Retention characteristics of lanthanum-doped bismuth titanate films annealed at different furnaces

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Lanthanum-doped bismuth titanate thin films (Bi13.25La0.75Ti3O12 – BLT) were prepared by the polymeric precursor method and crystallized in the microwave and conventional furnaces. The obtained films are polycrystalline in nature and its ferroelectric properties were determined with remanent polarization P r and a coercive field E c of 3.9 μC cm −2 and 70 kV cm −1 for the film annealed in the microwave furnace and 20 μC cm −2 and 52 kV cm −1 for the film annealed in conventional furnace, respectively. Better retention characteristics were observed in the films annealed in conventional furnace, indicating that our films can be a promise material for use in the future FeRAMS memories.

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1. Introduction

Ferroelectric thin films have attracted considerable attention because of a wide range of applications, such as high dielectric constant capacitors, dynamic random access memories with low switching voltage, and electro-optic devices [1,2]. Bismuth titanate, Bi4Ti3O12, is a typical ferroelectric material with a layered perovskite structure and exhibits useful properties for optical memory, piezoelectric, and electro-optic devices. Bismuth titanate is potentially useful for device applications because of its relatively high dielectric constant, high Curie temperature, and high breakdown strength. The polarization vector in bismuth titanate lies in the a–c plane at an angle of about 4.5° to the a-axis. Hence there is a c-axis (P c = 4 μC cm −2 and an a-axis (P a = 50 μC cm −2) component of polarization. The low coercive field along the c-axis makes bismuth titanate an attractive gate electrode in a ferroelectric FET memory device of nondestructive readout (NDRO) mode [3]. Recently, La-substituted Bi4Ti3O12 (BLT) films have been very attractive for their larger ferroelectricity and good fatigue resistance when compared to the other bismuth layer structure compounds [11]. By substituting La for Bi, the essentially larger ferroelectricity of Bi4Ti3O12 came into use [4]. However, the reports of BLT films with large ferroelectricity are limited to the films prepared at relatively high temperature above 650°C [5,6].

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 has reported the preparation of thin films by the polymeric precursor method [7]. The overall process consists of preparing a coating solution based on metallic citrate polymerization [8]. The precursor film is deposited by dip or spin coating and then treated to eliminate the organic material and synthesize the desired phase. This method presents many advantages, such as the possibility to work in aqueous solutions with high stoichiometry control. Moreover, it is a low-temperature process and a cost-effective method with inexpensive precursors and equipments. Rapid thermal annealing (RTA) has been used in processing of materials, in order to reach the desirable heating temperature in a shorter time. The RTA has advantages such as reduction in surface damage and minimization of the film–substrate interaction [9–11]. Recently, the energy in the frequency of the microwave spectrum has been used for the processing of materials at high temperatures. This technology is comparable to RTA and provides some advantages as low investment, rapid and uniform heating, low sintering temperatures, improved product quality and the achievement of unique material properties, which cannot be reached using conventional processes [12,13]. In this work, BLT thin films were deposited by spin coating on Pt/Ti/SiO2/Si substrate by the soft chemical method. The films were heat treated in a domestic microwave furnace using a SiC susceptor to absorb the microwave energy and transfer the heat to the film. In order to evaluate the influence of annealing process on the crystallization, morphology and electrical properties of the films, we prepared a film in a conventional furnace.
2. Experimental procedure

The preparation of the BLT deposition solution was fully described elsewhere [14]. The films were deposited onto Pt/Ti/SiO₂/Si substrates by spinning the deposition solution at 5000 rpm for 30 s. To eliminate the organic material the films were treated at 350 °C for 2 h. The desired thickness was obtained by deposition of several cycles and thermal treatment at 350 °C for 2 h. The films were annealed at 700 °C for 10 min in a domestic microwave furnace (CCE, M301, 2.45 GHz, 900 W) by means of a SiC susceptor below the substrate in order to absorb the microwave energy and rapidly transfer the heat to the film. For comparison, BLT films were also annealed for 2 h at the same temperature in a conventional furnace. After crystallization, phase analysis of the films was characterized by X-ray diffraction (Rigaku, 20-2000), 40 kV and 150 mA from 2θ of 20 to 50°. Thickness of the annealed films was measured in a scanning electron microscopy (Topcom SM-300) at the transversal section. In this case, back scattering electrons were used. The film thicknesses were approximately 300 nm for the film crystallized in the conventional furnace and 250 nm for the film crystallized in the microwave furnace (Digital, Nanoscope 3A) was used to analyze the roughness and the average grain size. A 0.5 mm diameter top Au electrode for the electrical measurements were prepared by evaporation through a shadow mask at room temperature. The electric properties were measured by an Au/BLT/Pt/Ti/SiO₂/Si (100) capacitor structure. The capacitance-voltage characteristic was determined in a metal–ferroelectric-metal configuration using a small AC signal of 10 mV at 100 kHz. The AC signal was applied across the sample, while the DC was swept from positive to negative bias by using an impedance analyzer (model 4192 A, Hewlett Packard). Ferroelectricity was investigated using a Sawyer–Tower circuit attached to a computer controlled by standardized ferroelectric test system (Radiant Technology 6000 A). The retention characteristics of the films were measured by observing the time-dependent changes of P* (switching polarization) and P′ (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′, positive pulses were used for both writing and reading.

3. Results and discussion

Fig. 1a illustrates the XRD pattern of the BLT film annealed at 700 °C for 2 h in a conventional furnace. For comparison, XRD pattern of the film annealed in a microwave furnace at 700 °C for 10 min with the susceptor placed below the substrate is shown in Fig. 1b. Platinum coated silicon (1 1 1) substrate peak was observed in the range of 38° < 2θ < 41°, and no impurity phase was identified, indicating that the polycrystalline precursor method allows a single perovskite structure to be obtained. The main difference noted in the XRD spectra of both films comes from the peak heights of the perovskite structure. The short annealing time of the microwave sample may also be insufficient for all the atoms to attain their equilibrium position, affecting the number of peaks in the X-ray diffraction pattern. The film crystallized under influence of microwave energy with the SiC-susceptor placed below it, suggesting that the crystallization initiates at the film–substrate interface leading to a polycrystalline structure. Although the film presents a polycrystalline nature, the versatility of the microwave treatment in controlling the film structure is desirable since the time required to obtain the phase is reduced.

Changes in the surface morphology of the films submitted to different methods of crystallization were followed by AFM measurements. Fig. 2a and b present the micrographs for the films treated at 700 °C for 2 h in conventional furnace and at 700 °C for 10 min in the microwave furnace with the susceptor placed below the substrate, respectively. The morphology of the films annealed at 700 °C in a conventional furnace consists of small spheroidal grains with a plate-like microstructure presenting a crack-free and small porosity surface (Fig. 2a). The film annealed in the microwave furnace presents bigger grains surrounded by a heterogeneous region (center of the film with strong white contrast) which can be caused by the damage suffered by the electrode–film interface. Because the susceptor was placed under the substrate, the film was crystallized by an upward heat flux coming from the film–substrate interface, so these regions may have originated from the stress caused by the dissimilar thermal expansion rates of the substrate and the film. The microwave energy probably plays an important role in addition to simply heating the susceptor, but that role is not yet clear. It worth emphasizing that the microwave treatment leads to films with higher superficial roughness. This is not surprising because the films crystallized in a microwave furnace present a heterogeneous region caused by the stress between substrate and film dissimilar...
Fig. 3. P–E hysteresis loops for BLT thin film annealed at: (a) conventional furnace and (b) microwave furnace.

Hysteresis loops come from the residual stress arising from completely different processing methods adopted in the two cases. Reasons for this are not clear at the moment, but the following factors might contribute to the difference. Firstly, it is reported the polarization switching in films with finer grains is usually more difficult. The domain walls in larger and platelet grains are easier to be switched under external field, while smaller domains in peg-like shape seem more stable. Secondly, ferroelectric property has a strong dependence on film orientation. Different orientation might contribute to different hysteresis behavior. The polar axis of BLT is believed to lie nearly perpendicular to the c-axis, it is impossible to have high remnant polarization for the highly c-axis textured films. This explains the poor ferroelectric response of the film crystallized in the microwave furnace, in which the grains are fairly large and mainly c-axis oriented. It is therefore possible that the higher remnant polarization observed in the film crystallized in the conventional furnace results from the lower population of b-axis grains of the film.

The capacitance versus voltage (C–V) dependence is shown in Fig. 4. The butterfly-shape curves that characterize every ferroelectric material are consistent with the other electrical measurements and the microstructural data. The two peaks, which characterize spontaneous polarization switching, are clearly shown in Fig. 4. Also, the curve displays asymmetry in the maximum capacitance values that can be observed in the vicinity of the spontaneous polarization switching. The curve for the film annealed in the conventional furnace is symmetric around the zero bias axis, indicating that the film contain few movable ions or charge accumulation at the film–substrate interface. These defects affect the switch characteristics of the domains and arising from the interaction between the microwave energy and the platinum electrode. Besides that, the fast heating rate caused by annealing under the influence of microwave energy leads to ordered growth in a c-axis direction where a small polarization is evident. On the other hand, the films annealed in the conventional furnace present a more polycrystalline growth with some preferred orientation in a-axis. These results were similar to those reported by Chon et al. [15]. They observed that BLT thin films deposited on platinum coated silicon substrates and annealed in a conventional furnace showed typical ferroelectric behavior with $P_r$ of 14 $\mu$C cm$^{-2}$ and $V_c$ equal to 10 V. The films crystallized in the conventional furnace is free of imprint phenomena which causes a significant shift along the electric field axis towards the positive side. This indicates that our films contain a small concentration of space charges at the interface film–electrode. Other reason for differences in the shape of thermal expansion rates of the substrate and the film. The average surface roughness value is 8.5 nm with an average grain size of 82 nm for the film annealed in the microwave furnace and 8.0 nm with 140 nm for the film annealed in the conventional furnace.

Hysteresis loops of BLT films are shown in Fig. 3. Ferroelectricity of the lanthanum-doped bismuth titanate thin films was observed with remanent polarization ($P_r$) and a coercive field $E_c$ of 3.9 $\mu$C cm$^{-2}$ and 70 kV cm$^{-1}$ for the film annealed in the microwave oven and 20 $\mu$C cm$^{-2}$ and 52 kV cm$^{-1}$ for the film annealed in conventional furnace, respectively. From the obtained results, we have observed that the films crystallized in the microwave furnace present lower ferroelectric characteristics, mainly due the defects created at the film–substrate interface. These defects affect the switch characteristics of the domains and arising from the interaction between the microwave energy and the platinum electrode. Besides that, the fast heating rate caused by annealing under the influence of microwave energy leads to ordered growth in a c-axis direction where a small polarization is evident. On the other hand, the films annealed in the conventional furnace present a more polycrystalline growth with some preferred orientation in a-axis. These results were similar to those reported by Chon et al. [15]. They observed that BLT thin films deposited on platinum coated silicon substrates and annealed in a conventional furnace showed typical ferroelectric behavior with $P_r$ of 14 $\mu$C cm$^{-2}$ and $V_c$ equal to 10 V. The films crystallized in the conventional furnace is free of imprint phenomena which causes a significant shift along the electric field axis towards the positive side. This indicates that our films contain a small concentration of space charges at the interface film–electrode. Other reason for differences in the shape of
the film–electrode interface (Fig. 4a). On the other hand, when the capacitor was crystallized in the microwave furnace, the $V_m$ voltage at which the capacitance is at its maximum $C_m$ value is not located at the zero bias field, but shifted toward the positive bias region. This suggests that the existence of additional capacitance at the interface arises from the space charge, originating from thermal shock caused by the rapid heating of the SiC susceptor, which favors the accumulation of the static charges (at the interface film–substrate). These static charges are mainly composed of trapped charge \((O^{2-}_{\ell})\) species associated with other defects \((V_{O}^*\) or even defect dipole complexes such as oxygen vacancies associated to bismuth vacancies \((V_{Bi}^0-V_{O}^{2+})\). Besides that, changes in the shape of $C$–$V$ curve can be caused by increase in local current around the nucleation sites which can destroy the film–electrode interface and suppress the nucleation of oppositely oriented domains at the surface. In these films an increase in switching polarization leads to a local increase in conductivity at the film–electrode interface region.

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. Retention, like fatigue, is also dependent on the thickness of the film, nature of the electrodes, microstructure, temperature, etc. Fig. 5a and b shows the long-time retention characteristics of the BLT films annealed in the conventional and microwave furnaces, respectively. As shown \((P^+*)\) and \((P^-)\) was plotted as a function of retention time from 1 s to \(1 \times 10^4\) s at a constant applied electric field of 150 kV cm\(^{-1}\). For the films annealed in a conventional furnace, 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 \(1 \times 10^4\) 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 \(1 \times 10^4\) s, the polarization loss was only about 6% of the value measured at \(t = 1\) s for an applied electric field of 150 kV cm\(^{-1}\). 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. 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 [16]. 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”. On the other hand, for the films crystallized in the microwave furnace, a strong decay is noted at a low infant periods indicating that there exists pinning of domain walls in the film which plays an important role in the polarization decay after 1 s writing. In other words, although the retained charge is similar in films annealed in conventional and microwave furnaces, the pinning of the domains walls at low retention time periods can be prejudicial for memory applications. 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. Conclusions

The microwave furnace reduces significantly the time required to crystallize the BLT phase when compared to a conventional furnace. We have shown that the annealing process affects the polarization mechanism of BLT thin films deposited on Pt/TiO$_2$/SiO$_2$/Si substrates obtained from the polymeric precursor method. Polarization charge compensation by the redistribution of defect charges should be considered to explain the retention loss in lanthanum-doped bismuth titanate thin films for memory applications. The retention failure tests showed that the BLT films deposited on conventional and microwave furnaces have quite good long-time retention characteristics, retaining 94% of the values measured at \(t = 1 \times 10^4\) s for an applied electric field of 150 kV cm\(^{-1}\). However, due to the strong decay at low time periods the films crystallized in a microwave furnace are undesirable for random access memories applications. The source of the strong decay are under investigation and can be attributed to the pinning of domain walls due to the interaction between microwave energy and platinum substrate.

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References