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Ceramics International 39 (2013) S513–S516

CERAMICS INTERNATIONAL

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Preparation and energy-storage performance of PLZT antiferroelectric thick films via sol–gel method

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Available online 16 October 2012

Abstract

In this work, sol–gel-derived $Pb_{0.97}La_{0.02}(Zr_{0.97}Ti_{0.03})O_3$(PLZT 2/97/3) antiferroelectric (AFE) thick films were fabricated on $LaNiO_3$-bottom electrodes through a two-step heat-treatment process. The effects of the heat-treatment process on the crystalline structure and the energy-storage performance of the AFE films were investigated in detail. While all the PLZT 2/97/3films crystallized into a pure perovskite phase, the film pyrolyzed at 600 °C shows a relatively more homogeneous surface morphology. As a result, the film pyrolyzed at 600 °C possesses the highest energy-storage efficiency of 64.4%. However, the film pyrolyzed at a lower temperature exhibits a larger energy storage density because of its large saturated polarization.The maximum energy storage density of 20.1 J/cm^{3}was obtained at 1158 kV/cm for the films pyrolyzed at 550 °C.

Keywords: A. Sol–gel processes; C. Dielectric properties; D. PLZT; E. Capacitors

1. Introduction

With the rapid development of current microelectronic devices toward the trend of miniaturization, lightweight and integration, capacitors with a larger energy-storage density are eagerly desired because they occupy the largest proportion of volume and weight in power system [1]. Generally speaking, antiferroelectrics (AFEs) usually display an improved energy-storage performance, compared with ferroelectrics (FEs) and linear dielectrics (DEs), due to a higher saturated polarization and a smaller remnant polarization [2–4]. Besides, AFE materials also possess faster charge–discharge speed and enhanced fatigue against performance owing to their unique field-induced AFE-FE phase switching [5]. Therefore, it is expected that AFEs have the potential for applications in high-energy-storage capacitors.

Recently, the energy-storage behaviors of lead zirconium oxide (PZ) based on AFEs in bulk ceramics and thin films have received increasing attention [1,6,7]. However, AFE bulk ceramics are usually not compatible with semiconductor integrated circuit technology. In addition, the higher operating voltage also makes AFE bulk ceramics unsuitable for practical applications. Although AFE thin films possess a lower driving voltage and are easily integrated, their overall stored energy is quite small because of thickness limitation. Comparatively, AFE thick films could avoid above disadvantages that are existed in thin films and bulk ceramics. Therefore, the investigation on the energy-storage performance in AFE thick films should be more meaningful for driving their application in capacitors.

However, the energy-storage behaviors in AFE thick films have rarely been reported because it is difficult to obtain uniform and crack-free thick films. It is believed that the quality of the thick films is strongly affected by their fabrication procedure. In this paper, sol–gel-derived lanthanum modified lead zirconate titanate AFE thick films with improved microstructure are deposited on $LaNiO_3$/Si(100) substrates by an optimum two-step heat-treatment process.The energy-storage properties of AFE thick films are investigated.

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http://dx.doi.org/10.1016/j.ceramint.2012.10.124

2. Experimental procedure

$Pb_{0.97}La_{0.02}(Zr_{0.97}Ti_{0.03})O_3$ (PLZT 2/97/3) thick films with stable AFE phase were prepared by a sol–gel method. Lead acetate trihydrate, lanthanum acetate, zirconium propoxide, and titanium iso-propoxide were used as raw materials. Acetate was selected as a solvent. In order to compensate the lead loss during annealing and to prevent the formation of a pyrochlore phase, 20% excess lead were added. The concentration of the final solution was about 0.5 M. More detailed synthesis of the sol could be found in our recent work [8]. The PLZT 2/97/3 solution was aged for 24 h.

PLZT 2/97/3 films were deposited on $LaNiO_3$/Si(100) substrates by the spin-coating method. It should be noted here that $LaNiO_3$ bottom electrodes on Si(100) substrates were also prepared by a chemical solution deposition route, which was similar to the reference [9].The $LaNiO_3$ layer was about 150-nm thick and showed a random orientation. Each PLZT 2/97/3 layer was spin-coated at 3000 rpm for 40 s. In order to obtain dense and crack-free thick films, a two-step heat-treatment process was adopted in this work. Namely, each wet layer was first fired at temperature A ($A = 350$ °C) for 10 min, and then pyrolyzed at higher temperature B for 10 min. Here, the selected temperature B was 550, 600 and 650 °C. The spin coating and heat treatment processes were repeated several times to obtain the desired thickness. A capping layer consisting of 0.4-M PbO precursor solution was coated before the films were finally annealed at 700 °C for 30 min to form a perovskite phase.The final thickness of the PLZT 2/97/3 thick films was about 1.7 μm, as determined from the cross-section picture.

Phase structure of the thick films was examined by a Bruker D8X-ray advance diffractometer (XRD) at a rate of 2°/min within the 2θ ranging from 20°to 60°. The surface microstructure and cross section of AFE thick films were observed by scanning electron microscopy (SEM). For the measurements of electrical properties,gold pads of 0.2 mm in diameter were coated on the films surface as top electrodes by dc sputtering.The polarization-field hysteresis (P–E) loops of PLZT 2/97/3 AFE thick films were measured at 1 kHz by a Radiant Technology Ferroelectric tester. The energy-storage performance of these films was studied from the P–E results.

3. Results and discussion

Fig. 1 gives the XRD patterns of PLZT 2/97/3 AFE thick films with different pyrolyzed temperatures of 550, 600 and 650 °C. All the thick films had crystallized into a single perovskite phase after final annealing at 700 °C for 30 min. The obtained films show a random orientation, and stronger peaks lie along the (110), (111), and (211) directions in all the cases. No obvious difference in the XRD curves was detected, indicating that the pyrolyzed temperature had little influence in the phase structure of AFE thick films. The surface pictures of PLZT 2/97/3 films are also shown in Fig. 1. It is seen that the surface microstructures of the obtained films had a close

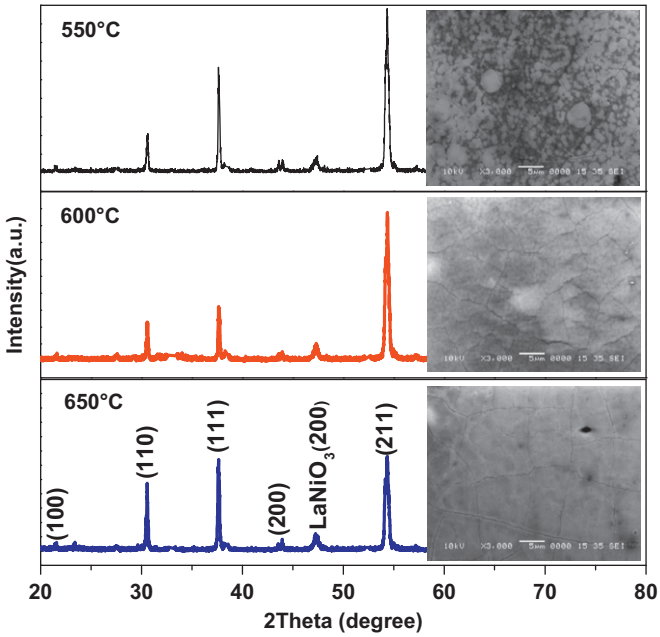

Fig. 1. XRD patterns and surface SEM pictures of PLZT 2/97/3 AFE thick films pyrolyzed at 550, 600 and 650 °C.

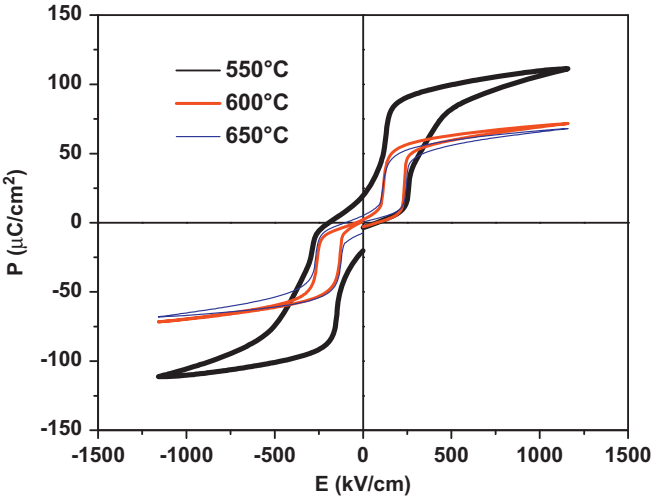

Fig. 2. The room-temperature P–E loops of PLZT 2/97/3 AFE thick films pyrolyzed at 550, 600 and 650 °C.

relation with their pyrolyzed temperature. Comparatively, the films pyrolyzed at 600 °C possessed a more uniform and denser surface structures. It could be predicated that the final energy-storage behaviors of the three samples would be unavoidably affected by their different microstructures.

The P–E loops of AFE thick films measured at 1158 kV/cm at room temperature are given in Fig. 2. The double P–E loop characteristic demonstrates the AFE nature of PLZT 2/97/3 films. As the electric field increases, all the PLZT AFE films display a sudden increase in polarization, representing a sharp phase switching from AFE to FE phases. The larger remnant polarization and saturated polarization values were observed in the films pyrolyzed at 550 °C, which was supposed to be caused by the interface layer, space charge and some unstable

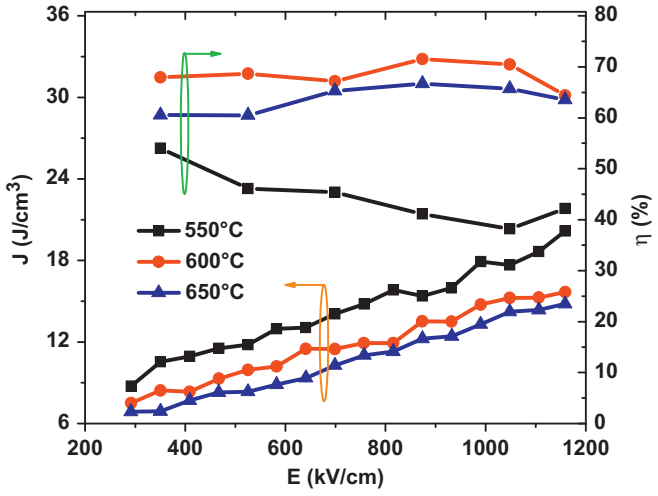

Fig. 3. The electric-field-dependent energy-storage density (J–E) and energy-storage efficiency of PLZT 2/97/3 AFE thick films pyrolyzed at 550, 600 and 650 °C.

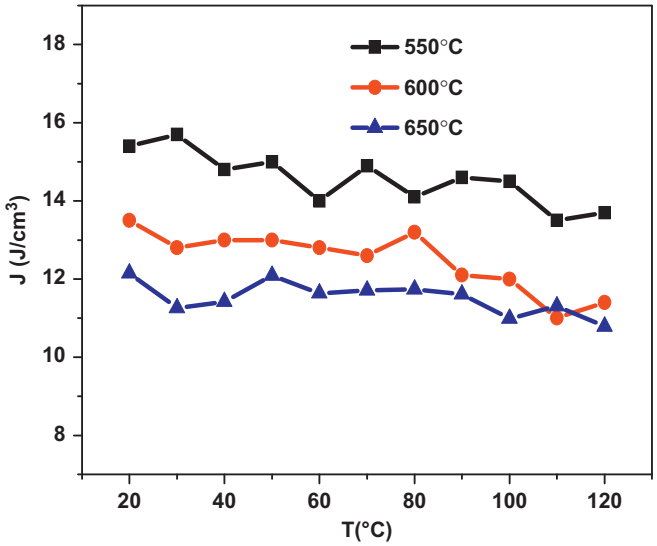

Fig. 4. The temperature-dependent energy-storage density (J–T) of PLZT 2/97/3 AFE thick films measured at E=873 kV/cm.

AFE regions. As the pyrolyzed temperature increasing, the hysteresis loops become sharper and thinner, indicating a reduction of the hysteresis loss. The saturated polarization values were 111.2, 71.7, and 68.0 μC/cm^2 for the thick films pyrolyzed at 550, 600 and 650 °C, respectively.

In order to compare the energy-storage performance of PLZT 2/97/3 AFE thick films that were pyrolyzed at different temperatures, the room-temperature recoverable electric-field-dependent energy-storage density (J–E) curves are given in Fig. 3. According to the definition of energy-storage density by P–E loops [10], the recoverable energy-storage density J ($J = \int EdP$, where E=applied electric field and P=polarization) can be obtained by numerical integration of the area between the polarization axis and the back switching curve of P–E loops. More detailed description on this could be found in reference [11]. As expected, the J values for all the PLZT 2/97/3 AFE films increase with the increase of electric-field. Moreover, it was also found that the films pyrolyzed at higher temperatures possessed smaller J values, which was contributed to the decreased saturated polarization values. The maximum J values obtained at E=1158 kV/cm were 20.1, 15.6, and 14.8 J/cm^3 for the thick films pyrolyzed at 550, 600, and 650 °C, respectively. These values were slightly larger than the previously reported results in pure, La- and Sr-doped $PbZrO_3$ AFE thin films [6,11].

In the practical application, a higher energy-storage efficiency (or lower energy loss) is also desired. The energy-storage efficiency η could be calculated according to the formula:

$$\eta = J/(J+J_{loss}), \quad (1)$$

where J_{loss} is the energy-loss density. The energy-loss density was calculated by numerical integration of closed area of the hysteresis loops. Accordingly, the room-temperature energy-storage efficiency of these thick films at various applied fieldswas calculated according to Eq. (1), as depicted in Fig. 3. It could be seen that the energy-storage efficiency of the films was also strongly influenced by the pyrolyzed temperature but showed a different tendency with J–E curves. Clearly, the films pyrolyzed at 550 °C possessed the lowest η of less than 54% in the measurement range because of a higher hysteresis loss. The highest η value was obtained for the thick film pyrolyzed at 600 °C, which was changed between 64.4% and 71.5%, as the electric field increases from 350 kV/cm to 1158 kV/cm. These results indicate that the slim hysteresis loop is beneficial to increase the energy-storage efficiency.

The temperature-dependent stability of the energy-storage performance was also a very important parameter for the capacitor application. Thus, the energy-storage densities were measured in the operating temperature from 20 °C to 120 °C, as presented in Fig. 4. In order to avoid the electric breakdown at a higher temperature, the measurements for all the samples were carried out at a lower electric field of E=873 kV/cm. Evidently, all the PLZT 2/97/3 thick AFE films showed a good energy-storage stability in the measurement range, and only a slight degradation of J was observed for all the samples. For instance, the J values for the films pyrolyzed at 550 C were varied from 15.4 J/cm^3 to 13.7 J/cm^3, as the operating temperature was increased from 20 °C to 120 °C.

4. Summary

In conclusion, 1.7-μm PLZT 2/97/3 AFE thick films with random orientations were successfully fabricated on $LaNiO_3$-buffered Si(100) substrates by the sol–gel method. It was found that the pyrolyzed temperature had a strong influence on the surface microstructure and the energy-storage performance of AFE films. A uniform and dense surface microstructures were obtained for the PLZT 2/97/3 AFE thick film that pyrolyzed at 600 °C. Under the same applied fields, AFE films pyrolyzed at 550 °C possessed the

largest saturated polarization and the highest energy-storage density. However, the film pyrolyzed at 600 °C displayed the largest energy-storage efficiency of 64.4% due to a smaller hysteresis loss. Overall, all the AFE films showed a good energy-storage stability in the temperature range from 20 °C to 120 °C. Thus, it could be concluded that the AFE thick films had the potential for application in high energy-storage capacitors.

Acknowledgments

The authors would like to acknowledge the financial support from the National Natural Science Foundation of China under Grant no. 51002071,the Program for Young Talents of Science and Technology in Universities of Inner Mongolia Autonomous Region, the Natural Science Foundation of Inner Mongolia under Grant no.2010BS0802, the Opening Project of Xinjiang Key Laboratory of Electronic Information Materials and Devices under Grant no. XJYS 0901–2011-01, the Innovation Fund of Inner Mongolia University of Science and Technology under Grant no.2009NC007, and the Fund of Industry-Academia-Research Project of Inner Mongolia University of Science and Technology under Grant no. PY-201003.

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