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Electromechanical properties and fatigue of antiferroelectric (Pb,La)(Zr,Sn,Ti)O$_3$ thin film cantilevers fabricated by micromachining

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Abstract

Electromechanical cantilevers comprising antiferroelectric (Pb,La)(Zr,Sn,Ti)O$_3$ (PLZST) thin films were fabricated through bulk micro-machining process on silicon wafers, and their electromechanical properties including strain-fatigue behaviors of the antiferroelectric thin film cantilevers were investigated. The antiferroelectric cantilevers showed the distinct digital actuation characteristics with the strain generated due to the antiferroelectric-ferroelectric transformation. The maximum displacement per unit voltage around the phase switching field reached 16.7 $\mu$m/V, significantly larger than the typical piezoelectric cantilevers. Moreover, the antiferroelectric PLZST cantilevers exhibited superior strain-fatigue resistance compared to the similar piezoelectric microstructures. These results show the promising future of antiferroelectric materials in micro electromechanical systems.

Key words: Antiferroelectric thin films, Strain fatigue, PLZST, Actuator, MEMS
1. Introduction

Micro electromechanical systems (MEMS) with improved performance are demanded for a great variety of applications. Electromechanical on/off actuation and switch are often required in many MEMS as the basic operations [1, 2]. Due to the RC (resistance-capacitance) delay in electrical circuits, an ideal digital on/off electric signal can never be generated. Consequently conventional electrostatic or piezoelectric mechanisms often cannot effectively provide the real digital on/off states as required in high-speed digital switches. The stability of the digital actuation in MEMS under cyclic loadings is another issue to be solved.

Antiferroelectrics (AFEs) are promising for providing the on-off actuation as required, due to their strain resulted from the electric field induced AFE to ferroelectric (FE) transformation. Their strain behavior in response to the electric field simulates a real digital response to an electric signal with response time of about 90 ns as reported in literature, limited by the phase transition speed [3]. Although the response time of the actuator is limited by its mechanical resonance frequency and (resistance-capacitance) delay, optimization of the device parameters with highly miniaturized designs could be done to make use of the intrinsic fast response of the AFE thin films.

The strains in some AFEs induced during the phase transformations could be larger than those induced in piezoelectric materials [4-6]. In addition, some reports have shown that AFEs could possibly have higher electric-fatigue strength than piezoelectrics in ferroelectrics under bipolar voltage loading [7-11]. AFEs are mainly composed of 180° domains. During the AFE-FE switching, the direction of polarization changes only by 180° which results in smaller internal stress than those generated in FEs during the switching of spontaneous polarization by 90°. Consequently under a cyclic loading, less defects and micro-cracks could
be formed in AFEs, resulting in higher electric-fatigue strength. There is no depoling issue for AFEs as compared with ferroelectrics without a substantial bias. For applications of ferroelectric thin films even under unipolar condition, large bias could result in accelerated property degradation. It is reported that the remnant polarization of ferroelectric thin films under large bias above the coercive field could even decrease to 20% of its initial value after $10^5$ cycles [12]. In comparison to the ferroelectric thin films with bias, AFEs could show much larger fatigue strength due to the much smaller locally injected power density and consequently less phase decomposition probability in AFEs [12].

Beside large strain and potential high fatigue endurance, no electrical poling process is required for AFEs. This is another important advantage of AFEs over FEs, where FEs should usually be poled before the application in MEMS devices, which is a time and labor consuming process.

There have been many efforts made for investigating the structure and properties of AFE thin films [13-17]. However, the strain-fatigue behavior of AFE thin films has not been studied yet, which is very critical for device applications. The electromechanical responses of micro-machined structures comprising AFE thin film with on-off switch function need be investigated. To the best of our knowledge, there is no such a study either. Although Yang et. al. have recently suggested a fabrication process for AFE (Pb,La)(Zr,Ti)O$_3$ based micro-cantilevers, they have not reported any functional characteristics of the cantilevers [18]. Here, for the first time, we report the electro-mechanical responses and the strain-fatigue behavior of AFE (Pb$_{0.97}$La$_{0.02}$)(Zr$_{0.90}$Sn$_{0.05}$,Ti$_{0.05}$)O$_3$ (PLZST) thin film cantilevers micro-machined on silicon wafers.
2. Experimental procedure

The chemical solution deposition process, structure, and the electrical properties of the AFE \((Pb_{0.97}La_{0.02})(Zr_{0.90}Sn_{0.05}Ti_{0.05})O_3\) (PLZST) thin films were reported in our previous publication [19]. Cantilevers comprising thin layers of Si, SiO\(_2\), Ti/Pt, AFE PLZST, and Ni were fabricated on 4-inch silicon wafer through a series of thin film deposition, patterning, and Si bulk micromachining steps. The Ni and Pt layers were DC-sputtered to form the sandwich electrode structure. The top Ni electrode layers were patterned by a lift-off process. To define the cantilevers from the front side, a photo-resist layer was spin-coated to selectively protect the Ni and PLZST layers, while the PLZST, SiO\(_2\) and Si were etched by reactive ion etching (RIE) and the Pt/Ti bottom electrode was patterned by ion milling. Finally, deep reactive ion etching (DRIE) of the bulk Si from the back side was conducted to form the cantilever structure. The steps for the fabrication of the PLZST cantilevers are schematically illustrated in Fig. 1.

To analyze the electromechanical response of the PLZST cantilevers, numerical simulations were performed with finite element method (FEM) (ANSYS, Version 12.0). The finite element model consisted of the coupled-field solid elements for the PLZST layer and the solid elements for the substrates and electrode layers. Harmonic and static analyses were conducted to investigate the dynamic responses of the AFE cantilevers in frequency domain and the effective transverse piezoelectric coefficient \(d_{31,\text{eff}}\) of the PLZST films, respectively. The simulated results were compared with the experimental measurements. The electromechanical responses and strain-fatigue behaviors were investigated with a laser scanning vibrometer (LSV) [20] (OFV-056, PolyTech GmbH, Germany). The LSV system was mainly consisting of a laser scanning head, a scanning vibrometer controller, a communication junction box and a host computer. The vibration velocity and amplitude were
measured based on the Doppler shift. The deflection of AFE cantilever was detected with a photo-detector in the scanning head for each point in a specifically defined scanning grid and then the data were transmitted to the computer for processing.

Room temperature polarization-electric field (P-E) characteristics of the AFE PLZST films on the cantilevers before and after fatigue were evaluated with a standard RT66A (Radiant Technologies, USA) testing unit. Dielectric constant ($\varepsilon_r$) of the films was measured with an impedance analyser (HP4194A).

3. Results and discussion

The cross-section of the PLZST multilayer was examined with an SEM, as shown in Fig. 2(a). An SEM image for an obtained PLZST cantilever with bonding pads is shown in Fig. 2(b). The cantilevers were composed of 18-µm Si, 1-µm SiO$_2$, 0.5-µm Pt bottom electrode, 1.2-µm PLZST, and 0.1-µm Ni top electrode layers. The length and width of the cantilevers were fixed at 4 mm and 1 mm respectively. The residual stress measurements by XRD using $\sin^2\psi$ method [21] revealed a 60 MPa tensile residual stress in PLZST film, which, together with the residual stress in other layers, yielded in upwards bending of the cantilever. The stress gradient in the thickness direction of the cantilever beam can be expressed as:

$$\frac{\partial \sigma}{\partial t} = \frac{E}{(1-\nu)^2} \cdot \frac{d}{L^2}$$

where $\frac{\partial \sigma}{\partial t}$ is the stress gradient, $E$ is the Young’s modulus, $d$ is the deflection of cantilever due to the residual stress, $L$ is the length of cantilever and $\nu$ is the Poisson’s ratio. The deflection of cantilever, $d$, was found to be about 660 µm as measured by cross sectional SEM. Since the thickness of other layers are negligible compared to the thickness of Si, we
used the Young’s modulus and Poisson’s ratio of Si (130 GPa and 0.28 respectively) instead. Thus a stress gradient of about 10 MPa/µm, responsible for bending of the cantilever, was obtained from the calculation.

The dielectric constant of the PLZST thin film was about 318 at 1 kHz at room temperature. The mechanical resonance frequency of the cantilevers was determined with the laser scanning vibrometer. To avoid any damage to the samples, a small voltage of 1 V was applied. The measured resonance frequency was about 1018 Hz, which is in good agreement with the numerically simulated result of 1008 Hz, as shown in Fig. 3.

The electric field induced tip deflection of cantilevers was measured under a sine-wave voltage at a frequency of 400 Hz. The voltage dependent tip deflection and the tip deflection wave forms are represented in Fig. 4. At low voltages well below the AFE-FE switch field, the AFE phase was stable and only a very small tip deflection was observed. With increasing voltage, the AFE to FE transformation was initiated and accompanied by a large strain in the PLZST film due to the difference in the specific volumes of the two phases [13]. This was reflected by the large increase in the tip deflection of the cantilever, started at about 30 V. With further increasing voltage by a few volts, the tip deflection soon saturated at about 160 µm after all of AFE phase was transformed to FE phase. This phase transformation behavior of the AFE PLZST films resulted in a digital-type displacement in the AFE cantilevers, which is desired for digital switches and actuators with on/off states.

In addition to numerical simulation, effective transverse $d_{31,\text{eff}}$ of PLZST thin film was also calculated through an analytical approach [22], as an equivalent parameter in comparison with piezoelectric thin films. The $d_{31,\text{eff}}$ of unimorph cantilever can be expressed as:

$$d_{31,\text{eff}} = -\delta.K / 3s_{11}s_{11}(h^b + h^p)VL^2$$  \hspace{1cm} (2)
where \( \delta, s_{11}, h, V \) and \( L \) are the tip deflection, elastic compliance, thickness, applied voltage and cantilever length, respectively. The superscripts \( p \) and \( s \) denote the PLZST thin film and substrate, respectively. Since the thicknesses of top and bottom electrodes and \( \text{SiO}_2 \) are negligible compared to the thickness of \( \text{Si} \), we have neglected the mechanical properties of these layers and used the elastic compliance of \( \text{Si} \) \((7.72\times10^{-12} \text{ m}^2/\text{N})\) instead. Assuming the elastic compliance of PLZST film is the same as PZT 5-H \((16.50\times10^{-12} \text{ m}^2/\text{N})\) [23], the \( d_{31,\text{eff}} \) of PLZST can be estimated as shown in Fig. 4 (solid line). The numerical simulation results (dash line) were in good agreement with the analytical results (solid lines). From Fig. 4, three different stages can be distinguished in the voltage dependent \( d_{31,\text{eff}} \) curve of PLZST. At the first stage, the small voltage applied to PLZST film was not large enough to transform the AFE phase to FE phase and thus, the corresponding \( d_{31,\text{eff}} \) was extremely small. By increasing the voltage to reach the transformation value, the AFE to FE phase transformation was initiated and the \( d_{31,\text{eff}} \) was increased abruptly to a maximum value of \(-69.3 \text{ pm/V}\). This value is comparable to the \( d_{31,\text{eff}} \) values as reported for free standing polycrystalline \( \text{Pb(Zr,Ti)O}_3 \) (PZT) thin films ranging from \(-54 \text{ pm/V}\) to \(-90 \text{ pm/V}\) [24-27]. With the voltage further increasing, \( d_{31,\text{eff}} \) started to decrease with a slow rate as all of the AFE phase has switched to the FE phase [16].

As the deflection of cantilever is mainly due to the AFE to FE transformation, it is feasible to obtain a large tip deflection by a small AC voltage under a proper DC bias. The DC bias should be large enough to partially drive the AFE phase to FE phase (about 31 V). Since the transformation is reversible, the additional AC voltage (about 5 V) will be able to either transform the remained AFE phase to FE phase \((V_{\text{AC}} > 0)\) or drive back the FE phase to AFE phase \((V_{\text{AC}} < 0)\). For most actuator applications, the induced displacement at an applied
unit voltage is an important factor, which is the derivative of the voltage dependant tip deflection graph in Fig. 4 ($d\delta/dV$). As shown in Fig. 5, this value of $d\delta/dV$ of PLZST cantilever is very small before and after the AFE-FE transformation (less that 1 μm/V), but it increases abruptly to its maximum of 16.7 μm/V at the transformation onset (DC bias of 31 V), which is significantly superior to the $d\delta/dV$ reported for PZT cantilevers (about 4.6 μm/V) [26, 28].

The effective electromechanical coupling coefficient ($k_{\text{eff}}$) of the film can be obtained according to the following equation:

$$k_{\text{eff}}^2 = \frac{f_r^2 - f_a^2}{f_a^2}$$

where $f_r$ and $f_a$ are the resonance and anti-resonance frequencies as determined by impedance measurements. Using Equation 4, $k_{\text{eff}}$ of about 16.8% was obtained for our PLZST thin film cantilever.

Fig. 6 presents the strain-fatigue behavior of an AFE PLZST cantilever. A cyclic AC voltage of 35 V was applied to induce the AFE to FE transformation and the large tip deflection was measured against the cycle numbers. The tip deflection remained almost constant up to $3\times10^7$ cycles, and started to decrease after that. The tip deflection reached almost 80% of its initial value at $10^9$ cycles. Slight burning of the electric contact pads under the probes was observed after the fatigue in $10^9$ cycles. The localized breakdown of electric contacts might be due to the deterioration effect of the leakage current in the PLZST films after the one billion cycles of large electric field and mechanical vibration.
A polarization-electric field (P-E) hysteresis loop of the PLZST film on the cantilever before and after the fatigue at $10^9$ cycles is presented in the inset of Fig 6. Well saturated double hysteresis loops with a small remanent polarization were observed in both cases. However, after fatigue, the saturation polarization and the AFE to FE switching field decreased. In the previous material investigations on AFEs [11, 29], it is suggested that some charged species, especially oxygen vacancies, form due to severe cycling process. During AFE-FE transformation, the charged defects can gradually migrate and be captured by domain walls, grain boundaries, and electrode-film interfaces. The accumulation of the charged species can lead to residual micro-stresses that provide additional free energy for AFE to FE transformation thus decreasing the switching field.

Although electrical fatigue behaviors are widely investigated in many FE thin films mechanically-constrained on substrates, strain-fatigue is rarely reported for the micro-machined structures with partially free-standing FE films, although this issue is very critical to MEMS applications. One report that can be found in the literature is the study by Kobayashi et. al. on the strain-fatigue of a micro-machined piezoelectric PZT cantilever [30], in which the tip deflection dropped to zero after $10^7$ cycles and the polarization-electric field hysteresis loop degraded substantially suggesting that the cantilever be broken down. In another report, Polcawich et. al. found no measureable degradation in function of PZT MEMS switch architectures after $10^6$ cycles [31]. Compared to the counterpart piezoelectric PZT cantilevers, our AFE PLZST cantilevers exhibited superior strain-fatigue resistance.

As discussed, the actuation mechanism of AFE PLZST thin films provides a sharp change of AFE-FE phase transformation induced large strain (displacement) within very short time (nonlinear in time scale). This can be very useful for some applications, such as high speed mechanical switching and pulse mode actuation. Since piezoelectric materials working under
a fixed bias have linear response to voltage in time scale, they will not provide the same characteristics.

4. Conclusions

Antiferroelectric cantilevers comprising a laminate of Ni/PLZST/Pt/Ti/SiO₂/Si were fabricated through bulk micro-machining process on silicon wafers. The antiferroelectric cantilevers showed the distinct digital actuation characteristics with the strain generated due to the antiferroelectric-ferroelectric transformation. The maximum displacement per unit voltage around the phase switching field reached 16.7 μm/V, significantly larger than the typical piezoelectric cantilevers. The effective $d_{31,\text{eff}}$ could reach a value -69.3 pm/V. Moreover, the antiferroelectric PLZST cantilevers exhibited superior strain-fatigue resistance compared to the similar piezoelectric microstructures. The tip displacement of the cantilever remained unchanged up to $3 \times 10^7$ cycles and was reduced by 20% after $10^9$ cycles. The large strain with high fatigue resistance, digital characteristics, and no need of electric poling process show the promising future of antiferroelectric materials in many micro electromechanical systems.

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References:


Pb(Zr,Sn,Ti)NbO$_3$ thin films prepared by sol-gel process, Japanese Journal of Applied 


[10] J.H. Jang, K.H. Yoon, K.Y. Oh, Electrical fatigue of ferroelectric PbZr$_{0.5}$Ti$_{0.5}$O$_3$ and 


[13] D. Berlincourt, Transducer using the electric field-forced antiferroelectric-ferroelectric 
transition, Ultrasonics. 6 (1966) 48-51.

[14] D. Berlincourt, Transducers using forced transitions between ferroelectric and 


[16] K. Uchino, Digital displacement transducer using antiferroelectrics, Japanese Journal of 

[17] B. Xu, N.G. Pai, Q.M. Wang, L.E. Cross, Antiferroelectric thin and thick films for high-


List of Figures

Fig. 1  Schematic illustration for the micro-machining steps for the fabrication of the PLZST cantilevers on a silicon wafer. (a) Deposition of Pt and PLZST (Ti below Pt not shown), (b) deposition of Ni, (c) lift-off for patterning of Ni top electrode, (d) patterning of cantilever (front side RIE and ion milling), (e) micromachining of bulk Si (back side DRIE), and (f) removing photoresist layer for completing the cantilever fabrication.

Fig. 2  (a) SEM image of the cross-section of Ni/PLZST/Pt/Ti/SiO$_2$/Si multilayer. (b) SEM image of the PLZST cantilever with two bonding pads.

Fig. 3  Frequency response of the tip deflection of the PLZST cantilever.

Fig. 4  Tip deflection of the PLZST cantilever and effective transverse piezoelectric coefficient ($d_{31,\text{eff}}$) of PLZST thin film as a function of applied AC voltage. The inset presents the measured wave forms of tip deflection of the cantilever actuated at 400 Hz and 42 V.

Fig. 5  $d\delta/dV$ of the PLZST cantilever as a function of the DC bias.

Fig. 6  Fatigue characteristics of the tip deflection of the PLZST cantilever. The inset shows the polarization-electric field hysteresis loop of the cantilever before and after fatigue at $10^9$ cycles.
Fig. 1
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