Effects of aging time of sol on the microstructure and electrical properties of $(Pb_{0.5}Ba_{0.5})ZrO_3$ thin films

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ABSTRACT

In this work, $(Pb_{0.5}Ba_{0.5})ZrO_3$ (PBZ) thin films were prepared on $Pt(1\,1\,1)/TiO_2/SiO_2/Si(1\,0\,0)$ substrates after the starting sol was aged for 24, 192 and 528 h, respectively. The effects of aging time of sol on the microstructure and electrical properties of PBZ films were investigated systemically. The phase structure and surface micrograph of PBZ thin films were analyzed by X-ray diffraction (XRD) and atomic force microscopy (AFM), respectively. It was showed that all PBZ thin films had a pure cubic perovskite structure without obvious difference and that the surface roughness of films was decreased as the aging time of sol increasing. Electrical measurements illustrated that dielectric constant and dielectric loss of PBZ films were also gradually declined with the increase of aging time of sol. As a result, films with a longer aging time also had an improved figure of merit (FOM) value.

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1. Introduction

Recently, $(Pb_{1-x}Ba_x)ZrO_3$ $(0.45 \le x \le 0.65)$ thin films with a chemical composition near the ferroelectric (FE)-paraelectric (PE) boundary have attracted increasing attention because of their excellent dielectric performance, such as moderate dielectric constant, larger dielectric tunability, lower dielectric loss, and acceptable temperature stability, which were comparable to the well-studied tunable dielectric materials $(Ba,Sr)TiO_3$ (BST) and $Ba(Zr,Ti)O_3$ (BZT) [1–3]. Therefore, PBZ films could be taken as a candidate for the potential applications in tunable microelectronic devices, such as phase shifters, varactors, and oscillators. So far, a few investigations had been carried out to optimize the final dielectric properties of PBZ films. State of the art works mainly focused on the influences of chemical composition, oxide buffer layer, and conductive oxides electrodes on the structure and electrical properties of PBZ films [4–7].

It should be noted here that PBZ films in recent works were often fabricated via the sol–gel method. It is well known that the structure and electrical properties of sol–gel-derived FE films are strongly dependent on sol's quality, including starting materials, concentration and aging time. However, the study on sol's quality-dependent structure and properties of PBZ films was rarely reported. In fact, the study on this problem is also important in

practical manufacture because the stable production procedure is always desired. Therefore, in this work, $(Pb_{1-x}Ba_x)ZrO_3$ thin films with $x = 0.5$ are fabricated by the sol–gel process, and the effects of aging time of sol on the microstructure and dielectric properties are studied in detail. The aim of this work is to find the relationship between the aging time of sol and the dielectric properties of films. In order to exclude the influence caused by the thickness variation, all the PBZ thin films possess a similar thickness.

2. Experimental procedures

The syntheses of $(Pb_{0.5}Ba_{0.5})ZrO_3$ (PBZ) precursor was similar with our recent report [2]. Barium acetate, lead acetate trihydrate and zirconium isopropoxide were selected as raw materials. Glacial acetic and deionized water were used as solvents. 2-methoxyethanol was added to adjust the viscosity and surface tension. In order to compensate lead loss during annealing and prevent the formation of pyrochloren phase, additional 10% of lead acetate trihydrate were added to the sol. The final concentration of the sol was 0.2 M. After aged 24, 192 and 528 h of the sol, PBZ thin films were prepared on $Pt(1\,1\,1)/TiO_2/SiO_2/Si(1\,0\,0)$ substrates through a multiple-layer spin-coating procedure. Each layer was spin-coated at 3000 rpm for 20 s and then pyrolyzed at 450 °C for 10 min. The spin-coating and heat-treatment were repeated to obtain desired thickness. A capping layer of 0.2 M PbO precursor solution, which was prepared from lead acetate trihydrate, was added on the surface of PBZ films before the films were subjected to a final anneal at 700 °C for 30 min. This capping layer served the purpose of preventing the excessive lead loss, thereby ensuring the formation of a single perovskite phase. The final thickness of all the thin films was about 200 nm.

Phase structure of PBZ films were characterized by X-ray diffractometer (XRD, Bruker D8 Advance diffractometer, Karlsruhe, Germany). The surface morphology was observed by atomic force microscopy (AFM, SPA-300HV). For electrical measurements, gold pads of 0.50 mm in diameter were coated on the film surface as top electrodes by dc sputtering. The dc electric-field and temperature dependence of

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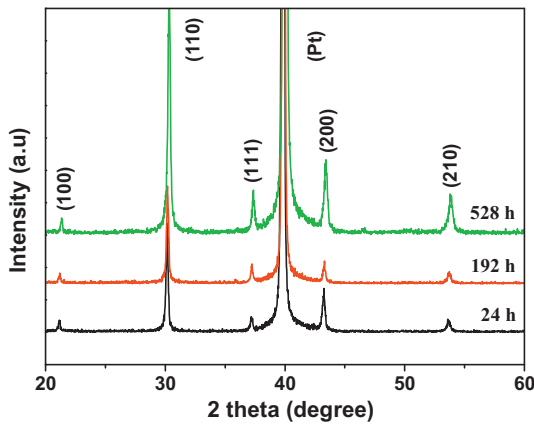E-mail address: xhhao@imust.cn (X. Hao).

Fig. 1. XRD patterns of PBZ thin films from same sol after aged 24, 192, and 528 h.

dielectric properties of PBZ films were measured by a computer controlled TH2828 analyzer (Tonghui Electronic, China) at 100 kHz with an AC drive amplitude of 50 mV. The room temperature leakage current was tested by Keithley 2410 electrometer.

3. Results and discussion

Fig. 1 gives XRD patterns of PBZ thin films prepared from the sol aged 24, 192, and 528 h, respectively. Clearly, the results showed that all PBZ films had crystallized into a pure polycrystalline cubic-perovskite structure with random orientation. There was no evidence of secondary phase formation, as no peaks other than the (1 0 0), (1 1 0), (1 1 1), and (2 0 0) peaks of PBZ were detected. Moreover, no evident difference in the curves was founded.

The surface AFM micrographs of PBZ thin films are shown in Fig. 2. The AFM images in tapping mode amplitude modulation were obtained by using an area of 5 μm × 5 μm. All the films displayed a smooth surface morphology, and the cracks and pinholes were absent. From Fig. 2, it could be also found that the particle

size of PBZ thin films decreased slightly as the aging time of sol increased from 24 to 528 h. As a result, the surface roughness of the films was declined. The measured roughness parameters (R_a) was 6.0, 5.3, and 4.5 nm for films with the aging time t = 24, 192, and 528 h, respectively. It could be predicated that the changed surface microstructure would inevitably lead to the difference in their final dielectric properties.

The dielectric properties of PBZ thin films with different aging time of sol were measured at room temperature and at 100 kHz, as a function of dc electric-field. Fig. 3(a) and (b) gives the field-dependent dielectric constant ($\varepsilon_r - E$) and dielectric loss (tan $\delta - E$) curves of PBZ thin films, respectively. Clearly, both $\varepsilon_r - E$ and tan $\delta - E$ curves showed a similar characteristic. Namely, the curves in both positive and negative biases were declined with the increase of field and were symmetric about the zero-bias axis. Moreover, no hysteretic behavior was observed in the curves. These results indicated that all the PBZ films were in PE state at room temperature. The variation of dielectric constant of PBZ films displayed a typical nonlinear behavior similar to BST and BZT films. The nonlinear characterization of $\varepsilon_r - E$ curves could be explained by phenomenological theory proposed by Johnson. Based this theory, in the case of $\varepsilon_r \gg 1$, the relationship between dielectric constant and the applied electric-field for perovskite-structure ferroelectric materials in PE state could be expressed as follows [8,9]:

$$\varepsilon_{r(T,E)} = \frac{\varepsilon_{r(T,0)}}{\left[1 + \varepsilon_{r(T,0)}^3 \alpha_{(T)} E^2\right]^{1/3}}, \qquad (1)$$

where $\alpha_{(T)}$ is the temperature-dependent constant which provides the information on the degree of anharmonic contributions of the polarization to the free energy, and $\varepsilon_{r(T,0)}$ and $\varepsilon_{r(T,E)}$ are the dielectric constant at temperature T without and with the applied electric-field E, respectively. Thus, according to this equation, the maximum values of dielectric constant for FE materials in PE state were obtained at zero electric-field. If a filed coefficient was defined as
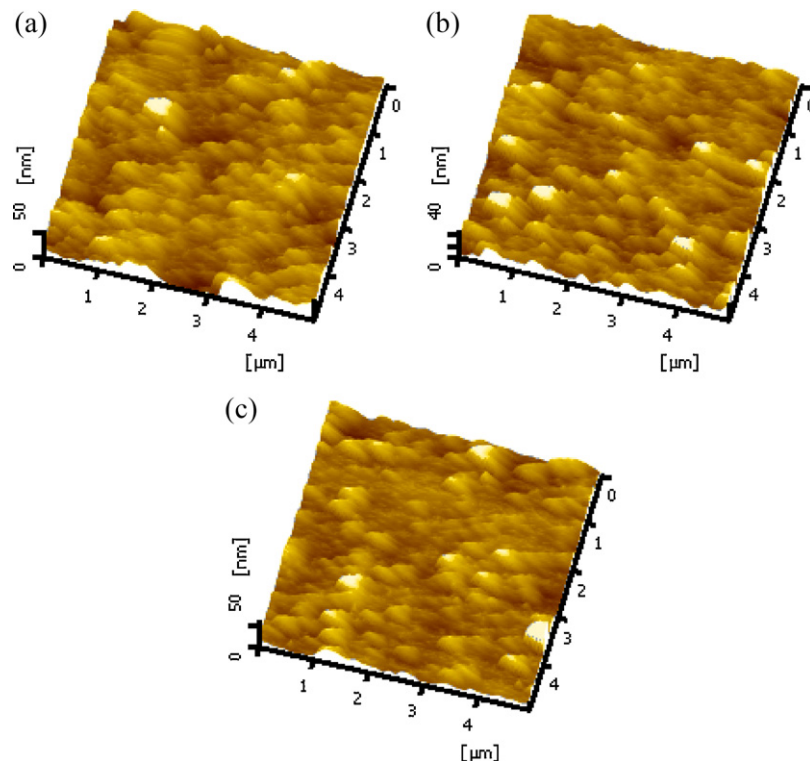

Fig. 2. AFE images of PBZ thin films from same sol after aged 24, 192, and 528 h.

Table 1
Electrical properties of PBZ thin films with different aging time of sol at 100 kHz and at room temperature.

Aging time (h)	Dielectric constant ($E = 0$ kV/cm)	$\tan\delta$ ($E = 0$ kV/cm)	Tunability (%)	FOM	Leakage current (A/cm^2)
24	216	0.01	61	61	1.5×10^{-2}
192	199	0.009	59	66	2.5×10^{-2}
528	146	0.006	55	92	3.7×10^{-2}

$b = \varepsilon_{r(T,0)}^3 \alpha_{(T)}$, Eq. (1) could be re-written as a linear equation about $[\varepsilon_{r(T,0)}/\varepsilon_{r(T,E)}]^3$ and E^2:

$$\left(\frac{\varepsilon_{r(T,0)}}{\varepsilon_{r(T,E)}}\right)^3 = 1 + bE^2. \qquad (2)$$

Here, field coefficient b represents the strength of dielectric nonlinearity. According to Eq. (2), the experimental data were well-fitted by linear fitting, as shown in the inset of Fig. 3(a). From the fitting parameters, the obtained b value was 6.3×10^{-5} (cm^2/kV^2), 5.6×10^{-5} (cm^2/kV^2) and 4.2×10^{-5} (cm^2/kV^2) for PBZ films with aging time $t = 24$, 192 and 528 h, respectively. Larger b value indicated a stronger strength of dielectric nonlinearity for the films with the shorter aging time of sol.

Table 1 summaries the electrical properties of PBZ thin films with different aging time of sol. The dielectric constant and dielectric loss at zero field were obtained from Fig. 3. Evidently, as the aging time of sol increasing, the dielectric constant and dielectric loss of PBZ films were decreased gradually. It is well known that dielectric properties of FE thin films are significantly affected by their microstructure. Generally, films with smaller particle size usually had a smaller dielectric constant. The smaller particle size also led to a smoother surface of the films. The declined surface roughness in turn decreased the interface layer between films and electrodes. Consequently, dielectric loss of FE films was also reduced [10,11].

In order to give a quantitative study on the strength of dielectric nonlinearity, the tunability (T) defined as $[\varepsilon_{r(T,0)} - \varepsilon_{r(T,E)}]/\varepsilon_{r(T,0)}$ was introduced [12], where $\varepsilon_{r(T,0)}$ and $\varepsilon_{r(T,E)}$ were defined as before. From $\varepsilon_r - E$ curves in Fig. 3, the calculated T values were 61%, 59%, and 55% for PBZ films with the aging time of 24, 192, and 528 h, respectively. The changing tendency of T was consistent with its strength of dielectric nonlinearity b. In practical application for dielectric films, besides lager tunability, lower dielectric loss was also necessary. Thus, for giving a overall evaluation on dielectric performance of present PBZ films, the figure of merit (FOM = $T/\tan\delta_{(T,0)}$) was also introduced [13]. According to this formula, the obtained FOM values at 100 kHz were 61, 66, and 92 for PBZ films with aging time of 24, 192, and 528 h, respectively. The improved FOM values for the films with longer aging time of sol were contributed to their smaller dielectric loss.

In addition to the dielectric properties, the leakage current of FE films was also very important property because it was closely related to the reliability of the devices. For practical application, the leakage current passing through the insulating layer should be as low as possible. Table 1 also gives the leakage current measured at 800 kV/cm. It was found that the aging time of sol had no obvious effect on the leakage current and that all the films possessed a similar value with a magnitude of 10^{-2} A/cm^2.

Fig. 4 shows the temperature-dependent dielectric constant curves of the PBZ films, which were measured at 100 kHz and on heating process. With temperature increasing, dielectric constant in all cases was decreased gradually. As expected there was no obviously steep change in the measurement range. The curves displayed a flatter profile, indicating a better stability over a wide temperature range. For giving a quantitative comparison, the temperature coefficient of capacitance (TCC), defined as TCC = $\Delta\varepsilon/(\varepsilon_0\Delta T)$, was introduced. $\Delta\varepsilon$ was the change in dielectric constant with respective to ε_0 at 25 °C, and ΔT was the change in temperature relative to 25 °C [14]. According to this equation, the calculated TCC values in the temperature range from 25 °C to 90 °C were -1.9×10^{-3} °C^{-1}, -1.2×10^{-3} °C^{-1}, and -1.8×10^{-3} °C^{-1} for PBZ thin films with the
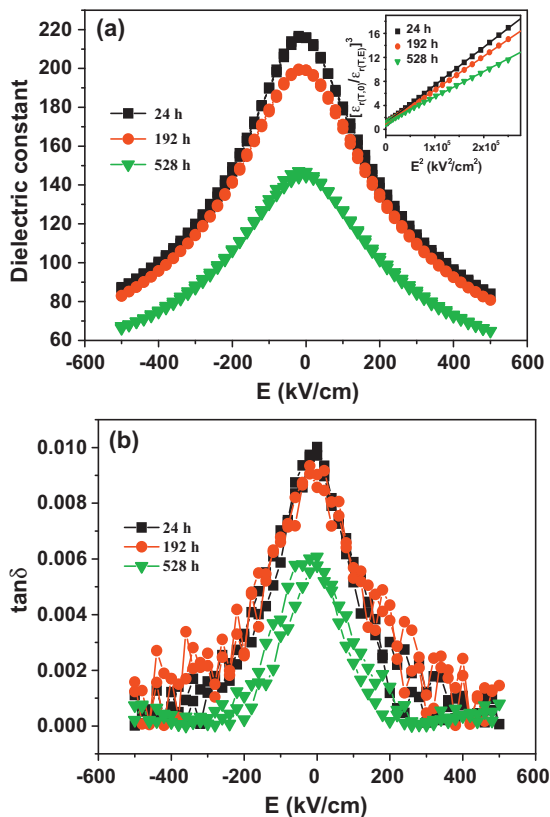
Fig. 3. Electric-field dependence of dielectric constant (a) and dielectric loss (b) of PBZ thin films from same sol after aged 24, 192, and 528 h. The insert in (a) showed the experimental data $[\varepsilon_{r(T,0)}/\varepsilon_{r(T,E)}]^3$ vs. E^2 and corresponding linear fitted curves.
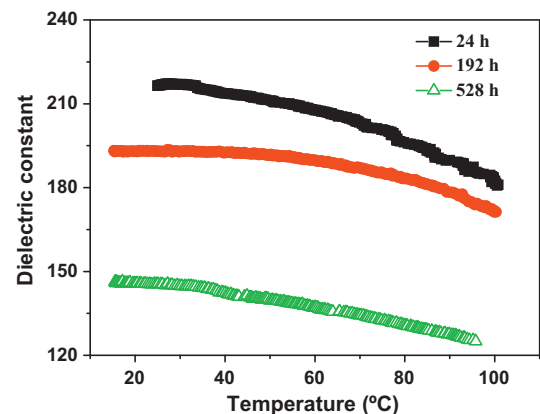
Fig. 4. Temperature-dependent dielectric constant of PBZ thin films from same sol after aged 24, 192, and 528 h.

aging time t = 24, 192, and 528 h, respectively. All the films showed a smaller TCC values comparable to BST and BZT [14,15]. Based on above results, it could be obtained that the final electrical properties of PBZ films were strongly dependent on the aging time of sol. The detailed study on this problem is still being carried out and will be given in further work.

4. Summary

In summary, $(Pb_{0.5}Ba_{0.5})ZrO_3$ thin films were prepared after the starting sol aged different time. It was found that all the films displayed a pure perovskite structure with random orientation and that films with longer aging time of sol possessed a smaller grain size and reduced surface roughness. As a result, the dielectric constant and dielectric loss was decreased gradually for PBZ films with longer aging time of sol. However, all the PBZ films showed good dielectric tunability with a larger T value above 50%. Due to the smaller dielectric loss, larger FOM values over 60 were obtained for the all films. Moreover, in the temperature range from 25 °C to 90 °C, all the PBZ films had an acceptable temperature-dependent stability. These results meant that PBZ films prepared from the sol with longer aging time were still suitable for practical application.

Acknowledgments

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