Synthesis and characterization of CaBi\textsubscript{4}Ti\textsubscript{4}O\textsubscript{15} thin films annealed by microwave and conventional furnaces

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Abstract

CaBi\textsubscript{4}Ti\textsubscript{4}O\textsubscript{15} thin films were deposited by the polymeric precursor method and crystallized in a domestic microwave oven and conventional furnace. The films obtained for microwave energy are well-adhered, homogeneous and with good specularity when treated at 700 \textdegree{}C for 10 min. The microstructure and the structure of the films can be tuned by adjusting the crystallization conditions. When microwave oven is employed, the films presented bigger grains with mean grain size around 80 nm. For comparison, films were also prepared by the conventional furnace at 700 \textdegree{}C for 2 h.

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1. Introduction

Ferroelectric materials have been extensively studied due to their potential applications mainly as thin films. The most popular ferroelectric material for nonvolatile memory applications is PbZr\textsubscript{x}Ti\textsubscript{1-x}O\textsubscript{3} (PZT), due to their high Curie temperature and large remnant polarization. In spite of these properties, these materials have serious fatigue degradation problems, which can be solved by changing the electrode [1,2]. As alternative materials, those belonging to the Aurivillius family Bi\textsubscript{2}O\textsubscript{2}\textsuperscript{+} (Am\textsubscript{1-x}BnO\textsubscript{3m+1}), among them SrBi\textsubscript{2}Nb\textsubscript{2}O\textsubscript{9} (SBN), SrBi\textsubscript{2}Ti\textsubscript{2}O\textsubscript{8} (SBT), Bi\textsubscript{4}Ti\textsubscript{3}O\textsubscript{12} (BIT), CaBi\textsubscript{4}Ti\textsubscript{4}O\textsubscript{15} (CBTi144), have received great attention.

CBTi144 is a member of the Aurivillius family, (Bi\textsubscript{2}O\textsubscript{2})\textsubscript{2+} (A\textsubscript{n-1}B\textsubscript{2}O\textsubscript{3n-1})\textsuperscript{2-}, in which A represents mono-, di-, tri-valent ions or a mixture there of, and B represents tetra-, penta- or hexa-valent ions. The compounds such as PbBi\textsubscript{4}Ti\textsubscript{4}O\textsubscript{15}, BaBi\textsubscript{4}Ti\textsubscript{4}O\textsubscript{15} and SrBi\textsubscript{4}Ti\textsubscript{4}O\textsubscript{15}, which have the n value of 4, have been studied for their anisotropic ferroelectricity [3–7]. Also, the thin films of these compounds have been synthesized via the chemical solution deposition techniques, such as the sol–gel and metalorganic decomposition method, and characterized for application to integrated systems such as ferroelectric random access memories because of their high resistance to fatigue [6,7]. Recently, it was reported that highly textured CBTi144 ceramics had enhanced piezoelectric properties [8–10]. The thin film of CBTi144 is expected for additional applications to the piezoelectric filters, resonators, and microelectromechanical systems.

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 [11]. The overall process consists of preparing a coating solution based on metallic citrate polymerization [12]. The precursor film is deposited by dip or spin coating and then treated to eliminate the organic material and synthesize the desired phase. The soft chemical
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 cation).

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 expensively and with greater control than is possible with conventional methods [13,14]. In this work, we investigated the effect of microwave energy to promote a rapid thermal way for film crystallization with the advantage of reducing the time and, in some cases, the temperature of the thermal treatment.

2. Experimental procedure

The preparation of the CBTi144 deposition solution was fully described elsewhere [13,14]. Briefly calcium citrate (Synth, 99%), titanium isopropoxide (Hulss AG, 99%) and bismuth oxide (Aldrich, 99.9%) were used as starting reagents. The metallic cations were dissolved in a citric acid aqueous solution followed by a polyesterification reaction with ethylene glycol. So, the homogeneous distribution of the cations in the polymeric chain leads to a very stoichiometric controlled compound. The films were deposited onto Pt(111)/Ti/SiO$_2$/Si substrates by spinning the deposition solution at 5000 rpm for 30 s. After deposition, the films were treated at 350 °C for 2 h to decompose the organic material by using several cycles of deposition. The films were heat treated at 700 °C for 10 min in a domestic microwave oven (CCE, M301, 2.45 GHz, 900 W) apparatus detailed in Ref. [15] by means of a SiC susceptor in order to absorb the microwave energy and rapidly transfer the heat to the film. The crystallization was performed placing the SiC susceptor below the substrate. For comparison, CBTi144 films were also heat treated for 2 h at the same temperatures in a conventional furnace. After crystallization, the films were characterized by X-ray diffraction (Rigaku, 20-2000), 40 kV and 150 mA from 2θ (10–60°) following the phase evolution. The thickness of the annealed films was determined by using scanning electron microscopy (Topcom SM-300) at the transversal section. In this case back scattering electrons were used. AFM (Digital, Nanoscope 3A) was used to analyze the surface topography and roughness. A 0.5 mm diameter top Au electrode for the electrical measurements was prepared by evaporation through a shadow mask at room temperature. The electric properties were measured by an Au/CBTi144/Pt(111)/Ti/SiO$_2$/Si(100) capacitor structure. The relative dielectric permittivity $\varepsilon_r$ was measured in an impedance analyser (model 4192 A, Hewlett Packard). The leakage current—voltage (I–V) characteristic was determined with a voltage source measuring unit (Radiant Technology 6000 A). The capacitance—voltage characteristic was measured in the metal–ferroelectric-metal (MFM) 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. Ferroelectricity was investigated using a Sawyer–Tower circuit attached to a computer controlled standardized ferroelectric test system (Radiant Technology 6000 A).

3. Results and discussion

XRD pattern of the films treated at 700 °C in conventional and domestic microwave furnace are displayed in Fig. 1. The peaks related to the perovskite phase are well defined in both cases. The films are polycrystalline and free of preferential orientation. This result is not satisfactory from a ferroelectric point of view, since the polarization occurs mainly in the $a$–$b$ plane, but still is a very interesting effect. The use of microwave furnace with the SiC susceptor placed below the film suggests that the crystallization initiates at the film–substrate interface leading to a polycrystalline nature of the film. Although the film presents a polycrystalline nature mainly due to the characteristics of the bottom electrode, the versatility of the microwave treatment in the control of the film structure is desirable since the time required to obtain the phase is reduced.

The changes in the surface morphology of the films submitted to different type of thermal treatment were followed by AFM measurements. Fig. 2a and b depicts the micrographs of the films treated at 700 °C in microwave oven for 10 min and in conventional furnace at 700 °C for 2 h, respectively. The microstructure of the film treated in the microwave furnace presents bigger grains coexisting with very small spheroid
grains. Meanwhile, the film treated at 700 °C in conventional furnace presented a microstructure with small spheroid grains, being crack-free and of small porosity. The average surface roughness is 7.0 nm with an average grain size of 80 nm for the film thermal treated in the microwave oven and 3.2 and 46 nm for the film thermal treated in the conventional furnace. It is worth emphasizing that the microwave treatment leads to films with higher superficial roughness. This is not surprising since the films crystallized in a microwave oven present some bigger grains coexisting with very small spheroid grains, while those obtained in a conventional furnace, are normally small rounded grains.

**Fig. 2.** AFM images for CaBi$_4$Ti$_4$O$_{15}$ thin film annealed at 700 °C for (a) 10 min and (b) 2 h.

**Fig. 3.** Dielectric permittivity and dissipation factor for CaBi$_4$Ti$_4$O$_{15}$ thin films annealed at 700 °C for (a) 10 min and (b) 2 h.

The $I$–$V$ measurements were taken using the Radiant Technology 6000 A tester in the current–voltage mode, with the voltage changing from 0 to 10 V. Low leakage current density is very important for memory device applications. A typical
leakage current density \( (J) \) vs the electric field \( (E) \) for CBTi144 thin film is given in Fig. 4. The curve was recorded with a voltage step width of 0.1 V and elapsed time of 1.0 s for each voltage. Two clearly different regions are observed. The current density increases linearly with the external electric field in the region of low electric field strengths, suggesting an ohmic conduction. At higher field strengths the current density increases exponentially, which implies that at least one part of the conductivity results from Schottky or Poole–Frenkel emission mechanism. The leakage current density at 1.0 V is close to \( 10^{7} \) A/cm\(^2\) for the film thermal treated in the microwave oven and close to \( 10^{7} \) A/cm\(^2\) for the film thermal treated in the conventional furnace. Since the conductivity is strongly affected by the characteristics of the film–electrode interface, the surface morphology of CBTi144 thin films is one of the major factors determining the leakage current in capacitors. The low leakage current value obtained for the film thermal treated in the conventional furnace can be attributed to the small surface roughness as was observed by AFM in Fig. 2.

The \( C-V \) results are shown in Fig. 5. The butterfly-shaped 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. 5. Also, the \( C-V \) curve displays a symmetry in the maximum capacitance values that can be observed in the vicinity of the spontaneous polarization switching. The \( C-V \) curve for the film thermal treated in the conventional furnace is symmetric around the zero bias axis, indicating that the films contain few movable ions or charge accumulation at the film–electrode interface. A slight change in capacitance values is observed for the films thermal treated in the microwave oven indicating that the platinum reflects the microwave energy leading to a overheating in some specific film area affecting the film–electrode interface and therefore the domain switching.

Hysteresis loops of CaBi\(_4\)Ti\(_4\)O\(_{15}\) films deposited on platinum coated silicon substrates and thermal treated at different conditions are shown in Fig. 6. A remnant polarization equal to 4 \( \mu \)C/cm\(^2\) and drive voltage of 2.7 V for the film thermal treated in the microwave oven and 12 \( \mu \)C/cm\(^2\) and to 2.2 V for the film thermal treated in the conventional furnace was acquired. Our findings suggest that the crystallization of CaBi\(_4\) Ti\(_3\)O\(_{15}\) films with platinum as a bottom electrode induces
a overheating in the film. This overheating is mainly caused by the thermal properties of the platinum bottom electrode. These results were similar to those reported by Kato et al. [20]. They observed that CaBi$_4$Ti$_4$O$_{15}$ thin films deposited on platinum coated silicon substrates showed typical ferroelectric behavior with $P_r$ of 7.1 µC/cm$^2$ and drive voltage of 2.8 V. The absence of imprint which causes a significant shift along the electric field axis towards the positive side indicates that our films present a small concentration of space charges in the electrode film interface. Our results indicate that the crystallization of CaBi$_4$Ti$_4$O$_{15}$ films by using microwave furnace reduces the electrical properties due to the overheating caused by the strong interaction between the bottom electrode and the source energy. This effect was not observed in films crystallized by the conventional furnace. In order to evaluate the efficiency of the microwave oven not only in the time required to obtain the phase but also in the films orientation is necessary to obtain bottom electrodes from conductors oxide.

4. Conclusion

A domestic low power microwave oven was used for crystallization of CaBi$_4$Ti$_4$O$_{15}$ films prepared by the polymeric precursor method. The films obtained are well-adhered and homogeneous even when treated at 700°C for 10 min. This method allows obtaining polycrystalline films with bigger grains surrounded by small spheroid grains when the susceptor is placed below the substrate. The time required for well crystallized films is drastically reduced (10 min) compared with the conventional way (normally 2 h). This is of great advantage for preventing undesired reactions between the film and the substrate and loss of stoichiometry of the film. Although the time required to obtain the film is reduced, the use of oxide electrode seems to be adequate to crystallize the CaBi$_4$Ti$_4$O$_{15}$ films in the microwave furnace.

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References