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PZT thin films produced by oxide precursors and crystallized by conventional and RTA process

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Abstract

Physical properties of ferroelectric thin films can be dependent on the preparation and crystallization process. This work reports studies on crystallinity, ferroelectric and dielectric properties of PZT thin films produced by an oxide precursor method and crystallized by conventional and RTA process. Grain sizes were estimated by scanning electron microscopy (SEM) to be around 100 nm. Films were deposited on Si and Pt/Si substrates and crystallized at 700°C for different times. For film crystallized by conventional furnace the remanent polarization (P_r) was about 7.8 μC/cm^2 and the coercive field (E_c) was 99 kV/cm. On the other hand, for PZT film crystallized at the same temperature by the RTA method, the remanent polarization and coercive field were about 16 μC/cm^2 and 73 kV/cm, respectively.

Keywords: Ferroelectric properties; Films; Perovskites; PZT

1. Introduction

Lead zirconate titanate, $PbZr_{1-x}Ti_xO_3$ (PZT), is probably the most studied perovskite-type ferroelectric material as bulk ceramics as well as thin films. PZT solid solution ceramics are known by excellent piezoelectric, dielectric and pyroelectric properties.[1] For compositions close to $x \cong 0.47$, region defined by Jaffe et al.[1] as morphotropic phase boundary (MPB), characterized in the last 40 years as being a coexistence of tetragonal and rhombohedral phases of PZT, most of the properties show their maximum values. The recent discovery of a stable monoclinic phase in the PZT system close to MPB[2,3] provides a new perspective to explain some results attributed before to the coexistence of tetragonal and rhombohedral phases, for example, the high piezoelectric response in PZT ceramics.[4] Thus, PZT remains as important and actual technological material, mainly explored as thin film.

There are many different deposition methods of PZT thin films such as DC planar magnetron sputtering,[5] RF sputtering,[6] sol–gel[7] and others. Among the various techniques to prepare ferroelectric thin films, chemical based processes are promising routes for integration of thin layer devices. Solution deposition enables better stoichiometric control of complex compositions other than physical techniques such as RF sputtering, laser ablation[8] or chemical vapour deposition (CVD).[9]

Recently, we proposed a hybrid chemical method for the preparation of ferroelectric thin films based on oxide precursors.[10] The oxide precursor method is an alternative chemical method for the preparation of ferroelectric thin films starting on a pre-calcination of oxides or carbonates. This method was applied initially to prepare PZT thin films of good quality. The method was also applied to produce other ferroelectric thin films such as bismuth titanate, $Bi_4Ti_3O_{12}$.[11]

This work reports studies on PZT thin films prepared by the oxide precursor method, with a Zr/Ti molar ratio of 53/47. Films were crystallized using conventional electric furnace and rapid thermal annealing (RTA). The main difference between RTA and conventional furnace crystallization is that the rise time for heating to

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the desired temperature is very short enabling to reduce the overall annealing period. This leads to reduction in surface damage and minimization of the film-substrate interaction.

2. Experimental procedure

Using the method that was described in our previous paper,[10] films of polymeric resin were deposited at room temperature on Si and Pt/Si substrates by spin coating. Films were crystallized using conventional furnace and RTA processes at heating rates of 5°C/min and 50°C/s, respectively. Using a conventional furnace, films were crystallized at 700°C for 1–2 h and using RTA at 700°C for 60 s.

The crystallographic structure of the films was examined by XRD analysis, using CuK_α radiation at room temperature. The dielectric constant and dissipation factor were measured using a HP 4194A impedance analyzer. To measure the dielectric constant and dissipation factor a small ac signal of 10 mV amplitude was applied across the sample while the frequency was swept from 100 Hz to 10 MHz. The electric field ($\sim$ 0.18 kV/cm) used for dielectric measurements was considerable smaller than the coercive field of the PZT such that polarization state remains unchanged and effects of the domain wall contribution are minimized. The ferroelectric properties include measurements of P–E hysteresis loops obtained at a frequency of 100 Hz. These properties were measured using a Sawyer–Tower circuit attached to a Tektronix 2232 digital oscilloscope. Scanning electron microscopy (SEM) was used to study the surface morphology of the PZT films. A micrograph was made using a JEOL JSM-5800 microscope. All measurements were conducted at room temperature.

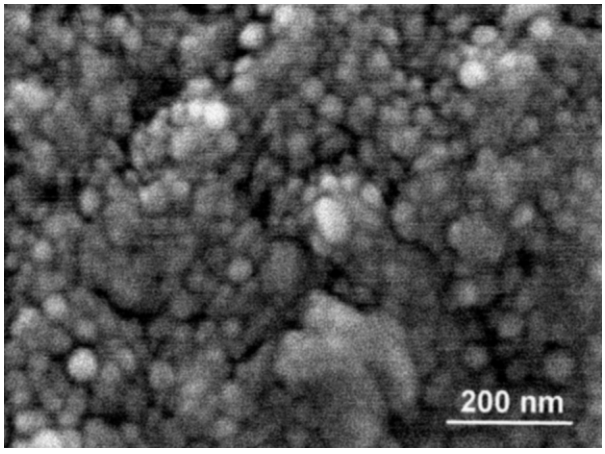

Fig. 1. Scanning electron microscopy of the PZT thin film deposited on Pt/Si substrate and crystallized in conventional furnace at 700°C for 1 h.

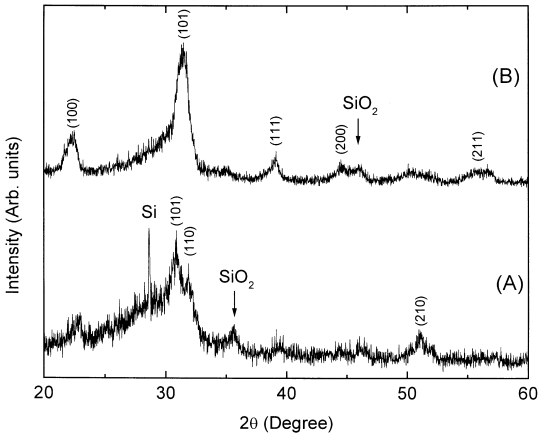

Fig. 2. X-ray diffraction pattern of the PZT thin films crystallized at 700°C for 2 h (A) and at 700°C for 60 s (B). Films were deposited on Si substrate.

3. Results and discussion

Crystallized films were crack-free, uniform and adhered well on both substrates. Fig. 1 shows the surface morphology of a PZT film, deposited on the Pt/Si substrate and crystallized in a conventional furnace at 700°C for 1 h. It can be seen that the film exhibits a dense microstructure. The film shown in Fig. 1 was prepared with 10 layers coating. Thickness of the film was about 550 nm. The grain size of the film was estimated to be 100 nm, on average. The film prepared by RTA presented essentially the same microstructure as the film prepared in conventional furnace.

Fig. 2 (A) shows the XRD pattern of a PZT film on Si substrate, fired at 700°C for 2 h using a conventional furnace. In this figure, we can identify peaks attributed to tetragonal phase of the PZT and substrate (Si). The lattice constants a_T and c_T were calculated using the (100), (101), (110) and (210) peaks and were found 4.02 and 4.18 Å, respectively. Thus, the obtained tetragonality factor and the volume of tetragonal unit cell were $c_T/a_T \cong 1.04$ and 67.55 Å.[3] This c_T/a_T ratio is very close to those reported for bulk PZT ceramics with the same composition[1] and PZT thin films produced by DC magnetron sputtering.[5] Fig. 2 (B) shows the XRD pattern of PZT film annealed at 700C for 60 s using RTA. The lattice constants for PZT tetragonal phase were $a_T = 4.04$ and $c_T = 4.06$ Å, $c_T/a_T \cong 1.01$ and the volume of unit cell equal to 66.27 Å.[3]

Based on previous results, we can see that films crystallized by the RTA process presented better crystallization than films crystallized in conventional furnace. The definition of XRD peaks in Fig. 2 (B) confirms this. Considering Fig. 2 (A), the presence of the larger band for 2θ between 24 and 34°, characteristic of amorphous material, suggested that this film, crystallized in a

conventional furnace, may be only partially crystallized. Also as was observed the films crystallized by the RTA process [Fig. 2(B)] presented a more compact tetragonal unit cell. This fact may be attributed to the faster rise time of RTA to reach the desired crystallization temperature. For crystallization in a conventional furnace, due to the smaller heating rate (~5°C/min), the films start to crystallize at temperatures lower than 700°C and this fact may make the final densification difficult. That means, at 700°C the film is already partially crystallized. Similar characteristics were also observed on PZT thin films processed by metallo-organic decomposition, crystallized by the RTA process.[12]

The structure of the films deposited on the Pt/Si substrate was also studied using XRD. Fig. 3 shows XRD patterns of the PZT films crystallized at 700°C for 1 h [Fig. 3(A)] and 700°C for 60 s [Fig. 3(B)] by conventional and the RTA method, respectively. In both cases, based on (100), (101) and (200) peaks in Fig. 3, the lattice constants a_T and c_T were calculated for film crystallized in conventional furnace and the RTA process. The obtained tetragonality factors were $c_T/a_T \cong 1.01$ ($a_T = 4.05$ and $c_T = 4.08$ Å) and $c_T/a_T \cong 1.01$ ($a_T = 4.07$ and $c_T = 4.09$ Å), respectively. These c_T/a_T ratio was slightly smaller than those calculated for films crystallized on Si in conventional furnace, but films deposited on Pt/Si, crystallized by conventional furnace and RTA, presented essentially the same tetragonality factor. Differences observed here in tetragonality may be related with stress in films, since heating rates and substrates are different.

The frequency dependence of the dielectric constant (ε) and dissipation factor (tanδ) is shown in Fig. 4 for PZT films crystallized at 700°C for 1 h [Fig. 4(A)] and at 700°C for 60 s [Fig. 4(B)]. From Fig. 4(A), ε and tanδ values at a frequency of 100 kHz were 358 and 0.039, respectively. Considering the same frequency in Fig. 4(B), these values were 611 and 0.026, respectively. The main difference observed in both graphics is associated with the dielectric constant and dissipation factor at higher frequencies. Considering the film crystallized in conventional furnace (700°C for 1 h) the dielectric constant was relatively unchanged up to frequencies about 1 MHz, after that it dropped to a small value (145 at 10 MHz). At around the same frequency, the dissipation factor increased substantially up to 0.743. Dielectric constant of the film processed by RTA was relatively unchanged over all the measured frequency range [Fig. 4(B)]. This film did not show dispersion at high frequencies, such as that observed for film crystallized in conventional furnace. This fact may be associated with a better crystallization in the films prepared by RTA. Similar result was reported in others PZT films.[12] The observed frequency dispersion, often characterized by a Maxwell–Wagner type, is probably associated with interface effects. The obtained results suggest that films prepared by RTA process were more effective in

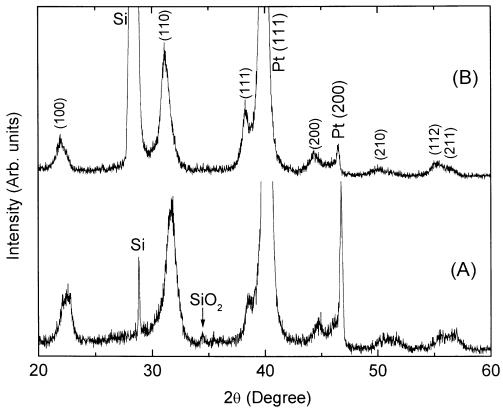

Fig. 3. X-ray diffraction pattern of the PZT thin films crystallized at 700°C for 1 h (A) and at 700°C for 60 s (B). Films were deposited on Si/Pt substrate.

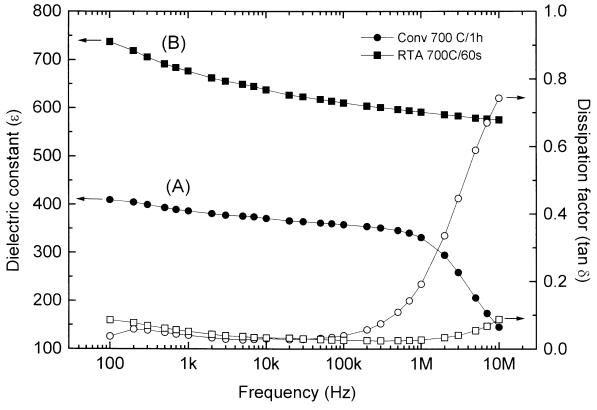

Fig. 4. Dielectric constant and dissipation factor as a function of frequency for PZT film deposited on Au/PZT/Pt/Si configuration. Films were annealed in conventional furnace at 700°C for 1 h (A), and by RTA at 700°C for 60 s (B).

minimizing the interface effects during crystallization reactions. Similar behavior was also reported in other ferroelectric films.[13]

Ferroelectric properties of PZT films were obtained from hysteresis loops for films crystallized on Pt/Si substrates. Fig. 5(A) and (B) shows hysteresis loops for film crystallized in conventional furnace at 700°C for 1 h and using RTA at 700°C for 60 s, respectively.

For film crystallized in conventional furnace [Fig. 5(A)] the remanent polarization (P_r) was about 7.8 μC/cm^2 and the coercive field (E_c) of 99 kV/cm. On the other hand, for PZT film crystallized by the RTA method [Fig. 5(B)], the remanent polarization and coercive field were about 15.7 μC/cm^2 and 73 kV/cm, respectively. For PZT films the values of P_r and E_c ranged from 1 to 7 μC/cm^2 and 26 to 80 kV/cm, respectively, obtained by sol–gel[7] or 3–30 μC/cm^2 and 25–64 kV/cm, for films obtained by dc magnetron sputtering.[5] As we can see, the remanent polarization presented by the film crystallized by the RTA process is almost two times greater

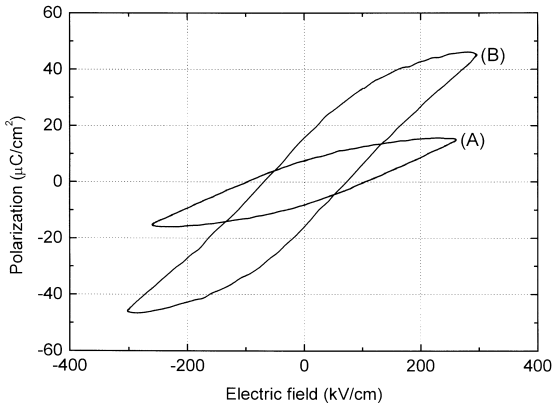

Fig. 5. Hysteresis loops of the PZT thin films measured at 100 Hz. Film crystallized in conventional furnace at 700°C for 1 h (A) and crystallized by RTA process at 700°C for 60 s (B). Films were deposited on Pt/Si substrate.

than that obtained for film crystallized in conventional furnace while the coercive field was reduced to about 2/3 in magnitude. There are many works about ferroelectric properties as a function of grain size for different ceramic materials.[14,15] In general, the observed slightly lower P_r and higher E_c in films may be associated with smaller grain size in comparison with bulk ceramics.[1] In the specific case of this work, films prepared by different ways presented, in average, essentially same grain size. Thus, improved ferroelectric behavior may be attributed to improved density, crystallization and reduction off the substrate-film interface of the PZT films prepared by the RTA process.

4. Conclusions

PZT films were deposited by an oxide precursor method and crystallized in conventional furnace and RTA method. Studies on crystallinity, dielectric and ferroelectric properties were carried out to understanding the effect of crystallization process on these properties. For films deposited on Si substrates, film crystallized by RTA process presented better crystallization than film crystallized by conventional furnace. For films deposited on Pt/Si substrates, better dielectric and ferroelectric properties (higher P_r and lower E_c) were observed in film crystallized by the RTA process than films crystallized in conventional electric furnace. These data will be fundamental to a future optimization of ferroelectric properties of these films.

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