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# Influence of Pb excess on the properties of lead lanthanum titanate ferroelectric thin films on Pt and LaNiO<sub>3</sub> electrodes

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## Abstract

The influence of Pb excess on the properties of lead lanthanum titanate (PLT) ferroelectric thin films on Pt and LaNiO<sub>3</sub> electrodes is studied in this paper. Electron probe analysis results show that there is still quite an amount of excess Pb in PLT films after annealing at 550 °C for one hour. The distribution of excess Pb in the films is investigated by an Auger electron spectroscopy (AES) depth profile. It is found that the bottom electrodes have significant effects on both the content and the distribution of excess Pb in the PLT films. Meanwhile, the bottom electrodes have great effects on the size of the grains and also on the distribution of the excess Pb. The excess Pb and its appearance at grain boundaries and accumulation at the interface between the film and bottom electrodes may act as pinning centres and have a pinning effect on domains, which can be observed by abnormal  $P$ – $E$  hysteresis loops and abnormal  $C$ – $V$  curves. The excess Pb content in the films and Pb accumulation at the interface is high in the PLT films deposited on Pt/Ti/SiO<sub>2</sub>/Si; their pinning is severe. This is one of the primary reasons why the films have a high fatigue rate. While LaNiO<sub>3</sub> has absorbed most of the excess Pb in PLT films, the content of excess Pb in the films deposited on LaNiO<sub>3</sub>/SiO<sub>2</sub>/Si is very low: the pinning effect is hardly observed. This is one of the primary reasons that the films have good fatigue properties.

## 1. Introduction

Much effort has been made on the studies of ferroelectric thin films with regard to their application in integrated circuit (IC) memories, optical waveguides, pyroelectric imaging sensors and microactuators [1–4]. Many deposition technologies are currently used for preparing ferroelectric thin films, and among them, the metal–organic deposition (MOD) process is a well accepted method due to advantages such as composition control and homogeneity, large-area deposition, low cost and short fabrication process. To date, fabrication

of lead lanthanum titanate (PLT) thin films by the MOD process has yielded quite successful results [5, 6]. But Pb is a volatile element in the Pb-based perovskite system; some of the Pb will volatilize during thermal treatment and cause Pb deficiencies in the films. Excess PbO is then added during synthesis of the films to compensate for the Pb deficiency and to promote the formation of perovskite phase in the films.

Doi and Atsuki [7] investigated PZT films with different excess PbO, and they believed that the fatigue of the PZT is closely related to the movement of defects generated from interdiffusion of atoms through the ferroelectric/electrode interface. Kim *et al* [8] studied structural and electrical properties of excess PbO doped PZT thin films, and they considered that excess Pb content can play a key role in reducing the deposition temperature. With the increase of post-annealing temperature, the ferroelectric properties gradually increased. The fatigue resistance of Pb excess PZT films was enhanced very much. Chen *et al* [9] investigated PZT thin films spin-coated onto a (100)-textured LaNiO<sub>3</sub> (LNO) electrode. They found that the annealing temperature for obtaining a perovskite PZT film was reduced by 50 K compared with that for direct deposition on a Pt electrode. Use of the LNO layer as a bottom electrode was also found to greatly improve the fatigue properties of PZT films.

PLT thin films, with or without excess PbO, deposited on Pt and LNO electrodes are investigated in this paper. Abnormal electric properties were explained by pinning effects caused by excess PbO in the PLT films. The LNO electrode has a similar structure to the PLT film and can absorb a large amount of excess Pb; the content of excess Pb in the PLT film is very low and no accumulation of excess Pb is found at the interface between the film and electrode: the pinning effect is very weak. The results suggest that an LNO electrode can improve the fatigue behaviour of PLT films effectively.

## 2. Experiment

A surface-oxidized (111) silicon wafer was chosen as substrate. After washing and drying in a clean room, the substrate was coated first with a layer of Ti film (30 nm thick) and then with a layer of Pt film (200 nm thick) by the dc sputtering method. Conductive oxide LaNiO<sub>3</sub> (LNO) thin film (250 nm thick), prepared by the thermal decomposition of water-based solution [10], was deposited on a silicon wafer and formed the LNO/SiO<sub>2</sub>/Si substrate.

The PLT thin films were prepared on silicon wafers by the metallo-organic decomposition (MOD) process. The PLT films were synthesized according to the formula Pb<sub>1-x</sub>La<sub>x</sub>Ti<sub>1-x/4</sub>O<sub>3</sub> with  $x = 0.1$  (abbreviation PLT10). Two kinds of PLT10 precursor solution were prepared in the experiment. In the first solution, 20 mol% of excess PbO was added, and no excess PbO was added in the second solution. The excess percentage of PbO is compared with A sites, not with  $(1 - x)$  Pb in A sites. The 0.5 M PLT precursor solution was prepared from lead acetate trihydrate, titanium *n*-butoxide and lanthanum nitrate. 2-butoxyethanol was chosen as a solvent. The details of the preparation procedure of the precursor solutions can be seen in [6].

The precursor solutions were spin-coated on the substrates in a clean room. The 'wet' films were thermally treated at 180 and 400 °C for 30 min respectively at a heating rate of 3 °C min<sup>-1</sup>, the coating and heating processes were repeated eight times and the final films were heated to 550 °C for 1 h at a heating rate of 3 °C min<sup>-1</sup>. The total thickness of the PLT films after annealing heat treatment was about 1 μm.

The morphologies of the PLT films were analysed by atom force microscopy (AFM). The compositions of the films were analysed by a JEOL JCXA-733 electron probe x-ray microanalyser (EPMA) operating at a voltage of 15 kV and a current of 20 nA. The incident electron beam was about 3 μm in diameter. A crystal wavelength dispersive spectrometer was used for x-ray wavelength and intensity analysis. Three spots in each film sample were chosen

in the measurement. Each element for the analysis in the thin films was calibrated by using a standard sample. The measured results were modified by ZAF correction. A Perkin–Elmer PHI600 Auger electron spectroscopy (AES) was used to investigate the AES depth profile of PLT10 films. The incident electron beam with an operating voltage of 3 kV, a current of 1  $\mu\text{A}$  and a beam diameter of 0.1  $\mu\text{m}$  was used. The argon beam with an energy of 3 keV, a current of 6  $\mu\text{A}$  and a beam diameter of 2 mm was adopted to etch the film samples. For the electric measurements, an Au top electrode (100 nm thick) with a diameter of 1 mm was deposited by dc sputtering. The ferroelectric  $P$ – $E$  hysteresis loops were measured by a modified Sawyer–Tower circuit at a frequency of 1 kHz, like the fatigue properties at a frequency of 10 kHz. The  $C$ – $V$  curves were measured by an HP4192A LF impedance analyser.

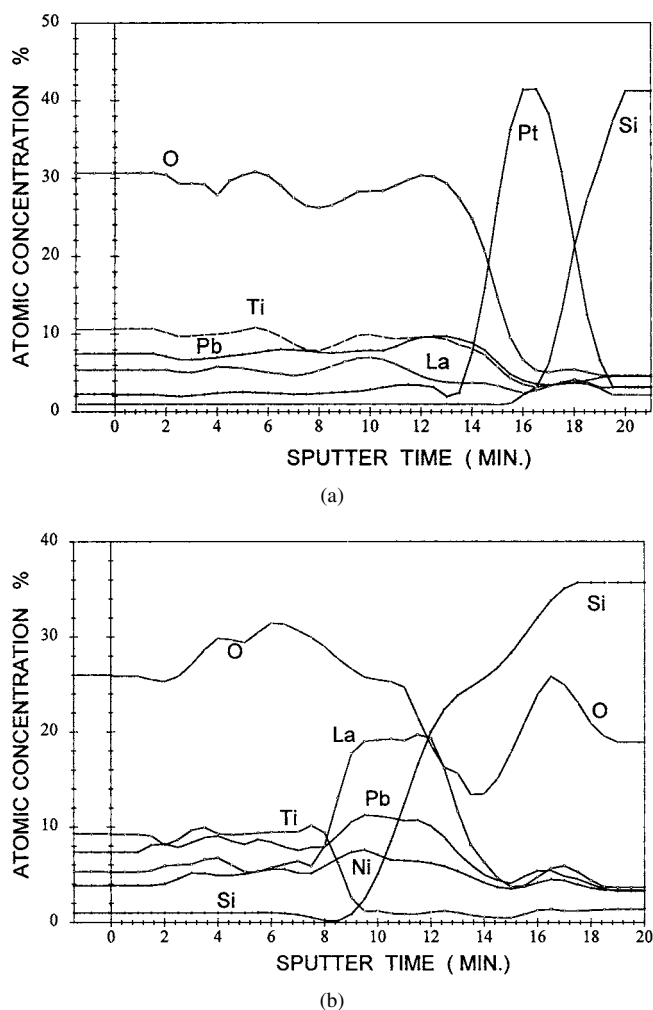
### 3. Results and discussion

Table 1 shows the EPMA results for compositions of PLT10 films with 20 mol% or without excess PbO. The measured Pb/Ti ratios for PLT10 films with 20 mol% excess PbO on Pt and LNO substrate are 0.963 and 0.943, respectively. The data are larger than 0.923, which is the calculated ratio without excess PbO according to the front formula, while the measured Pb/Ti ratios for the films without excess PbO on Pt and LNO substrate are 0.878 and 0.920, respectively. The data are smaller than 0.923. From the above experimental data, if 0.923 is a normal Pb/Ti chemical composition ratio in the PLT films as in the front formula, the PLT films with 20 mol% excess PbO still contain excess Pb after annealing at 550 °C for 1 h; the excess Pb quantity of the film on the Pt electrode is larger than that on the LNO electrode. Meanwhile, the PLT10 films without excess PbO lost Pb after the thermal treatment and cannot keep the normal chemical composition ratio, but the lost amount of the film on the Pt electrode is larger than that on the LNO electrode.

**Table 1.** EPMA results for compositions of PLT10 deposited on Pt or LNO electrodes, with or without excess PbO.

Excess Pb	Electrode	mol%			Pb/Ti		La/Ti	
		Pb	La	Ti	Calculated	Measured	Calculated	Measured
Pb 0 mol%	Pt	11.82	1.38	13.47	0.923	0.878	0.103	0.105
Pb 20 mol%	Pt	12.01	1.31	12.47	1.108	0.963	0.103	0.105
Pb 0 mol%	LNO	14.43	2.15	15.68	0.923	0.920	0.103	0.137
Pb 20 mol%	LNO	15.43	1.80	16.37	1.108	0.943	0.103	0.110

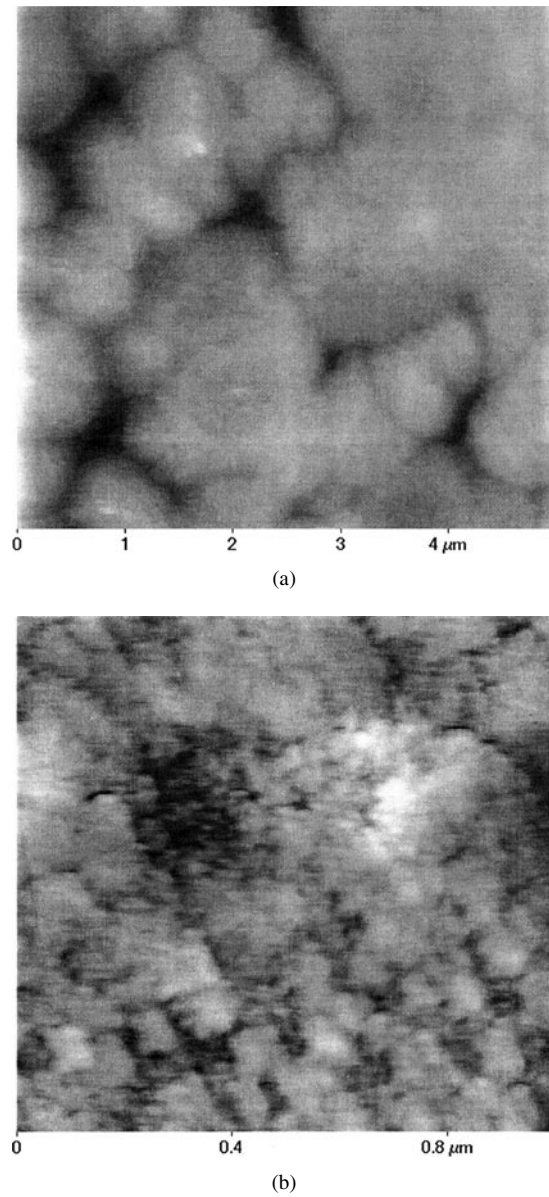
The AES depth profile of a PLT10 film with 20 mol% excess PbO on the Pt or LNO electrodes is plotted in figure 1. We find that there is Pb accumulation at the interface between the PLT10 film and the Pt electrode from figure 1(a). The Pt electrode has a low tolerance for Pb; thus most of the Pb diffused from the film will go through the Pt electrode into the Si substrate, and only a small part of the Pb remains inside the Pt electrode. From figure 1(b), it has been shown that the LNO electrode has a high tolerance for Pb. Most of the Pb diffused from PLT10 films is retained inside the LNO, and only a little amount of the Pb diffuses into the Si. It can be seen from figure 1 that the concentration of Pb inside the PLT10 films varies along the thickness direction. This is probably related to the inner interfaces formed inside the films by the multi-coating process. It seems that there is Pb accumulation at the inner interfaces in PLT10 films. From the above EPMA results, the films on LNO have a lower content of excess Pb than the film on Pt because Pt and LNO electrodes have different tolerances for Pb.



**Figure 1.** AES depth profiles of PLT10 films with 20 mol% excess PbO on a Pt electrode (a) and an LNO electrode (b).

The AFM photographs of PLT10 without excess PbO on a Pt electrode are shown in figure 2. The films were very smooth, but have some pinholes. Crystalline grains could not be distinguished in figure 2(a): only dense clusters were seen and their scale was about  $1\ \mu\text{m}$ . Further inspection show that dense clusters were made up of uniform nano-crystals. The grain size of the film is about 30–60 nm. The PLT10 film with 20 mol% excess PbO on a Pt electrode is shown in figure 3. Compared with figure 2, the films were smooth, free from pinholes and not showing clear boundaries of clusters in figure 3(a). Further inspection will find uniform nano-crystals. The grain size is about 40–80 nm, which is larger than the size of the film without excess PbO. The PLT10 film with 20 mol% excess PbO on an LNO electrode is shown in figure 4. Compared with the PLT10 films with 20 mol% excess PbO on a Pt electrode, the film has clear boundaries of clusters and has larger grains. From the above results, the sort of electrode and amount of excess PbO will affect the morphologies of the PLT films. Because the grain boundary may be the main place in which there exist some impurities such as excess

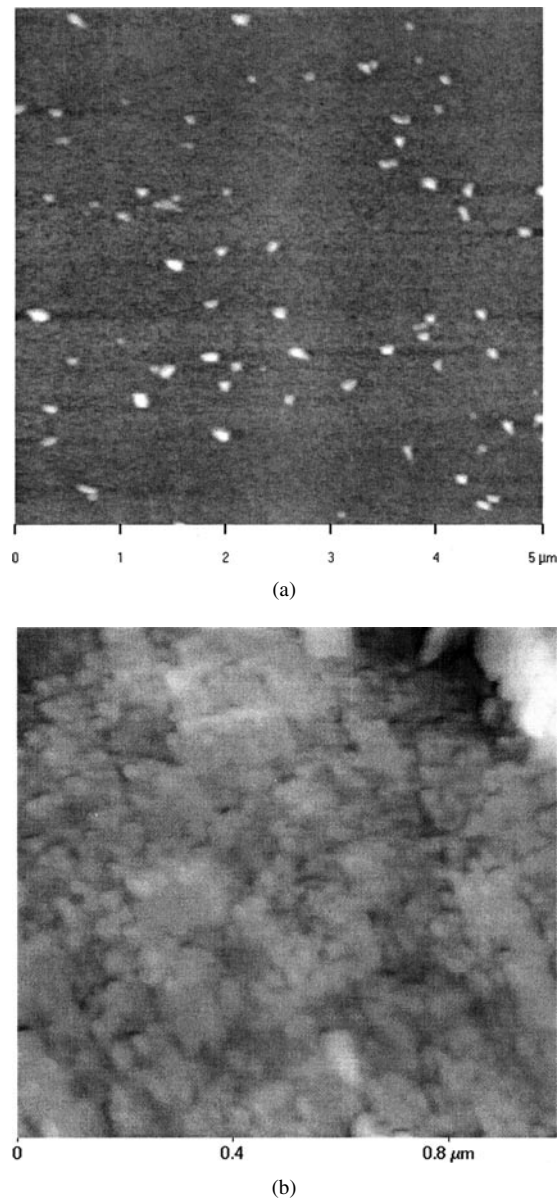
PbO, the different morphologies will result in differences of excess Pb distribution in those films.



**Figure 2.** AFM photographs of the PLT10 without excess PbO on a Pt electrode.

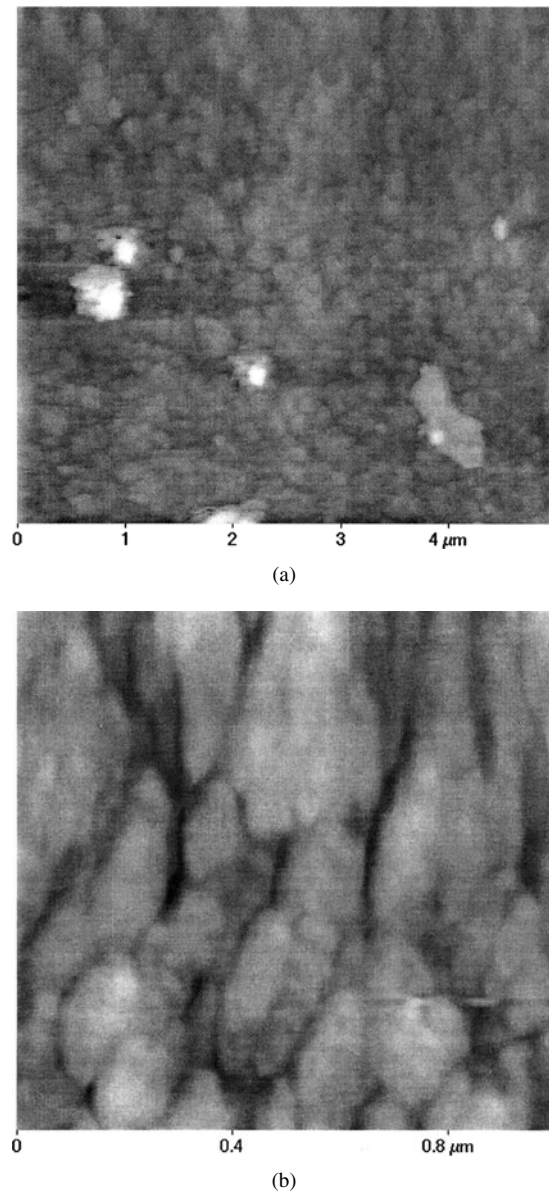
Au top electrodes with a diameter of 1 mm were sputtered onto the surface of the samples by a shadow mask. A sandwich structure of Au/PLT/Pt or Au/PLT/LNO was formed and used to measure electric properties.

Figure 5 shows the  $P$ - $E$  hysteresis loops of the PLT10 films with 0 or 20 mol% excess PbO on Pt or LNO electrodes. The sine-wave voltage applied was 30 V peak-peak. At this voltage, the films had not been saturated. It can be seen in figures 5(a) and 5(c) that the



**Figure 3.** AFM photographs of the PLT10 with 20 mol% excess PbO on a Pt electrode.

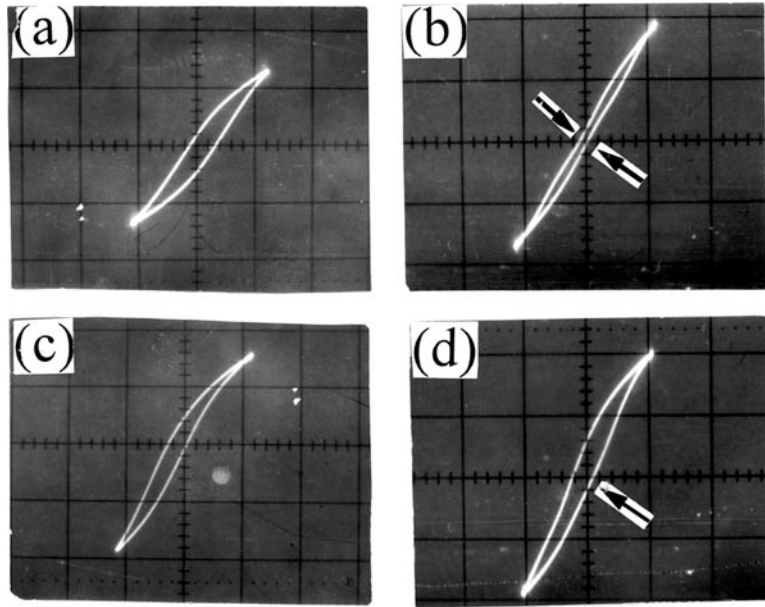
normal hysteresis loop was observed in the PLT10 films with no excess PbO on the Pt or LNO electrodes. But after adding 20 mol% excess PbO, abnormal hysteresis loops appeared in the PLT films and these loops were calabash shaped, which means that the loops became narrow in the middle part. The abnormal level was different with different electrodes. The loop on the Pt electrode has a more severe calabash shape compared with the loop on the LNO electrode in figures 5(b) and 5(d). The abnormal hysteresis loops can be turned into normal ones by applying a higher poling voltage [6].



**Figure 4.** AFM photographs of the PLT10 with 20 mol% excess PbO on an LNO electrode.

For the  $C-V$  curve measurement by an HP 4192A LP impedance analyser, a 0.5 V sine-wave voltage at a frequency of 10 kHz was overlapped on a dc bias voltage which scanned linearly from  $-15$  V to 15 V and vice versa with a step of 0.5 V and a speed of  $0.5 \text{ V s}^{-1}$ . Figure 6 shows  $C-V$  curves of the PLT10 films with 20 mol% excess PbO on Pt or LNO electrodes. The  $C-V$  curve of the PLT10 with no excess PbO on Pt or LNO electrodes was a normal two-peak (butterfly) shape as shown in figures 6(a) and 6(c). The values of the bias voltages for the two peaks were nearly equal. The different heights of the peaks may be attributed to the different interfaces of top and bottom electrodes with the films. For the



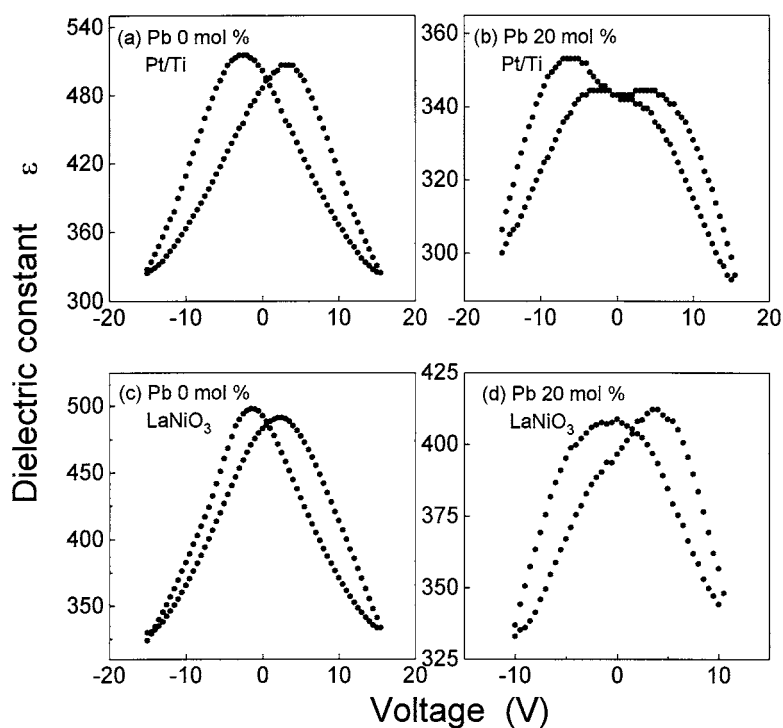


**Figure 5.** The  $P$ - $E$  hysteresis loops of the PLT10 films with 0 or 20 mol% excess PbO and on Pt or LNO electrodes: (a) 0 mol% excess PbO on Pt substrate, (b) 20 mol% excess PbO on Pt substrate, (c) 0 mol% excess PbO on LNO substrate, (d) 20 mol% excess PbO on LNO substrate (all of the pictures in this figure,  $x$ -axis:  $16 \text{ kV cm}^{-1}/\text{division}$ ,  $y$ -axis:  $22 \text{ } \mu\text{C cm}^{-2}/\text{division}$ ).

PLT10 films with 20 mol% excess PbO on Pt electrode, the abnormal four peaks instead of two peaks as in the normal case are observed in the  $C$ - $V$  curves, as is shown in figure 6(b). In the positive scanning (from  $-15 \text{ V}$  to  $15 \text{ V}$ ), a small peak appeared before the bias voltage reached zero and the second large peak appeared at a positive bias voltage. The height of the second peak was smaller than that of the first peak. In the negative scanning (from  $15 \text{ V}$  to  $-15 \text{ V}$ ), two similar peaks were also found. For the PLT10 films with 20 mol% excess PbO on the LNO electrode, under the above scanning voltage, a normal  $C$ - $V$  curve was observed, but under an even lower scanning voltage (from  $10$  to  $-10 \text{ V}$ ), slight abnormality of  $C$ - $V$  curves was seen, as in figure 6(d). Similarly, increasing bias voltage will transform all the abnormal  $C$ - $V$  curves to normal ones [6].

Summarizing the measuring results of the  $P$ - $E$  hysteresis loops and  $C$ - $V$  characteristics, we may obtain the following facts: the abnormal  $P$ - $E$  hysteresis loops and  $C$ - $V$  curves were caused by excess PbO addition. The abnormality of  $P$ - $E$  hysteresis loops and  $C$ - $V$  curves was different with different electrodes. From the above EPMA and AES results, the films on LNO have lower content of excess Pb than the films on Pt because Pt and LNO electrodes have different tolerances for Pb. Meanwhile, according to the results of the AES depth profile analysis, there is Pb accumulation at the film/Pt electrode. Such Pb accumulation is not found at the film/LNO electrode. From figures 3 and 4, the grain size of the PLT film on the LNO electrode is larger than on the Pt electrode. This will affect excess Pb distribution in the films. Therefore, the abnormalities of the  $P$ - $E$  hysteresis loops and the  $C$ - $V$  curves were different with Pt and LNO electrodes because of the difference of excess Pb content, distribution and accumulation at the interface.

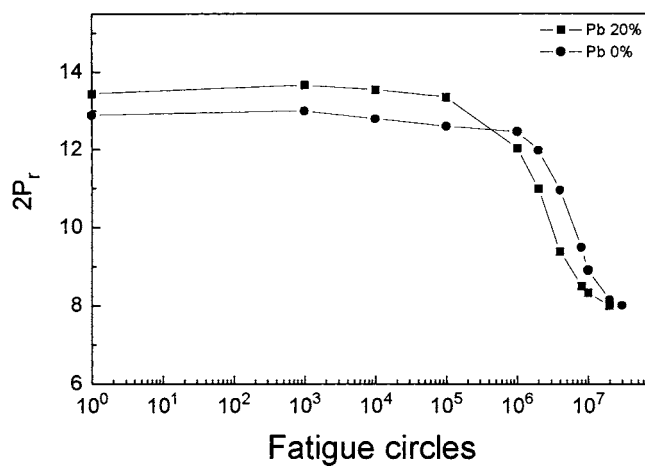
Figure 7(a) shows fatigue properties of PLT films on the Pt electrode measured at  $1 \text{ kHz}$  and  $60 \text{ V}$ . The film with 20 mol% excess Pb shows a significant fatigue degradation with



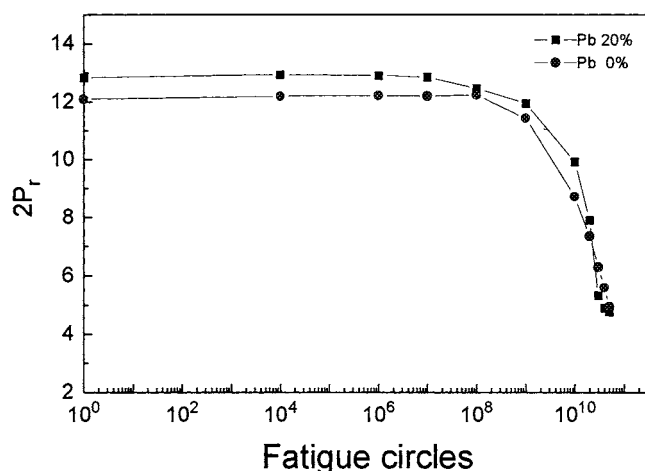
**Figure 6.**  $C$ - $V$  curves of the PLT10 films with 0 or 20 mol% excess PbO and on Pt or LNO electrodes.

increasing number of switching cycles. However, the film without excess Pb shows a better resistance to polarization fatigue. Figure 7(b) shows fatigue properties of PLT films on the LNO electrode measured at 10 kHz and 60 V. The films with 0 or 20 mol% excess Pb have better resistance to polarization fatigue compared with the films on the electrode. Compared with fatigue curves on the LNO electrode, the PLT film with 20 mol% excess Pb is a little better than the film without excess Pb. The difference in the fatigue rate of the PZT films on Pt or LNO bottom electrodes might be related to the different microstructure, different excess Pb and different interface between the PLT film and the bottom electrode. The good fatigue properties of the PLT films on the LNO electrode may be due to at least three contributions. First, the LNO electrode has a similar structure to the PLT film; therefore, there is no transition area from the PLT film to the LNO bottom electrode like the PLT/Pt interface [11]. The PLT film on the Pt electrode accumulates defects such as oxygen vacancies in the transition area due to lattice mismatch and chemical incompatibility. The defects such as oxygen vacancies may form charge traps, which lead to domain pinning and fatigue [12]. From PLT films to the LNO electrode, there is hardly any transition area due to the similarity in structure between the PLT film and the LNO electrode; therefore, there are smaller defects such as oxygen vacancies and good fatigue properties. Second, the LNO electrode has good compatibility with PLT films and good tolerance for Pb or oxygen deficiency. From EPMA and AES results, the LNO electrode acts as a Pb atomic adjustment. When there is a lot of excess Pb in the films, the LNO electrode can absorb a lot of excess Pb; when some of the Pb volatilizes during thermal treatment and causes Pb deficiencies in the PLT films, the LNO electrode can absorb less Pb or release Pb to compensate for the Pb deficiency. This can reduce excess Pb in the PLT

film to cause domain pinning [6]. Meanwhile, the LNO electrode has a large tolerance for oxygen deficiency and better effective sinks for oxygen vacancies. Third, the LNO electrode can improve grain growth of the PLT films and abate the pinning effect caused by excess Pb at grain boundaries.



(a)



(b)

**Figure 7.** Fatigue curves of the PLT films with 0 or 20 mol% excess PbO and on a Pt electrode (a) or an LNO electrode (b).

#### 4. Conclusion

The excess Pb and its appearance at grain boundaries and accumulation at the interface between the film and bottom electrodes may act as pinning centres and have a pinning effect on domains, which can be observed by abnormal  $P-E$  hysteresis loops and abnormal  $C-V$  curves. The excess Pb content in the films and Pb accumulation at the interface are high in the PLT films deposited on Pt/Ti/SiO<sub>2</sub>/Si: their pinning is severe. This is one of the primary reasons that the films have a high fatigue rate. The good fatigue properties of the PLT films on LNO

electrodes may be due to the LNO electrode having a similar structure to the PLT film: there is no transition area from the PLT film to the LNO bottom electrode like the PLT/Pt interface and smaller defects such as oxygen vacancies. The LNO electrode has good compatibility with PLT films and has good tolerance for Pb or oxygen deficiency and acts as a Pb atomic adjustment to keep a better chemical stoichiometry. Meanwhile, the LNO electrode has a large tolerance for oxygen deficiency and better effective sinks for oxygen vacancies. Third, the LNO electrode can improve grain growth of the PLT films and abate the pinning effect caused by excess Pb at grain boundaries.

### Acknowledgments

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### References

- [1] Scott J F and Araujo A P 1989 *Science* **246** 1400
- [2] No K S *et al* 1996 *Japan. J. Appl. Phys.* **35** 2731
- [3] Al-Shareef H N, Dimos D, Tuttle B A and Raymond M V 1997 *J. Mater. Res.* **12** 247
- [4] Seifert A, Sagalowicz L, Muralt P and Setter N 1999 *J. Mater. Res.* **14** 2012
- [5] Khan A R and Desu S B 1995 *J. Mater. Res.* **10** 2777
- [6] Song S T, Ren Wei, Zhang Liangyin and Yao Xi 1999 *Thin Solid Films* **347** 1
- [7] Doi H and Atsuki T 1995 *Japan. J. Appl. Phys.* **34** 5105
- [8] Kim T S, Kook D J, Lee J K and Jung H J 1998 *J. Mater. Res.* **13** 3436
- [9] Chen M S, Wu J M and Wu T B 1995 *Japan. J. Appl. Phys.* **34** 4870
- [10] Lin Y, Ren W, Wu X Q, Zhang L Y and Yao Xi 1998 *Thin Solid Films*
- [11] Song Z T, Wang S X, Wang L M, Wang L W and Lin C L 1999 Structural and abnormal electrical properties of excess PbO doped lead lanthanum titanate thin films *IUMRS-ICAM'99—F-138 (Beijing, 1999)*
- [12] Dimos D, Al-Shareef H N, Warren W L and Tuttle B A 1996 *J. Appl. Phys.* **80** 1683