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Ceramics International 30 (2004) 1509–1512

CERAMICS INTERNATIONAL

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A new and rapid heat-treatment process for fabricating lead zirconate titanate thin film

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Received 4 December 2003; received in revised form 10 December 2003; accepted 22 December 2003

Available online 7 May 2004

Abstract

A new and rapid heat-treatment process for fabricating lead zirconate titanate, $Pb(Zr_{0.52}Ti_{0.48})O_3$(PZT), ferroelectric thin films has been developed. The main equipment of this heat-treatment process is termed caterpillar furnace. The furnace is divided into three parts, including preheating, heating and cooling. This process offers several advantages over conventional thermal annealing, including rapid heat-treatment process (<10 min every layer film), pure film structure and better reproducibility. The precursor solution was synthesized by mixing and reacting lead acetate trihydrate, titanium isopropoxide, tetrabutyl zirconate, acetylacetone and 2-methoxyethanol. The precursor was investigated by DSC–TG, and the PZT thin film was investigated by XRD. XRD analysis shows that the thin films possess single-phase perovskite-type structure. A dielectric constant and loss tangent of thin film were measured about 231 and 0.02 at 10 kHz, respectively. The capacitance–voltage (*C–V*) and hysteresis loops of PZT films showed that the films possess fine ferroelectric properties.

Keywords: Ferroelectric; PZT thin film; Caterpillar furnace; Rapid heat-treatment process

1. Introduction

Recently, Ferroelectric thin films have received a great deal of attention in the preparation and application, especially lead zirconate titanate (PZT). Because of its excellent properties, PZT thin film has been widely used for preparing ferroelectric, piezoelectric, and pyroelectric devices [1–4], Among all the compositions of PZT, $Pb(Zr_{0.52}Ti_{0.48})O_3$, which is near the morphotropic phase boundary (MPB), is the most important one because of its excellent ferroelectric and electro-optic properties. Recently, PZT ferroelectric thin films have been prepared by using various techniques such as sol–gel [5], pulse laser deposition [6], metalloorganic chemical vapor deposition [7], and radio-frequency sputtering [8]. Among these various preparation methods of PZT thin films, the sol–gel process has gained much interest. Because of its many advantages for preparing thin films, including: (1) it is a simple process; (2) excellent control of the stoichiometry can be maintained; (3) a homogeneous film can be formed over a large area; and (4) a relatively low processing temperature is needed [9].

In this paper, the PZT thin films were prepared by sol–gel method. The impact of a new and rapid heat-treatment conditions on the structures and dielectric properties of the films were discussed. A new caterpillar furnace has been used to heat the PZT thin film in the experiment.

2. Experiment

PZT (Zr:Ti = 52:48) thin films were prepared using a sol–gel process. Lead acetate trihydrate, titanium isopropoxide, and tetrabutyl zirconate were used as raw materials, 2-methoxyethanol was used as solvent, and acetylacetone was used as chelating agent. The precursor preparing processes were: (1) chelating the titanium isopropoxide with acetylacetone in a mole ratio of 1:1 and stirring the mixture at room temperature for 2 h; (2) lead acetate trihydrate was dissolved in 2-methoxyethanol and dehydrated repeatedly at 124 °C for 30 min. After cooling to 70 °C, zirconium *n*-propoxide and titanium isopropoxide chelated with acetylacetone were added; (3) the resulting solution was refluxed at 132 °C for 2 h. Finally, light yellow PZT precursor solution was obtained. The sols were passed through a 0.22 μm in-line syringe filter directly before film preparation.

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doi:10.1016/j.ceramint.2003.12.126

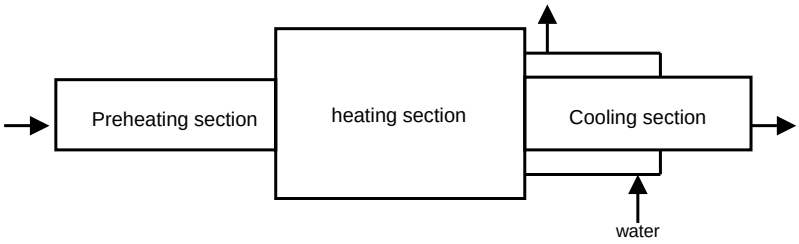

Fig. 1. Schematic diagram of the set-up for caterpillar furnace.

The precursor solution was spin-coated on a Pt(1 1 1)/Ti/SiO_2/Si substrates at 3000 rpm for 20 s. The gel films were put in the caterpillar furnace to evaporate and burn out the organic. Fig. 1 shows the schematic diagram of the set-up for caterpillar furnace. This procedure was repeated seven to eight times before further treatment. Experimentally, the temperature of heating section in the caterpillar is 450 °C. The sample moves from preheating section to cooling section in a slow speed and staying in the heating section for 5 min. Single layers with smooth surface can be prepared by subsequent coating/firing cycles. When a desired thickness was achieved, the film was heated to 600 °C in a rate of 3 °C/min and annealed for 60 min. The thickness of each layer was up to 90 nm with the 0.5 M PZT solutions. The resulting film was covered with Au (1 mm diameter) as top electrode that deposited by sputtering through a mask onto the film surfaces.

3. Results and discussion

TGA/DSC curves of the gel were measured at a heating rate of 10 °C/min, using a Netzsch STA 449C apparatus and Al_2O_3 as a reference. Fig. 2 shows the TG and DSC curves. As can be seen, the TG curve shows a strong weight loss between 200 and 350 °C, attributed to decomposition and vaporization of organic components. At 500 °C, 23% of the starting gel remains as decomposition products and weight loss has ceased. In the DSC curve three exothermic peaks are present at 238.3, 320.2 and 477.2 °C, respectively. The two peaks at 238.3 and 320.2 °C was probably due to the decomposition and vaporization of organic components. In the range of 400–600 °C, an expanded exothermic peak can be observed in the DSC spectrum. This peak is predominantly caused by the crystallization of pyrochlore phase and the phase transformation into perovskite phase [10]. In order to achieve a good resolution to detect the crystallization peak, the TG and DSC curves was obtained from room temperature to 700 °C, after completely burning of organic components. Based on these results, the heat treatment for each single layer at 450 °C for 5 min was applied to achieve maximum decomposition and vaporization of organic compounds before crystallization.

The structure of the film after annealing at different temperatures for crystallization was examined by X-ray diffraction (XRD) analysis. XRD patterns of the thin films are shown in Fig. 3. At 560 °C, the two characteristic phases of perovskite and pyrochlore peaks of PZT coexist in the

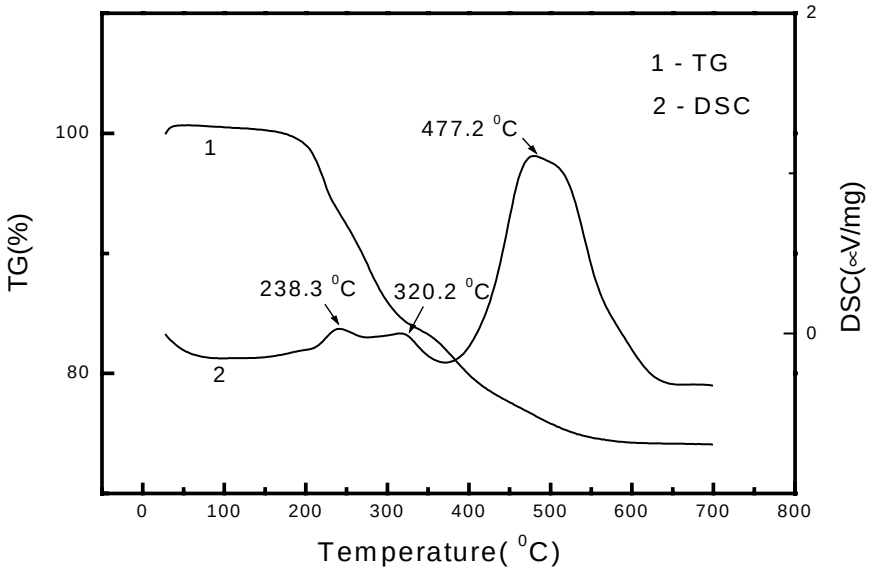

Fig. 2. The TG and DSC curves of PZT dried gels.

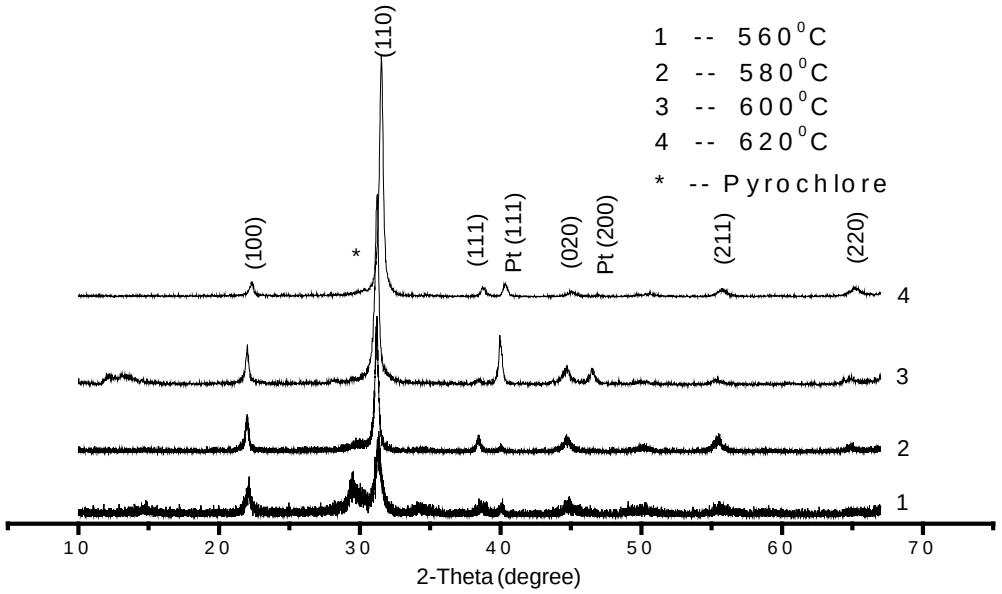

Fig. 3. X-ray diffraction patterns for the PZT thin film, annealed at various temperature for 1 h.

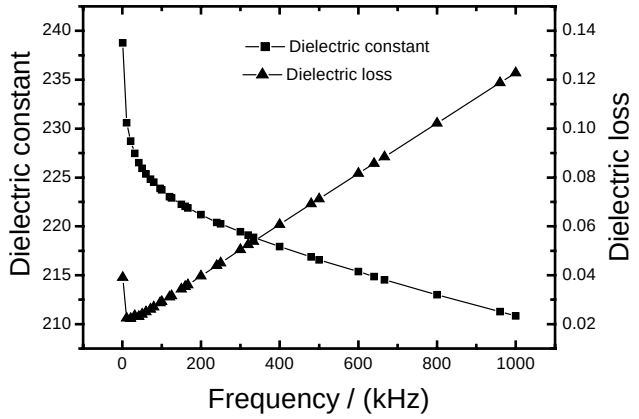

Fig. 4. The dielectric constant and dissipation loss as a function of frequency for PZT thin film, annealed at 600 °C for 1 h.

XRD pattern. It is evident that the pyrochlore phases are gradually disappearing with increasing of temperature. As the temperature increases above 600 °C, continuing refinement of peak shapes and intensity are observed, indicating crystallite growth of the PZT thin films is continuing.

The electric properties of the PZT thin film were evaluated using a capacitor structure of metal–ferroelectric-metal, onto which the Au (1 mm diameter) top electrode was deposited by sputtering through a mask onto the film surfaces. The dielectric properties of the PZT thin film annealed at 600 °C for 1 h are shown in Fig. 4. The dielectric constant and dissipation factor measured as a function of frequencies in the range of 1 kHz to 1 MHz. It is evident that the dielectric constant showed a decline and the dissipation factor has a minimum value in the 10 kHz. The dielectric constant and dissipation factor are 231 and 0.02 at 10 kHz, respectively.

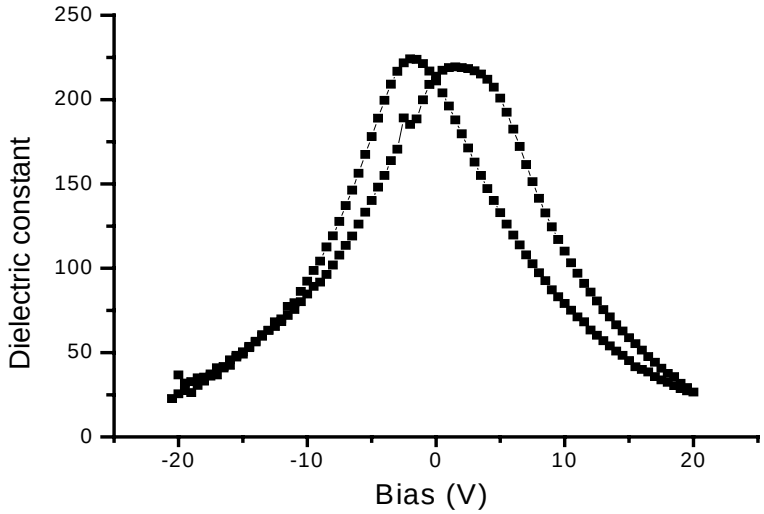

Fig. 5. The *C–V* curve for PZT film, annealed at 600 °C for 1 h.

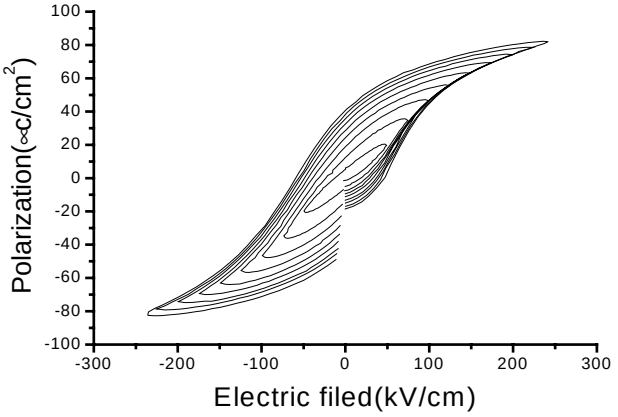

Fig. 6. The hysteresis loop for PZT thin film, annealed at 600 °C for 1 h.

The capacitance–voltage (*C–V*) properties were measured using a Hewlett-Packard (4284A) precision LCR meter at room temperature. The *C–V* characteristic curve of the PZT thin film annealed at 600 °C for 1 h are shown in Fig. 5. A small ac signal of 10 mV amplitude and 100 kHz frequency was applied across the sample while the dc electric field was swept from positive bias to negative bias and back again. Two maxima, which are due to ferroelectric polarization reversals, are clearly seen in Fig. 6. The two observed maxima can be regarded as double the coercive field (E_c). From this figure, E_c was obtained as 45.7 kV/cm. Generally, the coercive fields determined from the *C–V* measurements were somewhat smaller than E_c determined from the hysteresis loop measurements, due to the dependence of E_c on the applied voltage and frequency. In addition, the capacitance values of different dots on same substrate varied by less than 3% [11], indicating a good degree of uniformity of the thicknesses of the films.

Hysteresis loops were observed at 300 Hz using a Sawyer-Tower circuit (RT66A) at room temperature. Fig. 6 shows a typical *P–E* hysteresis loop for a film annealed at 600 °C for 1 h. The remanent polarization (P_r) and the coercive field (E_c) are 24.5 μC/cm^2 and 50 kV/cm, respectively. It is obvious that PZT thin films heat treated through caterpillar furnace possess fine ferroelectric properties.

4. Conclusion

Crack-free and uniform PZT thin films have been prepared by using sol–gel method and heat treated through a new caterpillar furnace. XRD analysis shows that the films possess single-phase perovskite-type structure, no pyrochlore phase exists in the films. The dielectric properties showed that the dielectric constant and dissipation factor are 231 and 0.02 at 10 kHz, respectively. The capacitance–voltage and hysteresis loops of PZT films showed that the films possess fine ferroelectric properties.

Acknowledgements

This work was supported by Shanghai Nano Fundamental Committee under contract No. 0152NM038 and the University Key Studies of Shanghai.

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