can cause several damages to the stack, leading to interdiffusion between the film and the substrate, and sometimes loss of stoichiometry (due to volatile element). So, it is important to decrease the temperature and time of the thermal treatment. Microwave energy is being developed as a new tool for high-temperature processing of materials. This technology has received great attention due to the advantages observed with microwave processing, which include: reduced processing costs, better production quality, new materials and product, among others. With proper understanding and control, many technically important materials can be heated rapidly, uniformly, selectively, less expansively and with greater control than is possible with conventional methods [10]. In this work, microwave energy to promote a rapid thermal way for the crystallization of the film was investigated with the advantage of reducing the time and, in some cases, the temperature of the thermal treatment. We have also examined the ferroelectric and dielectric characteristics of BLT films with definite conclusion and quality for the application in FeRAMS.

2 Experimental procedure

The RuO_2 and BLT thin films were prepared the polymeric precursor method, as described elsewhere [11]. The bottom electrodes thin films were spin coated on (100) Si/SiO_2 substrates by a commercial spinner operating at 5,000 rpm for 30 s (spin coater KW-4B, Chemat Technology). Each annealing layer was pre-fired at 400 °C for 2 h in a conventional oven. After the pre-firing, each layer was crystallized in a microwave oven at 700 °C for 10 min. Using the same procedure, the BLT thin films were deposited by spinning the precursor solution on the desired substrates. Through this process, we have obtained thickness values of about 150 nm for the bottom electrodes and around 300 nm for BLT, reached by repeating the spin-coating and heating treatment cycles. The microwave oven used was a simple domestic model similar to that described in literature [12]. Phase analysis of the films were performed at room temperature by X-ray diffraction (XRD) using a Bragg–Brentano diffractometer (Rigaku 2000 model) and CuKα radiation. The morphology and the thickness of the films were examined using atomic force microscopy (AFM) (Digital Instruments, Nanoscope IIIa) and scanning electron microscopy (Topcom SM-300), respectively. The electric properties were measured by an $Au/BLT/RuO_2/SiO_2/Si$ (100) capacitor structure. The upper electrodes of Au for the electrical measurements were prepared by evaporation through a shadow mask with 0.2 mm^2 dot area. Dielectric and ferroelectric properties of the capacitor were measured by an HP 4192A impedance/gain phase analyzer and a Radiant Technology RT6000 A in a virtual ground mode, respectively. For the fatigue measurements, internally generated 8.6 μs wide square pulses or externally generated square pulses were used with a 10 V amplitude. The retention characteristics of the films were measured by observing the time-dependent changes of P^* (switching polarization) and $P^\wedge$ (non-switching polarization) independently. For P^*, the capacitor was switched with a negative write pulse and read by a positive read pulse after retention time t. For $P^\wedge$, positive pulses were used for both writing and reading.

3 Results and discussion

The XRD pattern of BLT thin films annealed at 700 °C for 10 min is shown in Fig. 1. It was found that the film consisted of a single phase of bismuth layered structure showing preferred (00l) oriented grains. XRD analyses indicated that there is no evidence of secondary phase formation. This demonstrates that with the substitution of Bi ions by La ions up to 0.75, the single phase layered perovskite was preserved. The here discussed preferred orientations can be caused by differences in lattice parameters and thermal expansion coefficients between bottom electrode and ferroelectric thin film.

Figure 2 shows a typical surface morphology of BLT films deposited on RuO_2 electrodes. AFM study revealed a homogeneous surface indicating that the microwave furnace allows the preparation of films with controlled morphology. The average surface roughness value is 4.3 nm.

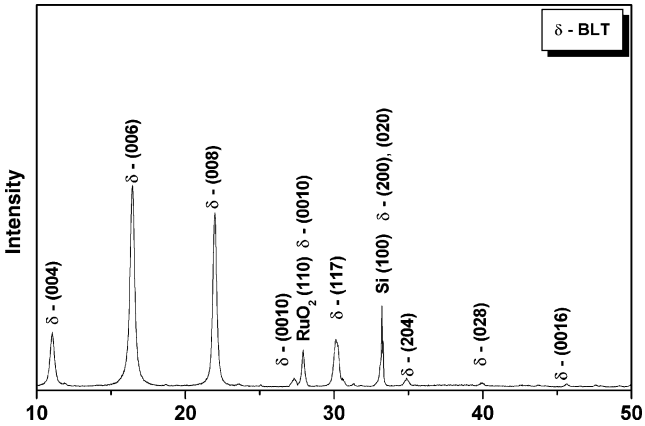

Fig. 1 X-ray diffraction for BLT film deposited on RuO_2 bottom electrode and annealed in microwave oven

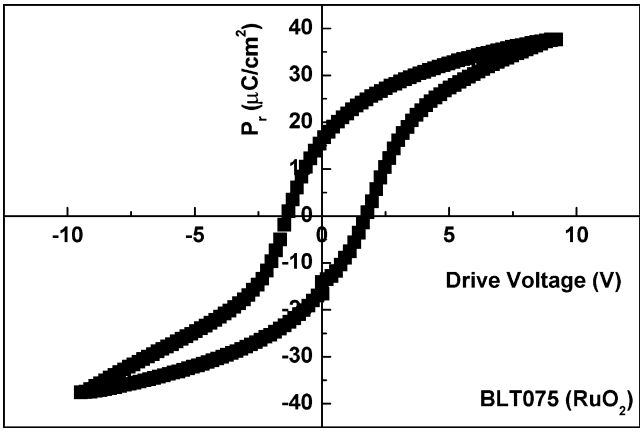

Fig. 3 P–E hysteresis loops for BLT film deposited on RuO_2 bottom electrode and annealed in microwave oven

BLT consisted of well developed rounded grains with considerable volume fractions of micrograins and the grains size are close to 58 nm. The observed rounded morphology of the grains which is not typical for BLT system may be related to the stress created during the film annealing due to the difference in the thermal expansion coefficient of bottom electrode and thin film.

The ferroelectric nature of the BLT thin film was confirmed by the polarization hysteresis loop, which is displayed in Fig. 3. The ferroelectric hysteresis loops of typical BLT films were measured at an applied electric field of 300 kV/cm. It exhibited a remnant polarization (P_r) of 17.2 μC/cm^2 and (V_c) of 1.8 V. The contribution of the La substitution to the large remanent polarization of the polycrystalline BLT films is not to enhance the intrinsic polarization but to bring out the polarization easily. It is considered that the pinned domain motion of the BIT is relaxed by La substitution and a saturate hysteresis is observed [13]. It may also be seen that the remanent polarization was much higher than that normally expected for a perfect *c*-axis oriented single crystal and may be ascribed to the presence of *a*-axis polarization components, as also seen from the XRD data.

The hysteresis behaviour was also reflected in the C–V characteristics of the BLT films, which is shown in Fig. 4. At 100 kHz, the applied voltage was swept from a positive bias to negative bias and back again. Two peaks are clearly seen in this figure. The BLT film capacitance changes from to with applied voltage bias. The presence of two peaks is attributed to the ferroelectric domains switching. The curve for the film deposited on RuO_2 electrode is symmetric around the zero bias axis, indicating that the films contain few movable ions or charge accumulation at the film-electrode interface. The narrowing of the C–V curves indicates that the process to switch the domains is faster in these electrodes and the saturation occurs with low energy for the ferroelectric domain alignment.

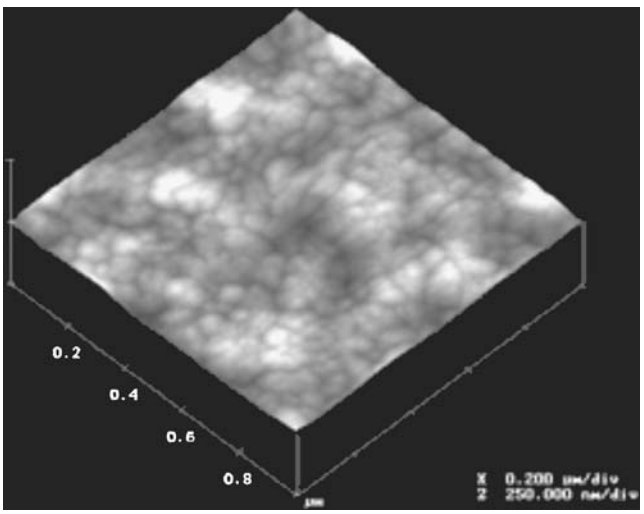

Fig. 2 AFM image for BLT film deposited on RuO_2 bottom electrode and annealed in microwave oven

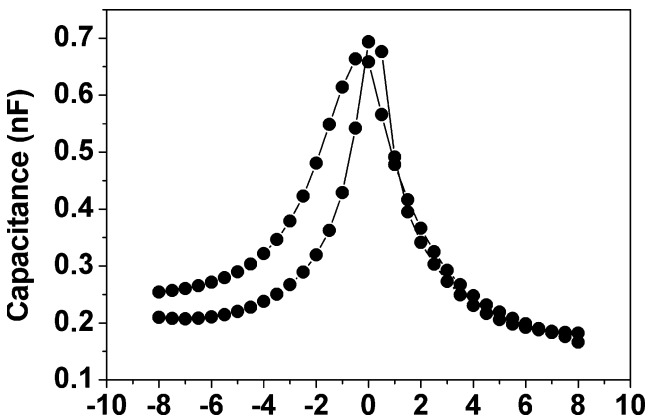

Fig. 4 C–V curves for BLT film deposited on RuO_2 bottom electrode and annealed in microwave oven

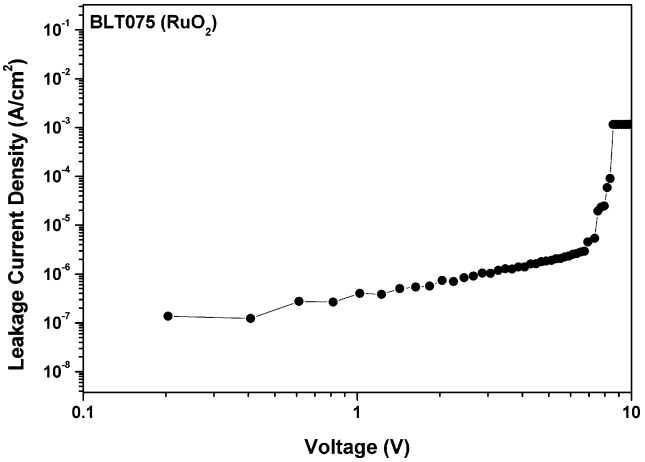

Fig. 5 log J vs log E characteristics for BLT film deposited on RuO_2 bottom electrode and annealed in microwave oven

One of the most important features for a material to be used as an alternative FeRAMS is the low leakage current density. Figure 5 shows the I–V characteristics of the BLT film annealed at 700 °C for 10 min. It is well know that BIT thin films prepared from stoichiometry composition suffer from high leakage current due to defects such as Bi vacancies accompanied by oxygen vacancies. To improve the leakage current properties in this experiment, the addition of lanthanum was verified. The low leakage current density observed in the film may be attributed to high oxygen affinity of the bottom electrode avoiding that oxygen will be depleted by the ferroelectric material, thus leaving an oxygen deficient layer of the electrode at the interface and increasing the contact resistance. Other reason is that the La substitution reduces the number of defect complexes that act as space charge in the pseudo-perovskite layer.

Figure 6 shows the fatigue behaviour of BLT films annealed at 700 °C for 10 min. The fatigue endurance was tested with 1 MHz bipolar pulses at 10 V. The BLT film demonstrated no fall of remnant polarization and exhibited no fatigue after 10^{10} switching cycles, respectively. The fatigue behaviour in perovskite thin films are generally explained on the basis of oxygen vacancy and electron/hole injection mechanisms [14]. Oxygen vacancies can be generated during annealing of BLT films which can be charge compensated by the higher oxygen affinity of the bottom electrode. It can be assumed that if oxygen vacancy accumulation near the film-electrode interface occurs during heat treatment, the conductive oxide can consume the oxygen vacancies near the interface preventing the fatigue behaviour.

Retention, which is the time dependent change of the polarization state of the ferroelectric film, is another factor which limits the life of a ferroelectric memory device. The tests on the retention characteristics of the ferroelectric capacitors were also carried out at room temperature by using a Radiant Technology RT6000 A test system. Figure 7 shows the long-time retention characteristics of the BLT films annealed in the conventional furnace. As shown, (P*) and (P^) was plotted as a function of retention time from 1 s to 1×10^4 s at a constant applied electric field of 150 kV/cm. The initial polarization decayed and approached a nearly steady-state value after a retention time of 10 s. The small decay of the retained charge in BLT thin films even after about 1×10^4 s is a favorable indication for memory applications. The overall retention time dependence of polarization retention for the BLT film is quite good. After a retention time of 1×10^4 s, the polarization loss was only about 16% of the value measured at t=1 s for an applied electric field of 150 kV/cm. Depolarization fields generated by the redistribution of space charge, defects and dipole charges could be the reason for the polarization decay after writing. For the infant period (within 10 s), depolarization fields could be the main contribution to polarization loss.

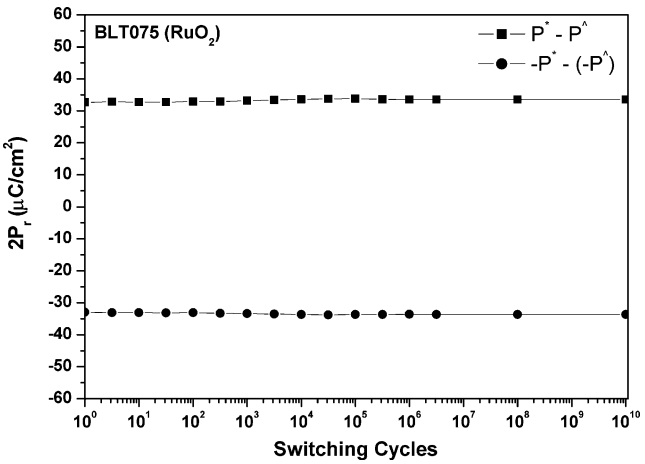

Fig. 6 Fatigue as a function of polarization cycles for BLT film deposited on RuO_2 bottom electrode and annealed in microwave oven

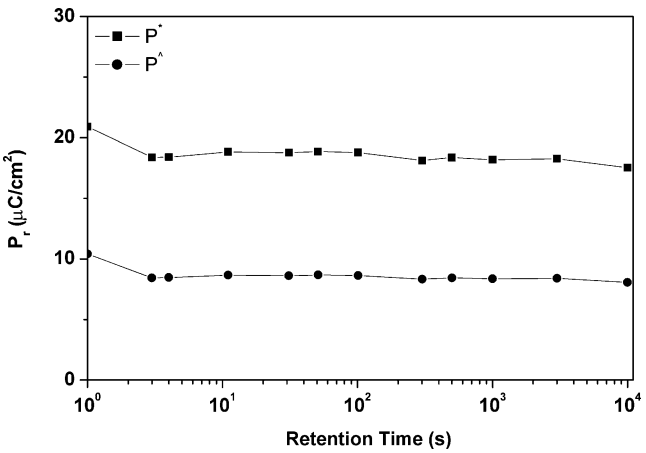

Fig. 7 P* and P^ of the BLT film for retention time up to 1×10^4 s and applied electric field of 150 kV/cm

The depolarization field increases with increasing the retained polarization and is time dependent. The long-time retention loss is attributed to the effects of redistribution of defect charges. This effect leads to a small decrease in the polarization by compensating the polarization charges when the redistribution of defect charges is driven by polarization [15]. Due to the dielectric relaxation, the retained charge is generally less than the switched charge measured from the P–E hysteresis loop and the difference between them should be small as possible to maintain enough margin between the digits "1" and "0." Since the lattice defect existed in the film, then the space charges due to the leakage current was not eliminated if the bias was retained during this retention period of time. Retention loss in ferroelectric was generally attributed to the presence of the internal electric field due to the bias effect originated from the incomplete screening of the depolarization field. Kang et al. [15] explained that the polarization charges were not completely compensated by the electrode charges due to the distribution between polarization and electrode charges are separated from each other. The origin of charge separation may be the existence of a spatial variation of polarization near the electrode. The residual depolarization field was polarization dependent and quickly changes its polarization reversal. At the same time, the field produced space charge, the screen field retains its polarity long after switching, since its decay rate was determined bt the RC time constant. Thus, space charge was created at the boundaries/interfaces, and retention occurs in the films. As a consequence, depolarization fields generated by the redistribution of space charge, defects and dipole charges could be the reason for the polarization decay after writing. Therefore, the understanding and improvement of the degradation behavior of ferroelectric thin films will have an essential impact on the future success of these films for device applications.

4 Conclusion

In summary, we have successfully shown the (00l)-oriented growth of the BLT films on SiO_2/Si using RuO_2 as a buffer layer. The BLT films are of pure peroviskite structure and show excellent ferroelectric properties. The C–V characteristics of the metal-ferroelectric-metal structure showed a typical butterfly loop that confirms the ferroelectric properties of the film, which is related to ferroelectric domain switching. High fatigue resistance was observed which proves that our films possess enough quality to be used in non-volatile random access memories. Retention loss in ferroelectric capacitors is generally attributed to the presence of the internal electric field such as oxygen vacancy and antisite defects. Due to its large spontaneous polarization, good fatigue and its satisfying retention characteristics, the BLT films could be a suitable material for integrated device applications in ferroelectric random access memories.

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