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Ferroelectric properties of PZT films on $LaNiO_3$ bottom electrode deposited under different oxygen partial pressure

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Abstract

$LaNiO_3$ (LNO) films were deposited on by RF magnetron sputtering of Ni metal target and La metal chips on top of it under Ar and O_2 atmosphere at different oxygen partial pressures (20, 25, 30, 35, and 40% oxygen). The resistivity of the LNO films increased with the increasing oxygen partial pressure. This is attributed to the reduction of oxygen vacancy concentration. About 150 nm thick $Pb(Zr_{0.35}Ti_{0.65})O_3$ (PZT) ferroelectric thin films were spin coated on the LNO films with subsequent post annealing. To find out the relationship, the electrical properties of the PZT/LNO thin film capacitors and the oxygen partial pressure, the *P–E* curve, X-ray diffraction, microstructure, leakage current density, and fatigue property were investigated as a function of oxygen partial pressure. An optimal remanent polarization and lowest leakage current density of the PZT capacitor has been obtained when its LNO thin film bottom electrode was deposited at 30% oxygen partial pressure. The microstructure of the LNO film deposited at 30% oxygen partial pressure had columnar structure, while the ones deposited under other conditions had granular structure. The ferroelectric properties of the PZT/LNO capacitor are critically affected by the structure of LNO bottom electrode, and they are excellent when optimally processed as discussed above.

Keywords: Fatigue; Ferroelectric properties; Perovskite; PZT; LNO

1. Introduction

Up to now, lead zirconium titanate (PZT) thin film has been one of the most intensively studied ferroelectrics for non-volatile random access memory (NVRAM) devices because it has high permittivity, remanent polarization, and low coercive field. Pt or Pt-based metal films are most often used as bottom electrodes in the fabrication of integrated ferroelectric capacitors for memory applications.[1] However, there have been several problems such as imprint, high leakage current, and especially short polarization fatigue life span with the PZT/Pt capacitor.[2] To extend the fatigue life span, conducting oxide electrodes such as $La_xSr_{1-x}CoO_3$ (LSCO), IrO_2, RuO_2, $YBa_2Cu_3O_{7-x}$ (YBCO) and $LaNiO_3$ (LNO) have been considered as alternatives for bottom Pt electrode, and they have been studied extensively.[3] Particularly, the LNO thin film has been developed as a new oxide electrode alternative because it grows easily in (1 0 0) orientation irrespective of substrate species and because its deposition temperature is relatively low.[4] Although a number of studies on the properties of reactive sputtered LNO films have been published so far, further investigations of the PZT/LNO capacitors are much needed.[1,5]

In our earlier work, we showed how the conductive LNO thin films could be successfully deposited on SiO_2/Si (1 0 0) substrates by reactive sputtering in particular of the Ni metal target and La metal chips on top of it instead of the usual LNO ceramic target.[6] On the other hand, there has been no effort made on the influence of oxygen partial pressure on the physical state of the LNO electrode sputtered on from the Ni/La metal target. Especially, optimization of this new LNO sputtering process is highly desired at this point.

It has been reported that oxide electrodes greatly mitigate fatigue problems, which are encountered in ferroelectric memory capacitors.[7] The most serious issue related to

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the oxide electrode, however, is their large leakage current. This problem appears to be related to the absence of the potential barrier between the ferroelectric film and the oxide electrode.[7]

In this work, the ferroelectric properties of Pb($Zr_{0.35}Ti_{0.65}$)O_3 films on the LNO bottom electrode deposited on under different oxygen partial pressures will be investigated. Dependence of ferroelectric hysteresis, leakage currents, and fatigue properties of PZT films on the oxygen partial pressure will be discussed.

2. Experimental

Pb($Zr_{0.35}$,$Ti_{0.65}$)O_3 (PZT) films were grown on $LaNiO_3$ (LNO) bottom electrode. First, LNO electrode was deposited on the SiO_2/Si (1 0 0) substrates by reactive RF magnetron sputtering at 300 °C at the 10 mTorr working pressure. Details of the LNO deposition were described elsewhere.[6] The oxygen partial pressure, $p(O_2)/p(O_2 + Ar)$, was varied from 20 to 40%. After the LNO deposition, about 150 nm thick PZT films were deposited on by common sol–gel technique. The PZT films were deposited by five multiple spin-coating to obtain the desired thickness. Each layer was coated on at 3000 rpm for 30 s, and then dried at 300 °C for 5 min to remove the residual organics. The PZT films were crystallized in ambient atmosphere at 600 °C for 30 min. The Pt top electrode was deposited by DC magnetron sputtering with a shadow mask (200 μm in diameter).

The resistivity of LNO films was measured using DC four-point probe method on a Keithley 238 high current source measure unit. The crystalline structure of PZT films on the LNO bottom electrodes of different oxygen partial pressure was examined by X-ray diffraction (XRD) on a Rigaku diffractometer. The in-plane and cross-sectional microstructure of the PZT and LNO films were observed by scanning electron microscopy (SEM). The ferroelectric properties were measured on a precision workstation ferroelectric tester (Radiant Technologies Inc.). The fatigue tests were performed using a triangular wave voltage with amplitude of 5 V and a frequency of 1 MHz.

3. Results and discussion

The resistivity of the bottom LNO films deposited at different oxygen partial pressures is shown in Fig. 1. It increases with the increasing $O_2/(O_2 + Ar)$ ratio. This trend suggests that the resistivity is strongly affected by the amount of excess oxygen incorporated in the films.[8]

Fig. 2(a) and (b), respectively, show the *P–E* curves of the PZT on the as-deposited LNO bottom electrode at different oxygen partial pressures and the remanent polarization, $2P_r$. An optimal $2P_r$, 101.4 μC/cm^2, is observed in the PZT/LNO film capacitor whose LNO electrode was deposited at 30% oxygen partial pressure. The remanent polarization of ferro-

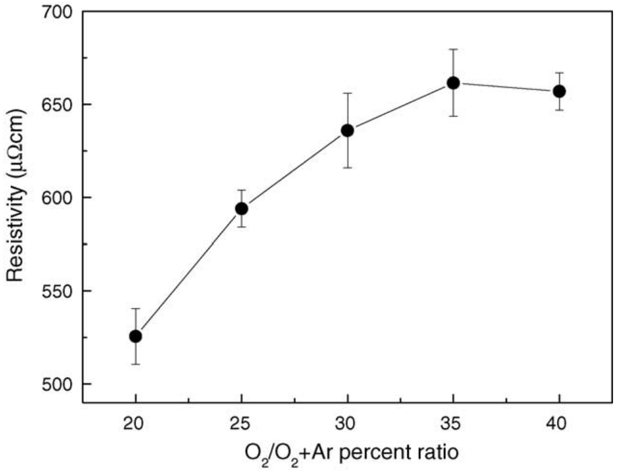

Fig. 1. The resistivity of the as-deposited $LaNiO_3$ films at different oxygen partial pressures.

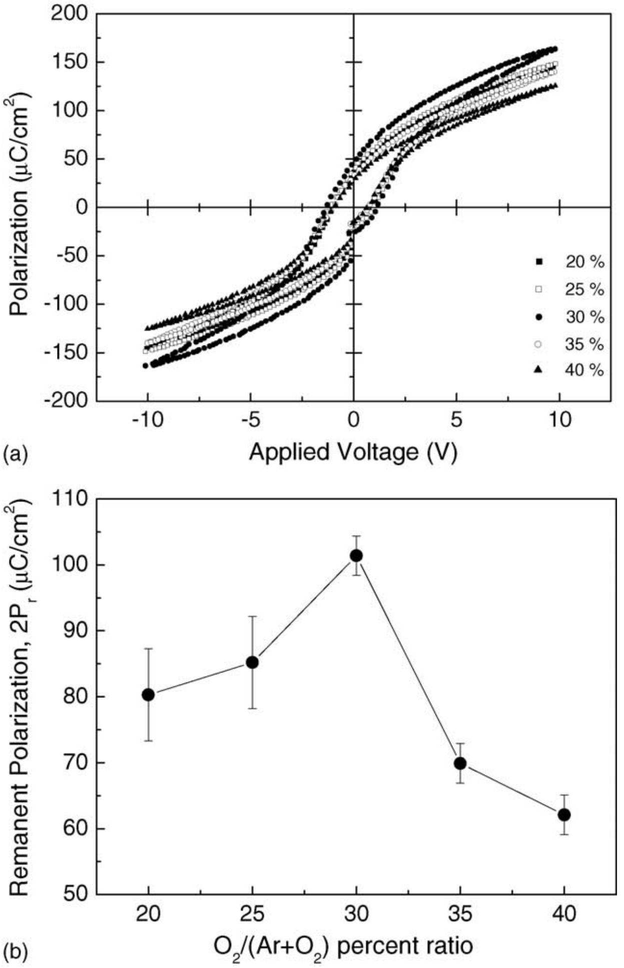

Fig. 2. Ferroelectric properties of the PZT films: (a) polarization–electric field (*P–E*) curves and (b) the dependence of remanent polarization, $2P_r$ of PZT films on the as-deposited LNO electrodes deposited at different oxygen partial pressures.

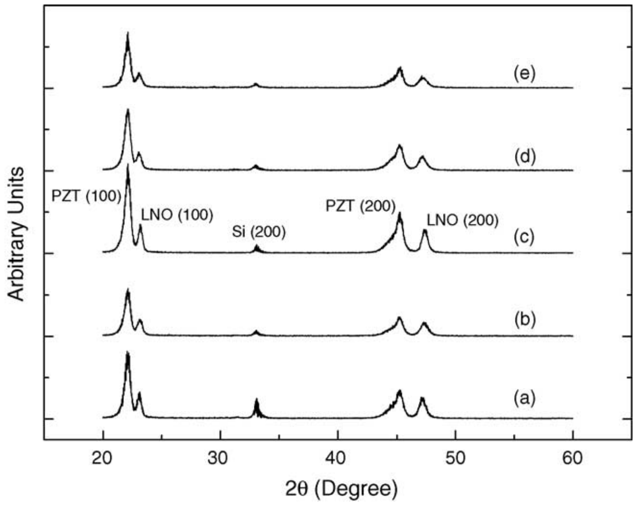

Fig. 3. XRD patterns of PZT films deposited on LNO electrodes deposited at different partial pressures: (a) 20%, (b) 25%, (c) 30%, (d) 35%, and (e) 40% oxygen partial pressure.

electric thin films is very often affected by their crystalline structure.[9] To establish the relationship between the remanent polarization and the crystallinity of the PZT film, we have investigated their XRD patterns.

Fig. 3 shows the XRD θ–2θ scans of PZT thin films deposited on LNO electrodes and they display predominant preferred (1 0 0) and (2 0 0) reflections. It indicates that the maximum P_r of the PZT thin film at 30% relative oxygen pressure also assumes the (1 0 0) texture. In addition, we have investigated the microstructure of LNO films.

The SEM microstructure of LNO films deposited at different oxygen partial pressures is shown in Fig. 4. The cross-sectional micrographs show that the film of Fig. 4(c) grew columnar. This film was grown at 30% oxygen partial pressure, while the rest at other than 30% oxygen partial pressure have granular structure. The maximum P_r derived from the LNO deposition at 30% oxygen partial pressure is definitely associated with the LNO's columnar microstructure. However, there is no grain size dependence of the LNO and PZT films on the oxygen partial pressure. The grain size of LNO films is about 30 nm and that of PZT films about 70 nm in all oxygen partial pressure.

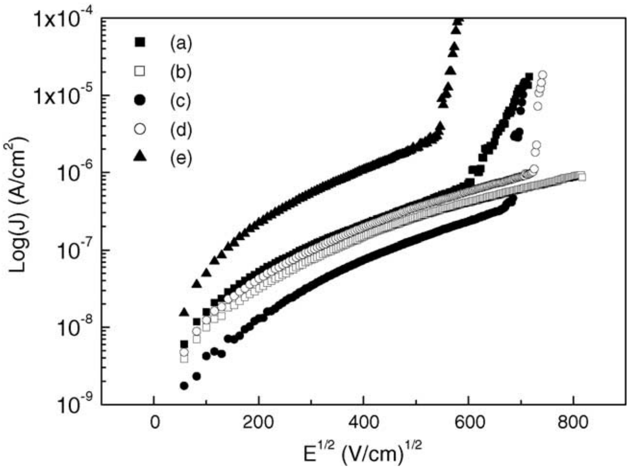

Fig. 5. Variations of log(J) of the Pt/PZT/LNO capacitors as a function of $\sqrt{E}$ deposited whose LNO electrodes at different oxygen partial pressures from 20 to 40%.

Fig. 5 shows the variations of the leakage current density (J) as a function of the square root of the applied electric field (E) of LNO/PZT capacitors with the LNO electrodes

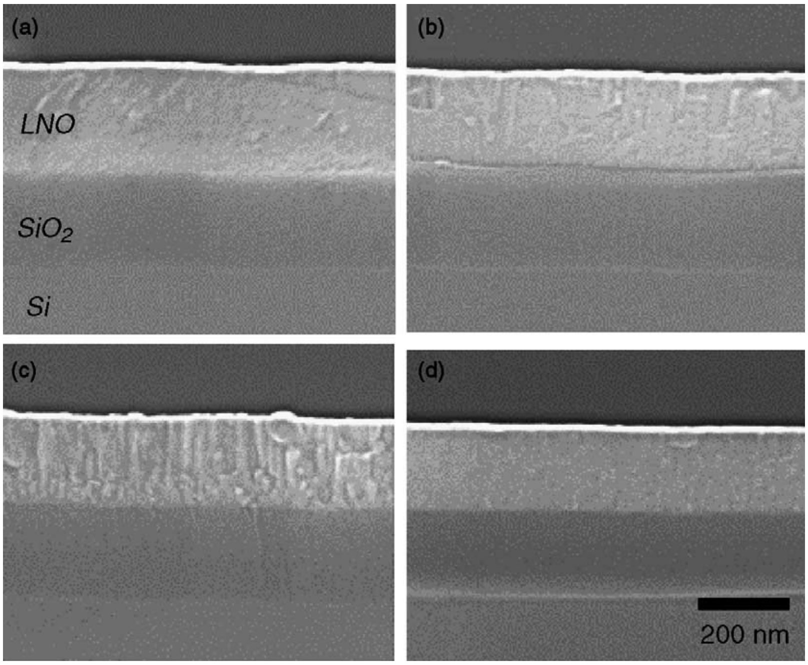

Fig. 4. SEM micrographs of the cross sectional view of LNO films on SiO_2/Si (100) substrate: (a) 20%, (b) 25%, (c) 30%, and (d) 40% oxygen partial pressure.

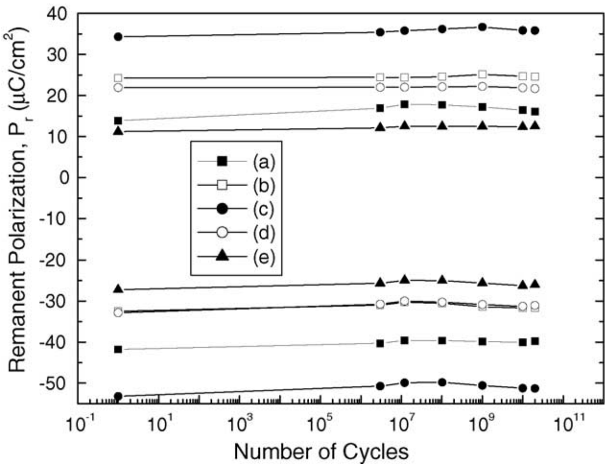

Fig. 6. Fatigue properties of the Pt/PZT/LNO capacitors with their LNO electrodes deposited at different oxygen partial pressures.

deposited at different oxygen partial pressures. The current density is dependent on the kind of LNO bottom electrodes, and it increases with the applied voltage. The capacitor of the LNO electrode deposited at 30% oxygen partial pressure has the lowest leakage current density. Another feature which should be noted is that the logarithm of the leakage current density in the low mid-field region increases almost linearly with the square root of the applied field, but in the high field region it increases abruptly. Furthermore, the leakage current densities of the capacitors in the high field regions show different behaviors depending on the LNO deposition condition. In other words, in the low mid-field region, the slopes of leakage current density remain almost same. However, in the high field region, the electrical break down happens in different fashion.

The fatigue properties of the LNO/PZT capacitors are given in Fig. 6. It shows the remanent polarization as a function of the applied fatigue cycles. We can clearly see that the PZT capacitors are almost free of fatigue up to 10^{10} switching cycles and the remanent polarizations and hysteresis loops are not changed after fatigue experiment. Also leakage current behavior is almost same after fatigue. It has been reported that the fatigue life span of ferroelectric thin films is dependent on the status of trapped oxygen vacancies at or near the electrode interfaces, which results in the suppression of further domain switching.[10] Our result suggests that conductive oxide LNO electrode can supplement oxygen to the oxygen vacancies of the ferroelectric thin films near the electrode/PZT interface. Thus, the fatigue life span may be extended.

4. Conclusions

We have investigated the ferroelectric and fatigue properties of sol–gel processed PZT capacitors on the RF magnetron sputtered $LaNiO_3$ electrodes. The LNO electrodes were deposited from the Ni metal target with La metal chips on top of it at 300 °C and 10 mTorr and at different oxygen partial pressures. The resistivity of the LNO bottom electrode increases with the increasing oxygen partial pressure. The remanent polarization of the capacitor has the maximum value in the capacitor whose LNO electrode was deposited at 30% oxygen partial pressure. The leakage current density of the capacitors takes up the lowest value in coincidence when the LNO electrode was also deposited at 30% oxygen partial pressure. The switched polarization value, that is, the fatigue property of all the capacitors remains almost constant up to 2×10^{10} switching cycles.

Acknowledgement

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