J Mater Sci (2007) 42:6956–6960
DOI 10.1007/s10853-006-1290-2

Investigation of $PbZr_{0.4}Ti_{0.6}O_3$ capacitors with room temperature as-grown $LaNiO_3$ electrodes

B. T. Liu · F. Li · C. S. Cheng · D. Q. Wu · X. B. Yan · F. Bian · Z. Yan · Q. X. Zhao · X. Y. Zhang

Received: 17 August 2006 / Accepted: 17 November 2006 / Published online: 26 April 2007

Abstract $LaNiO_3$ (LNO) film grown at room temperature (RT) by RF magnetron sputtering is used as the electrode for integrating $LaNiO_3/PbZr_{0.4}Ti_{0.6}O_3/LaNiO_3$ (LNO/PZT/LNO) capacitor on $SrTiO_3$ (STO) substrate. For comparison, LNO film grown at 250 °C is also used as the electrode of PZT capacitor. Reflection high energy electron diffraction (RHEED) technique is used to characterize the LNO film, it is found that LNO film prepared at 250 °C is epitaxial although no diffraction pattern is found for RT as-grown LNO. Ferroelectric properties of PZT films strongly depend on the LNO bottom electrodes. The remanent polarization (P_r) and coercive voltage (V_c), measured at 5 V, for the capacitors with LNO bottom electrodes prepared at RT and 250 °C, are 20 and 37 $\mu C/cm^2$, 1.67 and 1.95 V, respectively. No obvious degradation of polarization for PZT capacitors with RT as-grown LNO electrodes can be found. Room temperature as-grown LNO as both bottom and top electrodes to fabricate ferroelectric capacitors can save 2/3 thermal budgets, which may pay a way to decrease the potential challenges of devices resulting from the oxidation, interdiffusion or reactions during integrating ferroelectric capacitors with Si technologies.

B. T. Liu (✉) · F. Li · C. S. Cheng · D. Q. Wu · X. B. Yan · F. Bian · Z. Yan · Q. X. Zhao
College of Physics Science & Technology, Hebei University, Baoding, Hebei 071002, China
e-mail: btliu@mail.hbu.cn

X. Y. Zhang
Key Laboratory of Metastable Materials Science and Technology, Yanshan University, Qinhuangdao, Hebei 066004, China

Introduction

$Pb(Zr_xTi_{1-x})O_3$ (PZT) is currently one of the most widely studied materials, due to its favorable properties such as high dielectric constant, large remnant polarization and piezoelectric coefficient, for potential applications e.g., ferroelectric random access memories (FeRAM) [1, 2], micro-electro-mechanical systems (MEMS) [3, 4] and field effect transistor [5]. The decrease in switchable polarizations of PZT on metallic electrodes, such as Pt, has been greatly improved or even eliminated by replacing Pt with oxide electrodes in the capacitor structures. These oxide electrodes can be roughly divided into two categories: one is conductive perovskite oxide, such as $LaNiO_3$ (LNO) [6, 7], $La_{0.5}Sr_{0.5}CoO_3$ [8, 9], and $SrRuO_3$ [10], the other is non-perovskite metal oxide, such as IrO_2 [11]. Since the materials in the former group have similar crystal structure as that of PZT and have good chemical stability, they are regarded as the suitable candidates for the oxide electrodes. Among them, LNO is the most popular since it has a relatively lower electrical resistivity, and smaller lattice mismatch with PZT. On the other hand, much research has been done to integrate $Pb(Zr,Ti)O_3$ (PZT) ferroelectric capacitors as nonvolatile memory elements with the silicon based transistor technology to yield one transistor-one capacitor based memory architectures [12]. However, integration into high-density complementary-metal-oxide-semiconductor (CMOS) architecture is restricted by high processing temperature (typically 650 °C for sol-gel PZT film) since high growth temperature can introduce potential reactions, oxidation or interdiffusion of/between stack layers [13, 14]. Further lowering the processing temperature or even simplifying the annealing process of the capacitor stack should drastically reduce potential material challenge between different material layers. If room temperature (RT) as-grown oxide films can be used as both bottom and top electrodes of ferroelectric capacitor, this will not only save 2/3 thermal budgets but also greatly decreases the potential challenges of devices resulting from the oxidation, interdiffusion or reactions during fabricating such stacks. However, few results have been reported currently for RT as-grown LNO film used as the electrode of PZT capacitor. We therefore use a modified PZT solution to lower the annealing temperature of PZT film, and fabricate LNO/PZT/LNO capacitors with RT as-grown LNO electrodes. LNO film prepared at 250°C is also used as the bottom electrode of PZT capacitors in order to investigate the influence of LNO bottom electrode on the properties of the LNO/PZT/LNO capacitors.

Experimental procedure

Briefly, LNO (70 nm)/PZT (160 nm)/LNO (70 nm) ferroelectric capacitor heterostructures were fabricated on STO substrates with a combination of both sputtering and sol-gel methods. LNO bottom electrode layers were deposited by RF magnetron sputtering with a power of 50 W using a mixture of Ar:O_2 (3:1) at RT and 250 °C, respectively. After the deposition, the LNO film deposited at 250 °C was cooled to RT in a 0.8 atm oxygen atmosphere. PZT ferroelectric thin film was then grown on the LNO film using sol-gel method. In our experiments, a modified PZT solutions with 15% of Pb excess was used to compensate lead loss during annealing. PZT solutions were spin-coated at 4,000 rpm and baked at 350 °C for 5 min on a temperature-fixed hotplate. This deposition process was repeated four times. Then the PZT films were annealed at 550 °C for 1 h in a flowing-oxygen tube furnace. LNO and Pt films for Pt/LNO/PZT/LNO capacitor structure were subsequently deposited on top of the samples to obtain 9.6×10^{-4} cm^2 pads using a shadow mask. All of the LNO top electrodes for PZT capacitors were deposited at RT in order to simplify the effects of the LNO bottom electrode. The surface morphology and crystal structure of LNO bottom electrodes were characterized by atomic force microscope (AFM) and reflection high-energy electron diffraction (RHEED), respectively. The orientation and crystallinity of Pt/LNO/PZT/LNO/STO heterostructures were examined by X-ray diffraction (XRD). The ferroelectric properties of LNO/PZT/LNO capacitors were tested using Precision LC unit from Radiant Technologies.

Results and discussion

Figure 1 shows the RHEED patterns of LNO films prepared at both RT and 250 °C. We cannot find any diffraction pattern when LNO film was deposited at RT, as shown in Fig. 1a. While clear pattern could be observed for LNO film deposited at 250 °C, as shown in Fig. 1b, indicating that LNO film deposited on $SrTiO_3$ at 250 °C is epitaxial. LNO film deposited at RT is not well crystallinized, which is also confirmed by the XRD measurements.

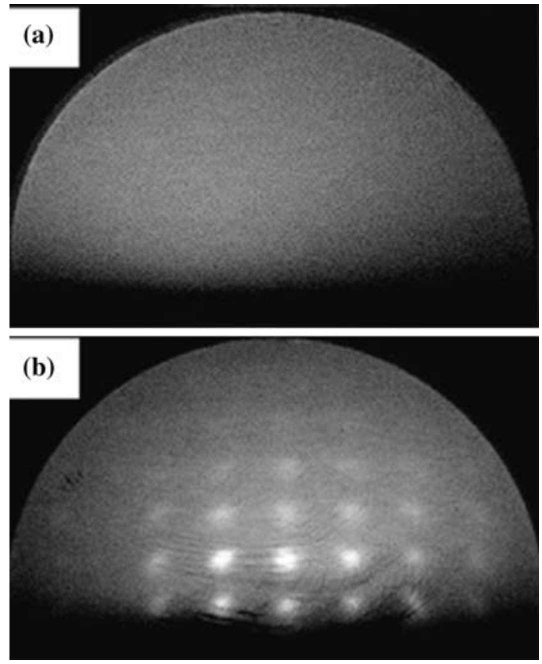

Fig. 1 RHEED patterns of LNO films prepared at temperatures of (**a**) RT and (**b**) 250 °C

The AFM images of the surface morphology of the above-mentioned LNO films are presented in Fig. 2. It can be seen that the surface of LNO films are smooth and uniform. The grain size of LNO film prepared at 250 °C is larger than that prepared at RT, as demonstrated in Figs. 2b and a, respectively; and the root mean square (rms) roughnesses for LNO prepared at RT and 250 °C are 0.237 and 0.466 nm, respectively.

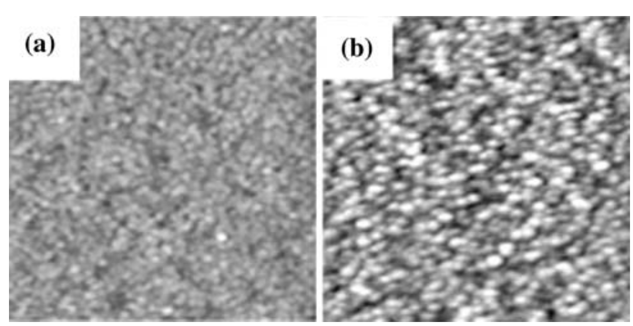

Fig. 2 AFM images for LNO films prepared at (**a**) RT and (**b**) 250 °C

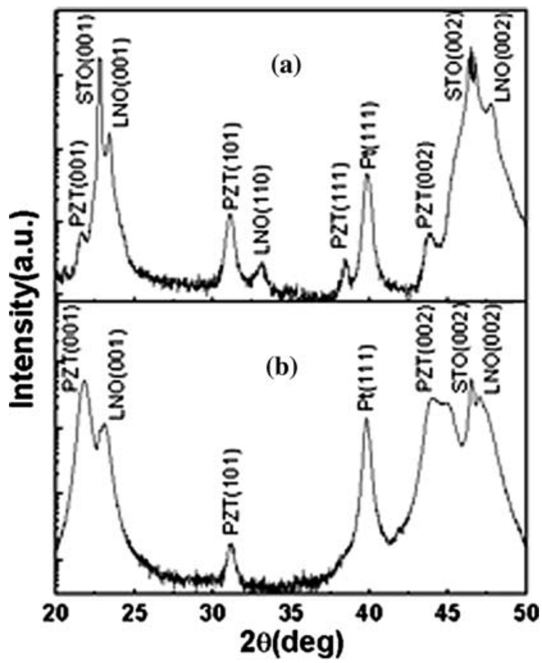

Fig. 3 XRD spectra of the Pt/LNO/PZT/LNO/STO heterostructures with LNO bottom electrodes prepared at temperatures of (**a**) RT and (**b**) 250 °C

Figure 3a and b show the XRD spectra of Pt/LNO/PZT/LNO/STO heterostructures obtained from the bottom LNO electrodes deposited at RT and 250 °C, respectively. (001), (002) and (110) LNO peaks can be found from Fig. 3a, implying LNO bottom layer is fully crystallized after the growth of PZT layer. In this case, PZT film is polycrystalline with strong (101) oriented peaks. In contrast, PZT film grown on epitaxial (001) LNO film is highly (001) oriented, as presented in Fig. 3b, indicating the LNO bottom electrode greatly impacts the microstructure of PZT capacitor heterostructure due to the interface effects (such as grain size and crystalline quality of LNO electrode). It is well-known that epitaxial film can be used as a template to grow highly oriented/epitaxial PZT film.

Hysteresis loops of LNO/PZT/LNO capacitors with different LNO electrodes measured at 5 V are shown in Fig. 4. The remanent polarizations and coercive voltages, corresponding to LNO electrodes prepared at RT and 250 °C, are 20 and 37 μC/cm^2, 1.67 and 1.95 V, respectively. Note that the well-saturated hysteresis loop, corresponding to curve (a) in Fig. 4, further convinced us that the PZT films annealed at 550 °C with RT as-deposited LNO bottom electrode are in the perovskite phase instead of pyrochlore phase. Moreover, it is found that capacitors with LNO bottom electrode deposited at 250 °C yields much larger polarization, as shown in curve (b) of Fig. 4. The switchable polarization ΔP, a parameter that can be directly read from Radiant ferroelectric tester, is defined as

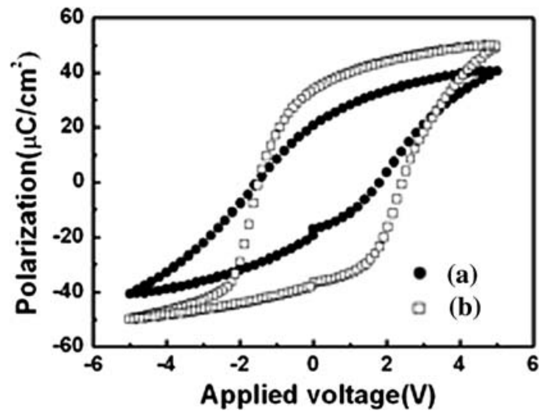

Fig. 4 Hysteresis loops for LNO/PZT/LNO capacitors with LNO bottom electrodes prepared at temperatures of (**a**) RT and (**b**) 250 °C

the difference between the switched (P*) and non-switched (P^) polarizations. Compared with the conventional P_r, ΔP is regarded to reflect the ferroelectric properties more accurately because the interference coming from the leakage current is removed. Figure 5 shows the pulse width dependence of switchable polarization (ΔP) measured by 5 V pulses with a 1 s delay. Both LNO/PZT/LNO capacitors with different LNO bottom electrodes show the similar trends with small slope of 6–8 μC/cm^2 per decade. The switchable polarization values at pulse width of 0.1 ms of the PZT capacitors with different LNO bottom electrodes are 25 and 57 μC/cm^2, respectively. The weak pulse-width dependence of polarization for the LNO/PZT/LNO capacitors implies that these capacitors prepared by this method are suitable for the high-speed ferroelectric random access memory application.

One of the most important concerns for the ferroelectric random access memory is retention, the ability of the memory element to store a given data state. Retention loss

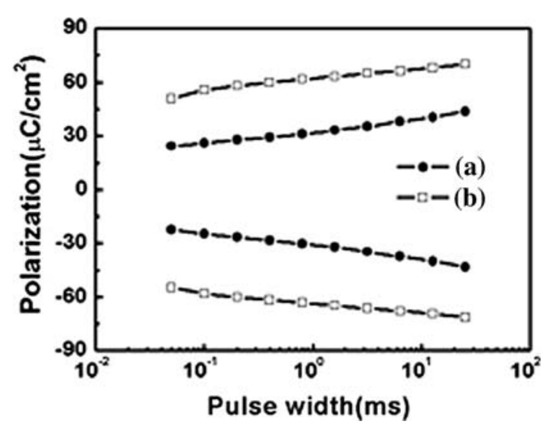

Fig. 5 Pulse width dependence of ΔP of LNO/PZT/LNO capacitors with LNO bottom electrodes prepared at temperatures of (**a**) RT and (**b**) 250 °C

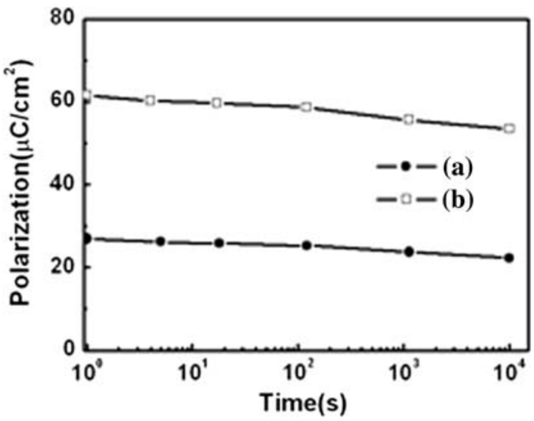

Fig. 6 Polarization of the LNO/PZT/LNO capacitors as a function of retention time

causes a reduction in the stored voltage signals, and leads to an inability to distinguish between the two logic states (1 and 0). Retention experiments were carried out with a write voltage of –5 V (1 ms pulse width) followed by a read at +5 V (1 ms pulse width). Figure 6 illustrates the dependence of switchable polarization (ΔP) versus retention time. There is little retention loss up to 10^4 s, and the ΔP of the capacitors keep at 22 and 53 μC/cm^2 for capacitors with LNO bottom electrodes prepared at RT and 250 °C, as demonstrated by curves (a) and (b) in Fig. 6, respectively.

Fatigue measurements were carried out using a 1 MHz triangular waveform with amplitude of 5 V. Figure 7 presents the relation of the switchable polarization (ΔP) values of the PZT capacitors versus fatigue cycles. The polarization of the PZT capacitors with LNO bottom electrode prepared at 250 °C decreased 8% after 10^{10} fatigue cycles, corresponding to curve (b), however, the PZT capacitors with LNO bottom electrode prepared at RT did not show obvious loss for ΔP value, as illustrated by curve (a). The differences of physical properties for the two kinds of capacitors should be attributed to impact of the LNO bottom electrode, which controls the microstructures of the PZT films. Imprint is described simply as the preference of a certain polarization state over the other in ferroelectric bistable states, and can be observed from the asymmetry of polarizations of different directions. Noted that symmetric polarization behavior along two voltage directions (positive and negative) shown in Figs. 5 and 7, besides the hysteresis loops, indicated that the LNO/PZT/LNO capacitor have a less preferred polarization state (i.e. little imprint).

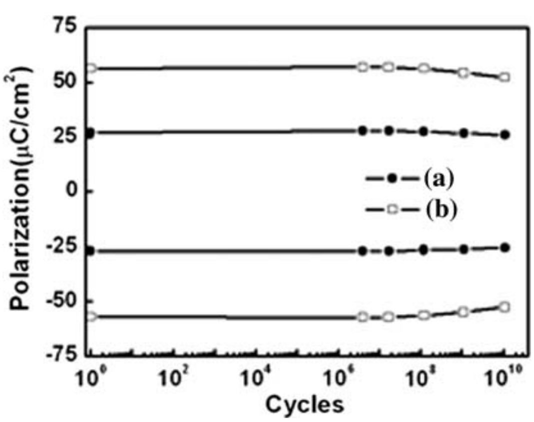

Fig. 7 Fatigue characteristics of LNO/PZT/LNO capacitors as a function of switching cycles

Conclusion

PZT capacitors with RT as-grown LNO electrodes were fabricated on $SrTiO_3$ substrates using combination of both magnetron sputtering and sol-gel method. The well-saturated hysteresis loops of PZT capacitors fully convinced us that PZT films are in the perovskite phase instead of pyrochlore phase. PZT capacitors possess reasonable polarization, and less fatigue compared to PZT capacitors with LNO bottom electrode grown at 250 °C. The promising results may be helpful to the viable integration of ferroelectric capacitors with silicon-based technology. Further work for fabricating Si-based ferroelectric capacitors with RT as-grown LNO electrodes is under way.

Acknowledgements This work is partly supported by the NSFC (No. 50572021), SRF for ROCS from both State Education Ministry and Ministry of Personnel, the NSF of Hebei Province of China (No. E2005000130), and Foundations of Hebei Provincial scientific/educational departments (No. 04213579 and No. 2005213), and Hebei University.

References

1. Liu BT, Cheng CS, Li F, Ma L, Zhao QX, Yan Z, Wu DQ, Li CR, Wang Y, Li XH, Zhang XY (2006) Appl Phys Lett 88:252903
2. Kim S, Koo J, Shin S, Park Y (2005) Appl Phys Lett 87:212910
3. Kang GY, Bae S-W, Park H-H, Kim TS (2006) Appl Phys Lett 88:042904
4. Ahn CH, Rabe KM, Triscone J-M (2004) Science 303:488
5. Zhao T, Ogale SB, Shinde SR, Ramesh R, Droopad R, Yu J, Eisenbeiser K, Misewich J (2004) Appl Phys Lett 84:750
6. Han H, Zhong J, Kotru S, Padmini P, Song XY, Pandey RK (2006) Appl Phys Lett 88:092902
7. Lin CH, Friddli PA, Ma CH, Daga A, Chen H (2001) J Appl Phys 90:1509
8. Wang Y, Ganpule C, Liu BT, Li H, Mori K, Hill B, Wuttig M, Ramesh R, Finder J, Yu Z, Droopad R, Eisenbeiser K (2002) Appl Phys Lett 80:97
9. Wang GS, Meng XJ, Sun JL, Lai ZQ, Yu J, Guo SL, Cheng JG, Tang J, Chu JH (2001) Appl Phys Lett 79:3476
10. Maki K, Liu BT, Vu H, Ramesh R, Fujimori Y, Nakamura T, Takasu H (2003) Appl Phys Lett 82:1263
11. Nakamura T, Nakao Y, Kamisawa A, Takasu H (1994) Appl Phys Lett 82:1522

12. Auciello O, Scott JF, Ramesh R (1998) Phys Today 51:22
13. Wang ZJ, Kokawa H, Takizawa H, Ichiki M, Maeda R (2005) Appl Phys Lett 86:212903
14. Liu BT, Maki K, Aggarwal S, Nagaraj B, Nagarajan V, Salamanca-Riba L, Ramesh R, Dhote AM, Auciello O (2002) Appl Phys Lett 80:3599