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Effect of electrode and substrate on the fatigue behavior of PZT thick films fabricated by aerosol deposition

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Abstract

10 μm-thick lead zirconate titanate (PZT) films with identical $LaNiO_3$ (LNO) top and bottom electrodes were fabricated on silicon and yttria-stabilized zirconia (YSZ) substrates by aerosol deposition (AD). A Pt electrode was also made for comparison. The dielectric, ferroelectric and fatigue behaviors at different fields were investigated. The PZT films on YSZ/LNO showed the highest dielectric and ferroelectric properties and good fatigue behavior under various fields. PZT films with a Pt electrode also showed good fatigue behavior up to 10^8 cycles as thicker film can minimize the effect of defect entrapment near the interface.

Keywords: A. Film; C. Fatigue; D. PZT; Aerosol-deposition (AD)

1. Introduction

The main limitation in the commercial applications of piezoelectric ceramic films is the degradation of polarization with increasing number of cycling [1]. Defect entrapment in the interface of metal electrode is believed to destroy the ferroelectric properties of films, resulting in fatigue behavior [2]. The remanent polarization of a Pt/PZT/Pt capacitor is reduced to less than half of initial value by 1×10^6 switching cycles [3].

There are many reports on the use of $SrRuO_3$, RuO_2, $LaNiO_3$ (LNO), Ir or IrO_2 electrode to improve the fatigue behavior of PZT films [4–7]. However, all of these were based on thin films, typically less than 1 μm, whose results are not suitable for thick film applications. In addition, most of them were asymmetrical structures, i.e., the top electrode was still Pt or Au metals. Therefore, it is difficult to attribute the improvement of properties to the structure or the electrode materials. Most importantly, thin film processes such as sol–gel or sputter methods are quite sensitive to the substrates. For example, PZT films deposited on LNO are prone to orientation due to the lattice matching [8]. Thus, the property enhancement may be due to this grain orientation rather than the electrode material itself.

Aerosol deposition (AD) can be used to fabricate polycrystalline films. In this study, up to 10 μm-thick PZT films were made on silicon and yttria-stabilized zirconia (YSZ) substrates by AD process. The LNO top and bottom electrodes were also deposited by AD process to ensure that the crystalline and interface states were identical. A comparable Pt electrode was also used.

2. Experimental procedures

Lanthanum oxide [La_2O_3, 99.9% purity, Aldrich Co., Milwaukee, WI] and nickel acetate [$Ni(CH_3COO)_2{\cdot}4H_2O$, 99.9% purity, Aldrich Co., Milwaukee, WI] were used to fabricate LNO powder. Nickel acetate was first dissolved in ethanol, then lanthanum oxide was adding into the sol to make a gel, which was dried and calcined at 850 °C/20 h. LNO bottom electrodes were deposited by AD on commercially available silicon wafer (P type boron doped Si <1 0 0>, roughness of 0.23 nm, produced by Inostek Inc., Korea) and homemade YSZ ceramic substrates (Tosoh TZ-3Y powder was cold isostatic pressed at 200 MPa and sintered at 1450 °C/2 h, then polished to $\Phi 30 \times 1\ mm^2$ plate by 1 μm diamond suspension).

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Following the LNO deposition, around 10 μm-thick PZT films were deposited on Si/LNO, YSZ/LNO or Si/Pt substrates using commercial PZT-based powder ($Pb(Al_{1/3}Nb_{2/3})O_3$–$Pb(Zr,Ti)O_3$, KP10, Kyungwon Ferrite Ind. Co., Shiheung, Korea). All the films were annealed at 700 °C/1 h. The Φ1 mm LNO top electrodes were deposited by AD, and Pt electrodes by DC sputtering. The AD process has been described in detail in our previous articles [9].

The film microstructures were observed using scanning electron microscopy (SEM: JSM-5800, Jeol Co., Tokyo, Japan). The residual stresses of the films were analyzed by high-resolution X-ray Psi scan diffraction system (HR-XRD, X'pert Pro MRD, Philips, Netherlands) based on PZT peaks at $2\Theta \sim 55°$. The dielectric properties were measured using an impedance analyzer (4294A, Agilent Technologies, Santa Clara, CA). The polarization-field hysteresis loops and fatigue were measured by a standardized ferroelectric test system (P-LC100-K, Radiant Technologies, Albuquerque, NM). Bipolar triangle pulses with a frequency of 10 kHz and a maximum value of either 150 kV/cm or the coercive field (Ec) of the films were used for fatigue measurement.

3. Results and discussion

All three samples showed similar perovskite phase by X-ray diffraction (XRD), although the patterns are not presented in this article. Fig. 1 shows the cross-sectional SEM micrographs of the annealed films on different substrates. The films were highly dense and maintained good adhesion with the substrates and the LNO layer, without any delamination (Fig. 1(a) and (c)). The energy dispersive X-ray spectroscopy (EDS) mapping results (Fig. 1(b)) revealed an LNO electrode thickness of less than 1 μm, and the absence of any reaction signature between the PZT, LNO and substrate. For more detailed examination of the interface and three-layered structure, we made thicker LNO (~7 μm) and PZT films on YSZ substrates, as shown in Fig. 1(c) and (d). The structure of YSZ/LNO/PZT was clearly seen and the EDS mapping also showed there is no interface reaction. The identical and dense films could be fabricated on different substrates by the AD process.

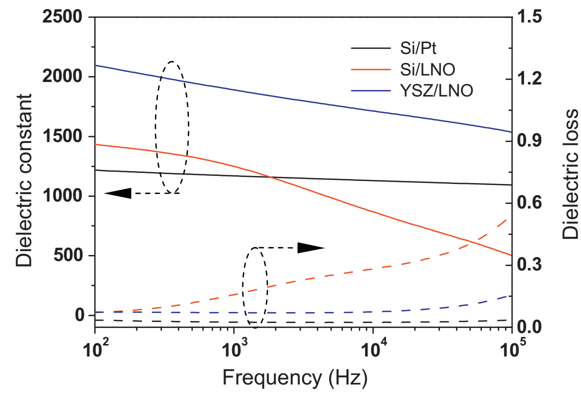

Fig. 2. Dielectric constants and losses according to the frequency of PZT films on the three different substrates.

Fig. 2 presents the dielectric constant and loss of PZT films varies with frequency for different substrates and electrodes. The dielectric constants gradually decreased and the dielectric loss increased with increasing frequency for all three substrates, but the dielectric constant decrement and loss increment were greater for the Si/LNO substrate. The dielectric properties of the PZT film on YSZ/LNO were extremely high relative to the other films. The dielectric constant and loss at 1 kHz were 1169

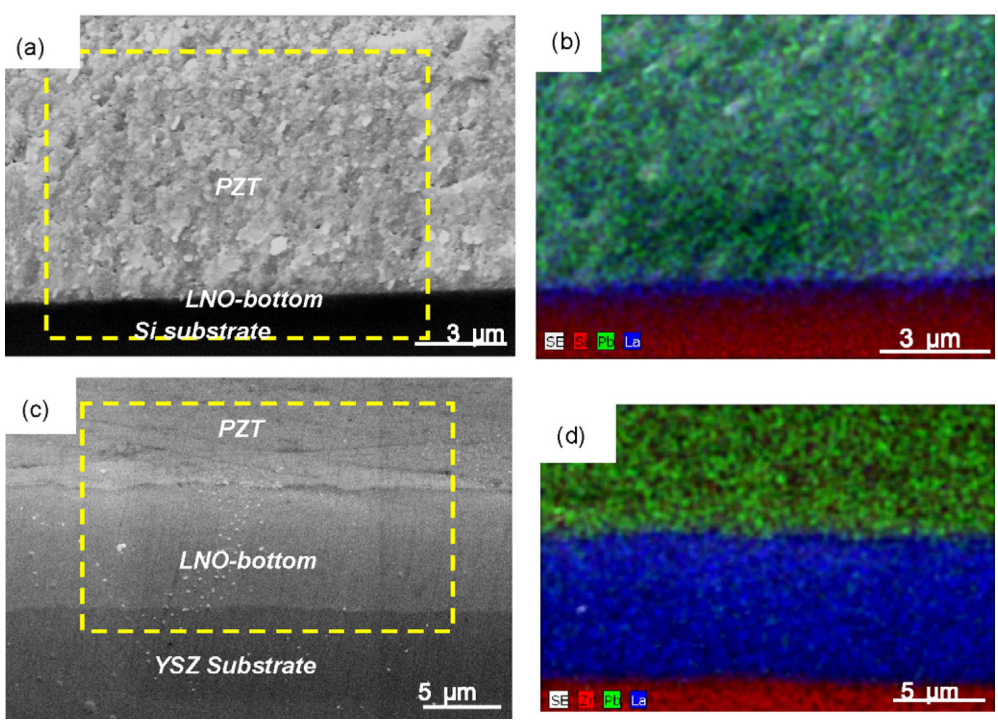

Fig. 1. Sectional SEM micrographs and EDS mapping of PZT films on (a and b) Si/LNO and (c and d) YSZ/LNO substrates.

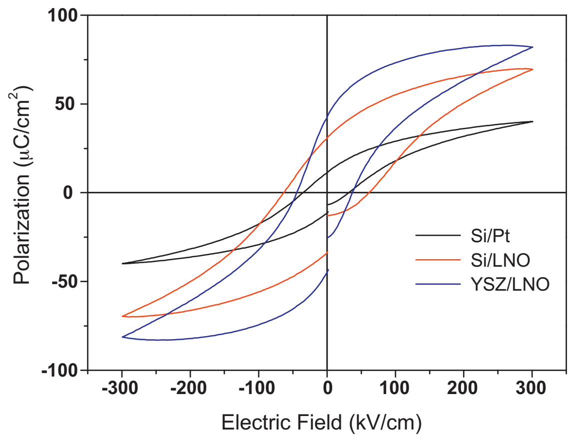

Fig. 3. *P–E* hysteresis loops of PZT films on different substrates.

and 0.0254 for Si/Pt, 1249 and 0.158 for Si/LNO, and 2268 and 0.0705 for YSZ/LNO substrate, respectively.

Fig. 3 shows the *P–E* hysteresis loops of PZT films on the three different substrates. All the loops showed typical ferroelectric characteristics. Comparing the results for the three different substrates, the remnant and saturated polarization of films on Si/Pt were lowest, which were almost half the values of those of films on YSZ/LNO. According to Chao and Wu [10], the films on the LNO electrode showed good ferroelectric properties, although no reason was given for the better properties of the LNO electrode.

In order to analyze this result, the surface stress states of the films were measured by high resolution XRD (HR-XRD). The films on Si/Pt and Si/LNO substrates exhibited tensile stresses of 89.5 ± 3.6 and 96.2 ± 3.7 MPa, respectively. However, the films on YSZ/LNO exhibited a compressive stress of -303.6 ± 5.6 MPa. These different stresses are mainly due to the difference of thermal expansion coefficients of PZT film and substrates, i.e., thermal expansion coefficient of PZT is higher than that of silicon but lower than that of YSZ. During cooling process after annealing, tensile and compressive stresses can be respectively induced in interface between the film and substrate. Such a compressive stress can induce a domain orientation in the thickness direction much easier [11]. Therefore, the films on the YSZ/LNO substrate showed much higher dielectric and ferroelectric properties. The much higher stress of thin films may markedly affect their ferroelectric properties.

Fig. 4 shows the fatigue behavior of the PZT films on different substrates under a driving field of (a) equivalent to Ec and (b) 150 kV/cm. The PZT films on the Si/Pt and YSZ/LNO substrates showed similar switching behavior at Ec, with the polarization (Pr or −Pr) after 10^9 switching cycles showing almost no change. However, after only 10^4 cycles, the Pr of films on the Si/LNO substrate was increasing, indicating that some leakage occurred. While switched at the relatively high field of 150 kV/cm, the Pr of the PZT films on Si/LNO gradually decreased with increasing fatigue cycling, as shown in Fig. 4(b). The film on YSZ/LNO was stable up to 10^7 cycles, after which a small Pr increment was observed. For the Si/Pt substrate, despite a small Pr increment after 10^4 cycles, the film showed no apparent fatigue phenomena until 10^8 cycles, which is higher than thin film of 10^6 cycles.

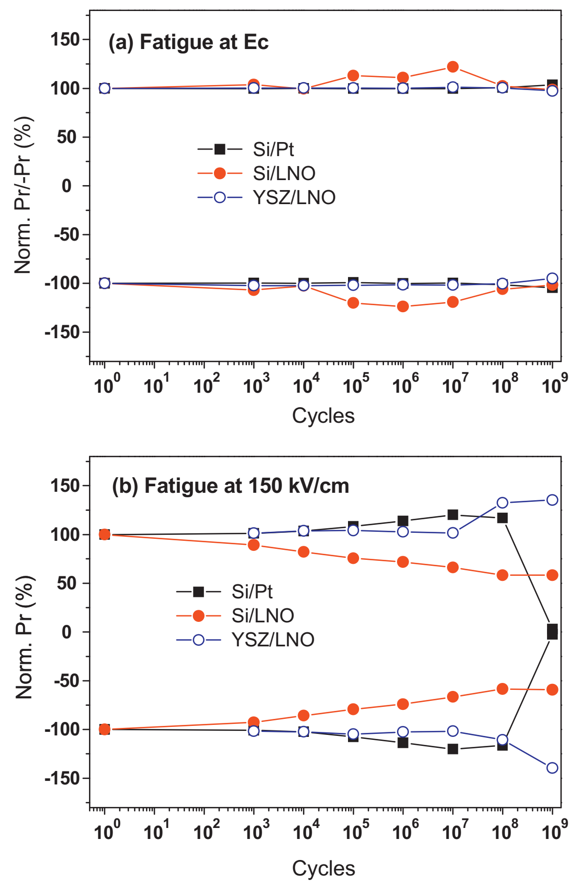

Fig. 4. Normalized remnant polarizations as a function of fatigue cycles of PZT films on the three different substrates, tested under a field of (a) Ec and (b) 150 kV/cm.

Generally accumulation of oxygen vacancies at the electrode interface degrades the film properties, leading to fatigue. In our case, the film was relatively thicker than those reported in the literature (<1 μm). The interface region of the present study was relatively small compared to the thick films. As the entrapment of defects at the electrode interface did not greatly affect the ferroelectric properties of our thick films, the Pt electrode could be used up to 10^8 switching cycles. Our previous work also demonstrated improved properties with increasing film thickness because of the decrease of the interface clamping effect [12]. This indicated that the fatigue behavior can be improved by increasing the film thickness to minimize the effect of defect entrapment in the electrode interface.

4. Conclusion

Thick PZT films were deposited and controlled by AD process on silicon and YSZ substrates with identical top and bottom LNO electrodes. The PZT films on YSZ substrate with LNO electrode showed the best dielectric and ferroelectric properties, with a dielectric constant and loss at 1 kHz of 2268 and 0.0705, respectively. The Pr of the PZT film with LNO electrodes was almost twice that of the film with Pt electrode. Both PZT films on Si/Pt and YSZ/LNO substrates showed no fatigue at a lower switching field equivalent to Ec of the films, and at a higher switching field of 150 kV/cm up to 10^8 cycles. This switching endurance was much higher than that of the traditional Pt electrode in thin films, which was attributed to the action of the increased film thickness in minimizing the effect of defect entrapment near the electrode.

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