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Piezoelectric PZT thick films on LaNiO₃ buffered stainless steel foils for flexible device applications

B P Zhu^{1,2}, D D Li³, Q F Zhou^{1,4}, J Shi², and K K Shung¹

¹NIH Transducer Resource Center and Department of Biomedical Engineering, University of Southern California, Los Angeles, CA 90089-1111, USA

²Department of Physics and Key Laboratory of Acoustic and Photonic Materials and Devices of Ministry of Education, Wuhan University, Wuhan 430072, People's Republic of China

³School of Materials Science and Engineering, Shanghai Jiao Tong University, Shanghai 200240, People's Republic of China

Abstract

In this paper, we report on 4.5μm piezoelectric Pb(Zr_{0.52}Ti_{0.48})O₃ (PZT) thick films deposited on flexible stainless steel (SS) foils with LaNiO₃ (LNO) buffer layers using a ceramic powder/sol-gel solution modified composite method. The polycrystalline thick films show a hysteresis loop at an applied electric field of 900 kV cm⁻¹ with remanent polarization and coercive electric field values of 27μC cm⁻² and 85 kV cm⁻¹, respectively. At 1 kHz, the dielectric constant is 653 and the dielectric loss is 0.052. The leakage current density of the film is lower than 1.55 × 10⁻⁵ Acm⁻² over the range of 0 to ±150V. The conduction current shows ohmic behaviour at a low electric field and space-charge-limited current characteristics at a high electric field.

1. Introduction

Piezoelectric lead zirconate titanate (PZT) thick films, at the morphotropic phase boundary (MPB), due to their high piezoelectric response, have been investigated in recent years for such applications as microfluid dynamics devices and ultrasonic transducers [1–3]. However, most PZT thick films are currently deposited on silicon with platinum as the bottom electrode, limiting their range of applications. To permit a broader range of applications, deposition on other substrates, such as flexible metallic foils, is of considerable interest for flexible devices.

PZT thick films deposited onto cheap sheets of stainless steel (SS) are particularly attractive, not only in terms of cost but also for so-called 'metal-based-MEMS' applications [4–7]. However, those PZT thick films have never been prepared on SS substrates whose thicknesses are less than 100μm. The thickness of the metal foil is crucial in maintaining the device flexibility; thinner substrates make the device more flexible. Therefore, the capability of depositing PZT thick films on a thinner SS substrate has generated much interest. Jen *et al* [8] built flexible transducers by depositing PZT thick films directly on 38μm SS substrates using a sol-gel spray technique. Unfortunately, the dielectric constant of flexible PZT thick films produced in this manner is very low ($\epsilon_r = 139$). It has been proposed that the reduction in the dielectric constant in these ferroelectric films may be explained by the existence of inter-diffusion of substances from the metal substrate to the films and the degradation of the metallic bottom electrode so as to form an interfacial 'dead layer', which would result in poor electrical

properties [9,10]. The measured capacitance is the sum of the film capacitance and the capacitance resulting from the dead layer, although it is always significantly lower than the former. The use of conductive oxide electrodes can minimize the thickness of the dead layer and thus enhance the dielectric constant [11–13]. A similar phenomenon has been observed in PZT thin films on SS substrates [14].

LaNiO₃ (LNO) is an n-type metallic conductor at room temperature, and its lattice constant ($a = 3.84$) matches well with that of many ferroelectric perovskite oxides. LNO can be fully oxidized at a lower oxygen pressure during annealing [15,16], which makes LNO a potentially good candidate for electrodes and buffer layers in ferroelectric memory and MEMS devices. To date, there has been no report published on flexible ferroelectric films with the LNO bottom electrode which could not only improve the electrical properties of the films but also maintain device flexibility.

In this work, 4.5 μm piezoelectric Pb(Zr_{0.52}Ti_{0.48})O₃ thick films were synthesized on flexible SS foils (thickness $d = 38 \mu\text{m}$ and area $S = 2 \text{ cm} \times 2 \text{ cm}$) with LNO as buffer layers and bottom electrode via a ceramic powder/sol–gel solution modified composite method [2,3]. The aim of this work is to examine the structural, ferroelectric, dielectric and leakage current characteristics of Pb(Zr_{0.52}Ti_{0.48})O₃ thick films.

2. Experiments

LNO thin films were derived by a metal-organic decomposition (MOD) technique. Lanthanum nitrate and nickel acetate were used as starting materials, and acetic acid and water were used as the solvents. Nickel acetate was initially dissolved in acetic acid at room temperature. Then an appropriate quantity of lanthanum nitrate was dissolved in water. The solutions were mixed under constant stirring at 45 °C. The concentration of the resulting solutions was adjusted to 0.30M for fabricating uniform films. The solutions were spin coated onto flexible SS foils at 3000 rpm for 30 s using a photoresist spinner. After deposition, each layer was annealed at 300 °C for 2 min to drive out the solvent and decompose organic compounds and annealed at 600 °C for 60 s using rapid thermal annealing (RTA). This procedure was repeated to achieve the desired thickness. Finally, the LNO film was furnace fired at 650 °C for 30 min to enhance the conductivity.

The PZT precursor solution was synthesized using lead acetate trihydrate, zirconium n-propoxide and titanium isopropoxide. 2-methoxyethanol (2-MOE) was used as the solvent. First, lead acetate trihydrate was dissolved in 2-methoxyethanol and refluxed at 120 °C for 2 h under a dry Ar atmosphere. The solution was cooled to 80 °C and a stoichiometric amount of zirconium n-propoxide and titanium isopropoxide (Zr : Ti, 48 : 52) were slowly added to the solution while stirring. The mixture was then refluxed at 120 °C for 2 h and the resulting PZT complex solution was cooled to room temperature. In the meantime, lead acetate trihydrate (20 mol% in excess of stoichiometry) was dissolved in 2-MOE and dehydrated at 110 °C. This was mixed with the PZT solution and refluxed at 120 °C for 5 h. Following the refluxed step, the solution was vacuum distilled at 120 °C. Finally, acetylacetone and 2-MOE were added to achieve a final PZT solution concentration of 0.4 M. The PZT piezoelectric ceramic powder (EC-64) was purchased from Piezo Technologies (Indianapolis, IN46268). The PZT composite solution was prepared from PZT powder and PZT solution in mass ratio (powder : solution, 1 : 4), followed by milling with ZrO₂ beads, using a SS twin-shell blender at room temperature for 24 h. Then the composite solution obtained was deposited on LNO buffered flexible SS foils by spin coating at 2000 rpm for 30 s. After deposition, each layer was subjected to 2 min heat treatment on a hot plate at 200 °C and 400 °C to drive out the solution and decompose the organic compounds. A 60s RTA at 600 °C was performed to crystallize the layer. The procedure

was repeated to achieve the desired thickness. Ultimately, thick films were crystallized to phase pure perovskite at 650 °C for half an hour in a conventional box furnace.

The crystalline structure of the PZT films was examined using a Rigaku x-ray diffractometer with Ni filtered Cu K_{α} radiation. Patterns were recorded at a rate of $4^{\circ} \text{ min}^{-1}$ in the 2θ range of 20° – 60° . The morphology of the films was monitored by a scanning microscope (SEM; Hitachi, S-3500N, Tokyo, Japan). To characterize the electrical properties of the films, 1.5 mm diameter circular Au-top electrodes were sputtered onto the film through a shadow mask. The dielectric permittivity and loss were measured using an impedance analyzer (HP4194A, Hewlett-Packard) with an oscillation amplitude of 30 mV. Low field leakage current and high field hysteresis properties were characterized using an RT6000 (Radiant Technology, Albuquerque, NM) ferroelectric test system with a voltage amplifier.

3. Results and discussions

Figure 1 shows the x-ray diffraction (XRD) pattern of PZT thick films on LNO buffered flexible SS foils annealed at 650 °C for half an hour in a conventional box furnace. Longer sintering time and higher sintering temperature will degrade the SS foils and make it lose flexibility. Hence, a temperature of 650 °C and a duration of 30 min are the optimum conditions. It can be seen that PZT thick films have been crystallized into the pure perovskite structure without detectable pyrochlore or second phases, indicating that PZT thick films exhibit the polycrystalline style and random orientation. The inset shows the flexibility of PZT thick films on LNO buffered SS foils.

Figure 2 depicts the SEM photograph of PZT thick films on LNO buffered flexible SS foils annealed for half an hour in a conventional box furnace. It can be seen from the surface image that the crack free PZT thick film is extremely dense and the grain size of film is from 50 to 150 nm.

A typical polarization–electric field (P – E) hysteresis loop for PZT thick films with LNO layers on flexible SS foils annealed at 650 °C is shown in figure 3. At an applied electric field of 900 kV cm^{-1} , the spontaneous polarization (P_s), remanent polarization (P_r) and the coercive electric field (E_c) obtained from this P – E loop are $60 \mu\text{C cm}^{-2}$, $27 \mu\text{C cm}^{-2}$ and 85 kV cm^{-1} , respectively. The PZT thin films directly deposited on SS substrates [14,17]; neither have a well-shaped P – E loop nor possess high remanent polarization (less than $17 \mu\text{C cm}^{-2}$), indicating that our PZT thick film exhibits better ferroelectric property.

Figure 4(a) represents the variation of the dielectric constant and loss of PZT thick films prepared on the LNO buffered flexible SS foils with a frequency from 1 kHz to 1 MHz at room temperature. With increasing frequency, the dielectric constant decreases for all frequencies; however, the dielectric loss decreases slightly at the beginning and then increases. At 1 kHz, the dielectric constant and loss of PZT thick films with LNO layers are 653 and 0.052, respectively. The dielectric constant is much higher than that of PZT thick films deposited directly on flexible SS foils [8]. Figure 4(b) shows the dielectric constant and dielectric loss of PZT thick films prepared on the LNO buffered flexible SS foils vary with temperature from room temperature to 300 °C at 10 kHz. The variations of dielectric constant and dielectric loss are the same and always increase with increasing temperature. At 300 °C, the dielectric constant and dielectric loss arrive at maximal values at 977 and 0.074, respectively. In contrast to PZT thin films directly deposited on SS substrates [14], the thick films prepared in this way show much better dielectric properties (higher permittivity and less loss) at the same temperature.

Figure 5(a) shows the leakage current density of thick films with a thickness of $4.5 \mu\text{m}$ as a function of voltage in the range -150 to 150 V . No significant difference in leakage current is observed in both forward and reverse bias conditions. The leakage current density is lower than

$1.55 \times 10^{-5} \text{ A cm}^{-2}$ over the range of 0 to $\pm 150 \text{ V}$. Although the origin of the observed leakage current is not known, several mechanisms, including Schottky emission [18], Frenkel–Poole emission [19] and space-charge-limited current (SCLC) [20], may simultaneously contribute to the leakage current with one of them playing a more major role. The SCLC can be expressed as $\log(J)$ proportional to $\log(E)$. To verify the conduction mechanism in the PZT thick films, the leakage current density is plotted against $\log(E)$ in semilog scale, in figure 5(b). The slope is close to 1.0 in the low electric field ($< 145 \text{ kV cm}^{-1}$) region, indicating that Ohm's law dominates conduction in the low electric field because the density of thermally generated carriers in films is predominant over the injected charge carriers. At the field over 145 kV cm^{-1} , the plot of $\log(J)$ versus $\log(E)$ shows a slope that is close to 2, which agrees well with SCLC theory [20].

4. Conclusion

In summary, PZT thick films with LNO buffer layers were fabricated on flexible SS foils using the ceramic power/sol–gel solution modified composite method. The thick film annealed at 650°C for half an hour has a grain size of about 50–150 nm. The polycrystalline film behaves better ferroelectrically and dielectrically, having a higher remanent polarization ($27 \mu\text{C cm}^{-2}$), lower coercive electric field (85 kV cm^{-1}), higher dielectric constant (653 at 1 kHz) and lower dielectric loss (0.052 at 1 kHz). At low electric fields ($< 145 \text{ kV cm}^{-1}$), Ohm's law dominates the conduction, while at high fields ($> 145 \text{ kV cm}^{-1}$), the conduction current shows SCLC behaviour. The results suggest that these thick films may be promising materials for fabricating piezoelectric devices that require flexibility.

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Figure 1.

X-ray diffraction (XRD) pattern of the PZT thick film on LNO buffered flexible SS foils annealed at 650 °C for half an hour in a conventional box furnace. The inset shows the flexibility of the PZT thick film.

(This figure is in colour only in the electronic version)

Figure 2.
SEM image of the PZT thick film on LNO buffered flexible SS foils annealed for half an hour
in a conventional box furnace.

Figure 3.

Typical polarization–electric field (P – E) hysteresis loop for the PZT thick film with LNO layers on flexible SS foils annealed at 650 °C.

Figure 4.

(a) Variations of the dielectric constant and the loss of the PZT thick film prepared on the LNO suffered flexible SS foils with a frequency from 1 kHz to 1MHz at room temperature. (b) Variations of the dielectric constant and dielectric loss of the PZT thick film prepared on the LNO suffered flexible SS foils with the temperature from room temperature to 300 °C at 10 kHz.

Figure 5.

(a) Leakage current density of the PZT thick film on the LNO suffered flexible SS foils versus dc bias voltage in the range of -150 to 150V. (b) Plot of $\log(J)$ versus $\log(E)$ of the thick film capacitor.