Effects of excess Pb on structural and electrical properties of $Pb(Zr_{0.48}Ti_{0.52})O_3$ thin films using MOD process

ZHITANG SONG
State Key Laboratory of Functional Materials for Informatics, Shanghai Institute of Metallurgy, Chinese Academy of Sciences, Shanghai 200050, People's Republic of China
E-mail: ztsong@itsvr.sim.ac.cn

JIANXIA GAO
Shanghai Institute of Nuclear Research, Chinese Academy of Sciences, Shanghai 201800, People's Republic of China

XIANGRONG ZHU, LIANWEI WANG, XIAORONG FU, CHENGLU LIN
State Key Laboratory of Functional Materials for Informatics, Shanghai Institute of Metallurgy, Chinese Academy of Sciences, Shanghai 200050, People's Republic of China

$Pb(Zr_{0.48}Ti_{0.52})O_3$ thin films at 20% excess Pb were synthesized on $Pt/Ti/SiO_2/Si(100)$ substrates at different annealing temperatures by a metal-organic decomposition process. The microstructure of the PZT films was investigated by x-ray diffraction and atomic force microscopy. The composition of the films was characterized by Rutherford Backscattering Spectroscopy (RBS). These results showed that The PZT films have perovskite phase coexisted with PbO_2 phase. The PbO_2 phase mainly was formed by excess Pb which congregate at boundaries of crystalline grains during the annealing process and may be absorbed part of oxygen ion at normal sites, thus leading to an increase of oxygen vacancies in the PZT film. PbO_2 phase and oxygen vacancies act as pinning centres, which has an effect on the ferroelectric domain switching. This eventually resulted in an increase of fatigue rate in PZT films. *© 2001 Kluwer Academic Publishers*

1. Introduction

Ferroelectric lead zirconate titanate (PZT) thin films have been intensively studied for a variety of electronic applications including nonvolatile memories and MEMS devices [1–3]. Varous fabrication techniques such as RF-sputtering [4], laser ablation [5], chemical vapor deposition [6], and the sol-gel [7] or metal-organic decomposition [8] (MOD) have been intensively investigated on the deposition of PZT thin films. Recently, there has been an increasing interest in the MOD technique because it has many advantages compared with others, e.g. excellent control of stoichiometry and compositional modification with liquid-mixed level homogeneity, lower treatment temperature, film uniformity over large area, and simple and inexpensive equipment. To obtain the films with desired electrical properties, a perovskite structure is required. One of a necessary condition for obtaining the perovskite phase is to maintain the stoichiometric composition of perovskite. However, the volatile of PbO tends to be deficient in the PZT film when annealed at high temperature. In order to solve this problem, the excess Pb was added to the precursor to compensate for the loss of lead oxide. But the excess amount of Pb needs to optimize. That means it is necessary to study the effect of excess PbO in the PZT films on electric properties.

In this study, PZT thin films contained excess Pb was prepared on $Pt/Ti/SiO_2$ substrate by MOD technique. It has been demonstrated by X-ray diffraction and Rutherford Backscattering Spectroscopy. Our results have shown that the excess Pb form PbO_2 phase and maybe induce an increase of oxygen vacancies in the PZT films, PbO_2 phase and the oxygen vacancies act as pinning centers, have an effect on the ferroelectric domains switching. This eventually resulted in an increasing fatigue rate of PZT films.

2. Experimental procedure

PZT (Zr : Ti ratio = 48 : 52) thin films were prepared using a metal-organic decomposition (MOD) process. The precursor solution used for PZT thin film preparation was based on lead acetate trihydrate, zirconium nitrate, and titanium n-butoxide. 2-butoxyethanol was chosen as a solvent. 20% excess Pb was added to the precursor to compensate for the loss of lead oxide during the annealing process.

The 0.3 M precursor solution was spin-coated on the $Pt(111)/Ti/SiO_2/Si$ substrates for 20 s at 3000 rpm. Deposited films fired at 450°C for 10 min to evaporate and burn out the organic. This procedure was repeated five times before further treatment. The film were cut four area equal piece and the piece were crystallized at different temperature in air for 1 hr. The thickness of the final film was about 0.3 μm. For electrical measurement, Au top electrodes ($A = 7.85 \times 10^{-3}$ cm^2) were deposited on the PZT thin film by dc-sputtering and post-annealing at 150°C for 30 min.

The crystal structures of the films were characterized by x-ray diffraction (XRD). The microsmorphologies of the films were analyzed using atomic force microscopy (AFM). The composition of the films was characterized by Rutherford backscattering spectroscopy (RBS). The ferroelectric properties of the films were measured by a RT66A standardized test system. The polarization fatigue test were performed using square wave of ±12 V at 100 kHz.

3. Results and discussion

Fig. 1 shows the RBS spectra of the PZT films with various annealing temperatures. The peaks of lead and zirconium in the PZT films are separable at various annealing temperature apart from the condition at 600°C. In order to calculate correct content of lead and zirconium, the overlapping peaks of zirconium and lead at 600°C were fitted and decomposed by Gaussian distribution. The RBS results of the PZT films are listed in Table I. In addition to the elemental analysis, the Zr : Ti and Pb : Ti ratios are listed. The contents of Zr and Ti almost keeps constant. But the content of Pb in the films decreases with the increase of annealing temperature. The measured Pb/Ti ratios for the PZT film with various annealing temperature are larger than 1.92. The data of 1.92 is the calculated ratio for the films according to stiochiometric ratio. Although the above results have about 10% relative error-bar of the measurement, but it is reasonable to say that PZT films still contain excess Pb and the content of excess Pb decreases with the increase of annealing temperature.

Fig. 2 shows XRD patterns obtained from PZT thin films with 20 mol % excess PbO with an increase of annealing temperature from 550°C to 700°C. The

TABLE I RBS results for PZT film with various annealing temperature

Annealing temperature °C	Pb (counts)	Ti (counts)	Zr (counts)	Pb/Ti Original	Pb/Ti Measured	Zr/Ti Original	Zr/Ti Measured
600	128060	4011	11334	2.31	2.24	0.922	0.880
650	82994	2773	8210	2.31	2.15	0.923	0.900
700	65365	2233	6773	2.31	2.10	0.923	0.918
750	32367	1211	3677	2.31	1.92	0.923	0.918

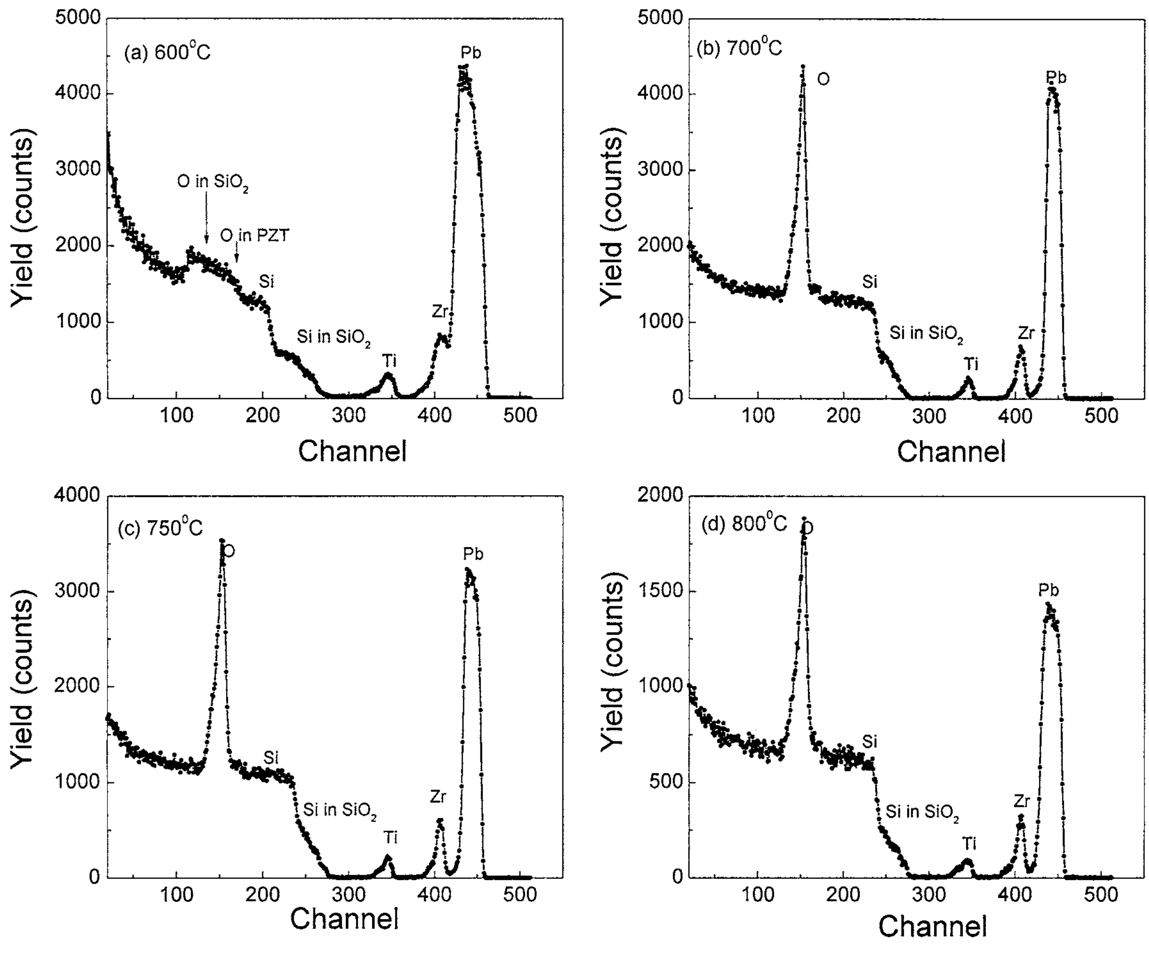

Figure 1 RBS results of PZT thin films as function of different annealing temperature.

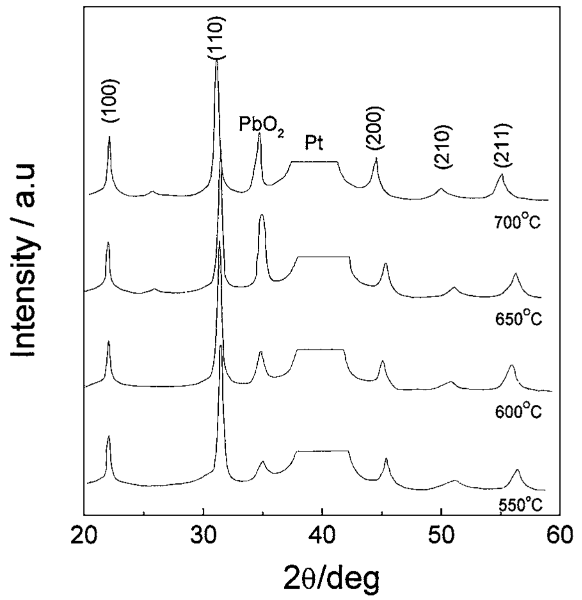

Figure 2 XRD patterns of PZT thin films as function of different annealing temperature.

orientation of PZT thin films indexed as (100), (110), (200), and (112) were randomly distributed regardless of annealing temperatures and slightly show (110) preferred orientation. Meanwhile, PbO_2 peaks were observed [5]. It means that the non-perovskite PbO_2 phase exist in the PZT films. Although the content of Pb in the films from the RBS results decreases with an increase of annealing temperature, but intensity of PbO_2 peaks do not decrease and have increasing trend. The results indicated that the films have perovskite coexist PbO_2 phase.

Fig. 3 shows the surface morphologies for the PZT films with various annealing temperature observed by AFM. With an increase of annealing temperature, the grain size of the films has an increase trend. Meanwhile, the volume percentage of grain boundaries has a conspicuous decreased feature. Interstitial atom and grain boundary mcriopores exist in the PZT films. Microporosity was also reported by Huffman *et al.* [9], who attributed the formation of pores to an increase in the excess amount of PbO. Based on the nucleation-growth

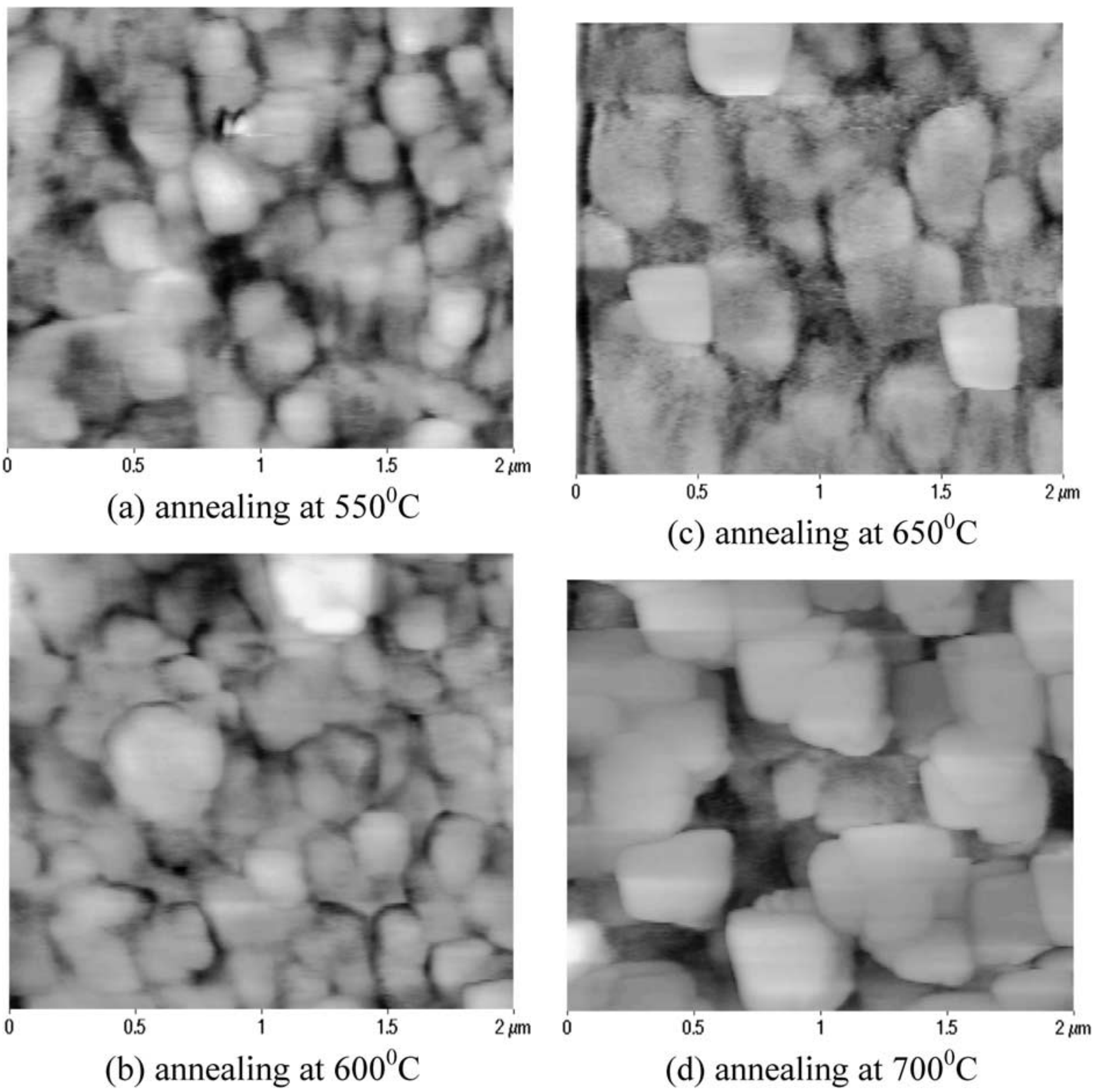

Figure 3 AFM photographs of PZT films as function of different annealing temperature.

model proposed by Lefever *et al.* [10], we can describe the formation process of interstitial atom and grain boundary mcriopores in the PZT films. For PZT films with excess PbO, because perovskite phase has a limited tolerance for excess Pb (usually within 1–2 mol % Pb tolerance), excess Pb would be rejected out by the perovskite phase during the nucleation and growth process, which emerges at the boundaries in the form of interstitial atom. Another part of the excess PbO_2 evaporates into the air though the film surface, such a process may lead to forming of mcriopores in the PZT film. The rest part of the excess Pb may diffuse toward the film/bottom-electrode interface [8]. Amount of interstitial atoms increases with an increase of PbO, therefore, a lot of interstitial atoms will accumulate to form PbO_2 phase in grain boundary. With an increasing of annealing temperature, firstly amount of excess PbO further evaporates into the air, thus interstitial atom and grain boundary micropores will decrease, secondly re- crystal and growth up of crystal grains, therefore the volume percentage of grain boundaries has a conspicuous decreased. Meanwhile, the excess Pb acting as ionic defect or interstitial atom may be absorbed a part of oxygen ion at normal sites, thus lead to an increase of oxygen vacancies in the films.

Fig. 4 shows the P-E hysteresis loops of the PZT films with various annealing temperatures. The sinewave voltage applied was 15 V in peak-peak. With an increasing of annealing temperature, a squarer P-E hysteresis loop and a larger remnant polarization were observed. The measured P_r value of the film are 11.6, 15.1, 22.1, and 22.5 $\mu C/cm^2$ respectively, and E_c values are 51.3, 69.5, 98.5 and, 84.1 kV/cm, respectively. P_r value increase with an increasing of annealing temperature, it maybe related with increase of grains size and exist PbO phase in the PZT films.

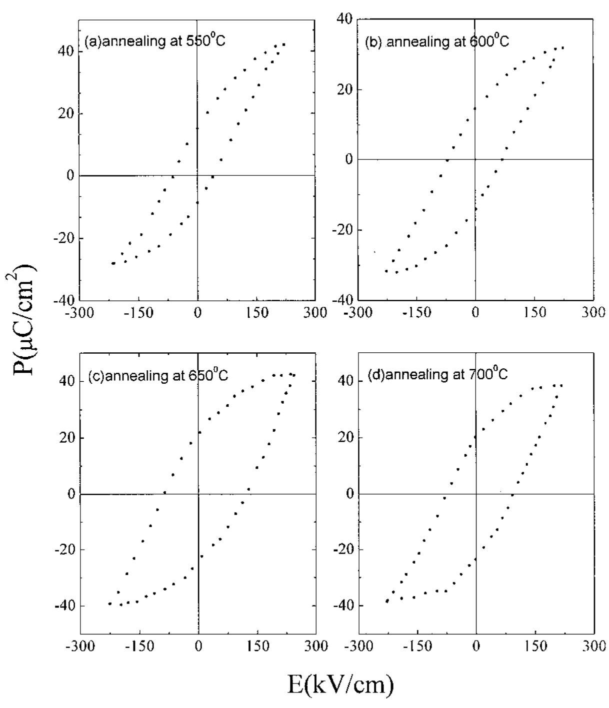

Figure 4 Saturated P-E hysteresis loops of PZT films as function of different annealing temperature.

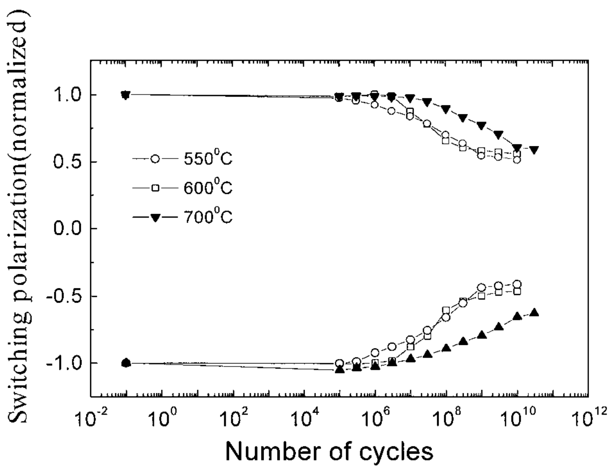

Figure 5 Fatigue properties of PZT film as function of different annealing temperature.

The loss of switchable polarization with the repeated polarization reversals that characterizes ferroelectric fatigue in the films is illustrated in Fig. 5 for the case of different annealing temperature. It was measured at 100 kHz and 10 V. Notice that the films prepared at 550°C and 600°C have similar fatigue property, which show an abrupt polarization decrease between 10^8 and 10^9 cycles. They have about 40%–50% of polarization loss at 10^{10} cycles. The film prepared at 700°C shows weak decrease of switching polarization between 10^8 and 10^9 cycles. With increasing cycles from 10^9 to 10^{10}, the film shows strong decrease of switching polarization and get about 20%–30% of polarization loss at 10^{10} cycles. Thus, the fatigue performance of the films can be summarized as follow: The dependence of fatigue rate on the annealing temperature. Fatigue rate of the PZT films at 550°C and 600°C is bigger than that of the PZT film at 700°C. With an increase of annealing temperature, Fatigue rate of the films has an tendency of decrease. Therefore, the excess Pb in the PZT films improves the fatigue rate of PZT films. Our results is similar with Doi's [11].

The RBS composition analysis shows that the measured Pb/Ti ratio in PZT films with higher than 1.92. This means that these films still contain excess Pb. The results of XRD demonstrated that excess Pb in the PZT films as formation of PbO_2 existed. According to and AFM analysis PbO_2 phases maybe exist in grain boundaries.

The excess Pb may congregate at boundaries of crystalline grains and the interface between bottom electrode and the film during the annealing process. Meanwhile, the excess Pb acting as ionic defect or interstitial atom may be absorbed a part of oxygen ion at normal sites, thus lead to an increase oxygen vacancies in the films. Pb inoic defects and oxygen vacancies acting as trapping electronic centres result in an increase of the trapping electronic charge and have an effect on the ferroelectric domains. It resulted in the abnormality of the P-E hysteresis loops and C-V curves of the PZT thin films [12]. It may impede domain switching. This eventually resulted an increase of fatigue rate in PZT films. With an increase of annealing temperature, grains of the films are increase and excess Pb of the PZT films are decrease, thus effect of pinning domains by PbO_2 phases in grain boundaries and oxygen vacancies is decrease and lead to decrease of fatigue rate of the films.

4. Conclusion

Pt/Ti/SiO_2/Si(100) substrate at a different annealing temperature by a metal-organic decomposition process. The microstructure and composition of the PZT films were investigated by x-ray diffraction, atomic force microscopy, and Rutherford backscattering spectroscopy. These results showed that there was still a certain mount of excess Pb in the PZT films. The excess Pb may congregate at boundaries of crystalline grains and form PbO_2 phase during the annealing process. Meanwhile, the excess Pb acting as ionic defect or interstitial atom may be absorbed a part of oxygen ion at normal sites, thus lead to an increase of oxygen vacancies in the PZT films. PbO_2 phase and oxygen vacancies have an effect on the ferroelectric domains switching. Because the PZT film prepared at 700°C has greater grain size and litter excess Pb than that of the films prepared at 550°C and 600°C, therefore, the film has litter pinning effect and has better fatigue property.

Acknowledgments

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