

Characterization and aging response of the d_{31} piezoelectric coefficient of lead zirconate titanate thin films

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The wafer flexure technique was used to characterize the d_{31} coefficient of a number of sol-gel and radio frequency (rf) sputtered lead zirconate titanate (PZT) thin films with thicknesses between 0.6 and 3 μm . Typical d_{31} values for well-poled 52/48 sol-gel films were found to be between -50 and -60 pC/N. The rf sputtered films possessed large as-deposited polarizations which produced d_{31} coefficients on the order of -70 pC/N in some unpoled films. The subsequent poling of the material, in a direction parallel to the preferred direction increased the d_{31} coefficient to values of about -85 pC/N. The aging behavior of the d_{31} coefficient was also investigated. For sol-gel films the aging rate was found to be independent of poling direction and to range from 4% per decade for a 2.5 μm film to 8% per decade for a 0.6 μm film. In contrast, the aging rate of sputtered films was strongly dependent on poling direction, with maximum and minimum rates of 26% and 2% per decade recorded. These aging rates are very high in light of the limited twin wall motion in PZT films, and are believed to result from the depolarizing effects of internal electric fields in the rf sputtered films and interfacial defects in the sol-gel films. © 1999 American Institute of Physics.

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I. INTRODUCTION

The design and development of novel microelectromechanical systems which utilize piezoelectric thin films requires explicit knowledge of the material's longitudinal (d_{33}) and transverse (d_{31} or d_{32}) piezoelectric coefficients. When prepared in bulk ceramic form, piezoelectric coefficients are characterized by numerous methods, the most common of which are the resonance and dynamic load techniques (e.g., the Berlincourt meter). Those techniques however, are inadequate for the piezoelectric characterization of thin film materials and for that reason a number of alternative techniques have been proposed.^{1,2}

Laser interferometers are the most well established method for the characterization of both the longitudinal and transverse piezoelectric coefficients of thin films. Interferometric methods however, require careful optical alignment and operation, and in the case of a d_{31} measurement, appropriate sample preparation (cantilever beam construction). In contrast, the wafer flexure technique was conceived as an alternative method for the characterization of the transverse piezoelectric coefficient (d_{31}) of thin films.³ The measurement is a direct technique (i.e., it utilizes the direct effect) and is based on measuring the charge produced as a film-coated wafer is flexed periodically. Details on the design and

calibration of the technique are given elsewhere.⁷ The wafer flexure technique was used here to compare the properties of sol-gel and sputtered lead zirconate titanate (PZT) films.

II. EXPERIMENTAL PROCEDURE

A. Sol-gel PZT thin films

PZT thin films were synthesized with 52/48 compositions using a variation of the procedure described earlier by Budd, Dey, and Payne.⁴ Lead acetate trihydrate was dissolved in 2-methoxyethanol, distilled and refluxed at 110 °C, and combined with titanium-IV isopropoxide and zirconium-IV propoxide. Solutions were made in 0.5 molar concentrations and spin coated at 3000 rpm on platinumized (100) silicon substrates. Each substrate had 1 μm of thermal oxide sputter coated with a 200 Å titanium adhesion layer and 1500 Å of (111) platinum. Following pyrolysis at 300–360 °C, additional layers were spin coated to build up the desired thickness. Lead volatilization was discouraged (during the subsequent annealing step) with 12% excess lead in the solution. Films were crystallized in an AG Associates, Heatpulse 210 rapid thermal annealer at 700 °C for 60 s. Individual crystallization steps were conducted for thicker films after every fourth coating to minimize cracking of the resulting film. Final film thicknesses ranged from 0.6 to 2.5 μm . Additional details on the processing are given

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TABLE I. Sputtering conditions for the deposition of 4 in. PZT thin films.

Target	[Pb(Zr _{0.53} , Ti _{0.47})O ₃] _{0.8} + [PbO] _{0.2} (Hot pressed)
Substrate	Pt/Ti/(SiO ₂)/Si [Pt/Ti=1000A/500A]
Stage temperature	600 °C
Target to substrate distance	10 cm
rf power	500 W
Gas flow	Ar/O ₂ =9.5/0.5 sccm
Pressure	1.0 Pa
Deposition rate	0.7–1.0 μm/h

elsewhere.⁵ Pt top electrodes were sputtered through a 1.5-mm-diam shadow mask and postannealed at 400 °C for 60 s.

B. rf magnetron sputtered 50/50 PZT films

Several 4-in.-diam radio frequency (RF) magnetron sputtered films were used in this investigation. The Zr/Ti ratio of the sputtered films was measured to be 50/50 using energy dispersive x ray. The two films studied were approximately 3.0 and 3.3 μm thick and both displayed strong (111) textures. Details of the deposition procedure are given in Table I.⁶ Pt top electrodes were sputtered through a 1.5-mm-diam shadow mask.

C. Wafer flexure method for transverse piezoelectric characterization

The principle of operation for the wafer flexure method and the details of the hardware used have been reported elsewhere.⁷ A schematic of the basic configuration is given in Fig. 1. In this investigation the uniform pressure rig was configured for both 3 and 4 in. wafer characterization. Fundamentally, the technique utilizes the direct piezoelectric effect. The audio speaker was excited with the reference signal [0.4 V_{rms} (rms=root mean square) at 4 Hz] from an EG&G 7260 lock-in amplifier fed through a Harman/Kardon HK770 stereo amplifier. The output of the audio speaker is fed to a cavity in the aluminum housing over which the film-coated wafer is fixed. The resulting pressure oscillation flexes the wafer, which subjects the film to a controlled planar stress, and induces a charge via the d_{31} coefficient of the film. The charge from the PZT sample is converted to a rms voltage (via the charge integrator) and together with the voltage from

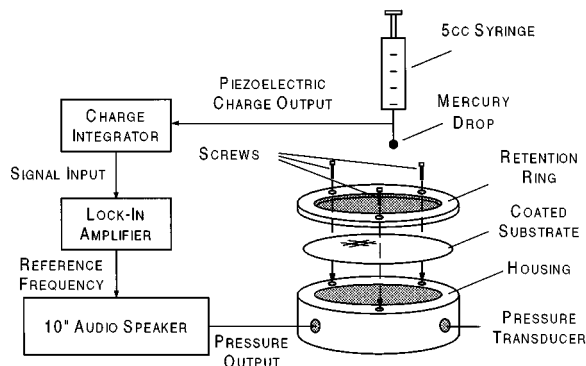


FIG. 1. Wafer flexure method for the transverse piezoelectric characterization of piezoelectric thin films.

a piezoresistive pressure transducer (Omega PX 170, 0.26 psig full scale) is fed into the lock-in and measured with respect to the internal reference. From the lock-in data, output charge and applied pressure are then calculated and used to determine; (1) the stress applied to the film (using classical mechanical plate theory), and (2) the film's d_{31} coefficient.

D. Effects of poling time and poling direction on the d_{31} coefficient

The wafer flexure technique was used to characterize the d_{31} coefficient of a number of PZT thin films. As a general rule, each PZT sample was characterized as a function of poling time and poling direction at room temperature. The magnitude of the poling field was typically two to three times the coercive voltage (as measured from the polarization hysteresis loop) and poling was done in 5 or 15 min increments to a maximum of 1 h. By analogy with piezoelectric ceramics,⁸ results from the experiments were expected to show a logarithmic increase with poling time. As such, data from the poling experiments were used to check the health of the d_{31} meter, the quality of the PZT films, and to identify/confirm the existence of internal bias fields (the d_{31} response is strongly asymmetric with respect to poling direction for films with large internal bias fields).

E. Aging rate of the d_{31} coefficient of PZT thin films

The aging of the piezoelectric response under closed circuit conditions without a direct current bias was measured and is reported as a function of film thickness and poling direction. A number of 3 in. sol-gel and 4 in. rf sputtered samples were tested. For each test, samples were poled with an electric field (typically two or three times their coercive field) for a time of 1–2 min. At the end of the poling period the oscillation on the measurement rig was started and the test begun. The output from the test capacitor was monitored continuously on the lock-in display and the voltages recorded every 5 min for times of 1–60 min after poling. Care was taken to insure that the pressure applied to the plate was the same over the course of the experiment.

III. RESULTS AND DISCUSSION

A. Effects of poling time on the d_{31} coefficient of PZT thin films

Four rapid thermally annealed sol-gel films with thicknesses of 0.6–2.5 μm were characterized in terms of their d_{31} coefficients as a function of both poling direction and poling time. The poling fields used for the experiments were taken to be three times the coercive field of the capacitor tested (where E_c was calculated from the average of the $\pm E_c$'s reported during earlier polarizing–electric field (P–E) measurements). The same spot on the sample was then poled for increasing lengths of time, up to 31 min, at this field level. For each set of experiments a virgin electrode was used. The results from the experiments with the top electrode made positive are given in Fig. 2 and show that the piezoelectric coefficient of all films tested increases in a logarithmic

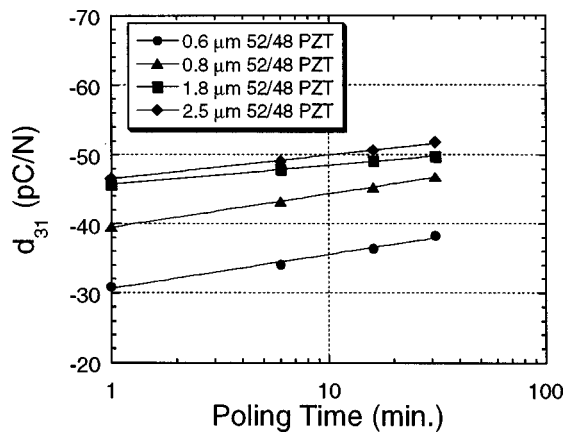


FIG. 2. Variation of d_{31} as a function of film thickness and poling time with the top electrode positive. Films tested had 52/48 compositions and were poled with fields equal to three times the coercive field of the film.

mic fashion with poling time. The maximum d_{31} coefficient was recorded for the 2.5- μm -thick film and had a magnitude on the order of -50 pC/N. Results collected with the top electrode made negative showed a similar response with the magnitudes comparable to those given in Fig. 2.

The piezoelectric characterization of the 50/50 rf sputtered films indicated that the films had large spontaneous polarizations which produced as-deposited d_{31} coefficients between -45 and -70 pC/N. d_{31} data taken from a 3.3- μm -thick film are presented in Fig. 3 as a function of poling time at ± 60 kV/cm. (This poling field is close to the average coercive field; higher fields could not be used due to delamination of the top electrode after prolonged high field exposure.) In Fig. 3, the data for the top electrode negative follow the expected logarithmic increase with poling time. However, poling the film for 1 min with the top electrode positive was insufficient to reverse the original polarization direction. As a result, the magnitude of d_{31} decreased from -70 to -20 pC/N, but the phase of the response with respect to the applied stress was unchanged. Only with extended poling did the remanent polarization change sign. For these longer times, the phase of the d_{31} response with the applied stress

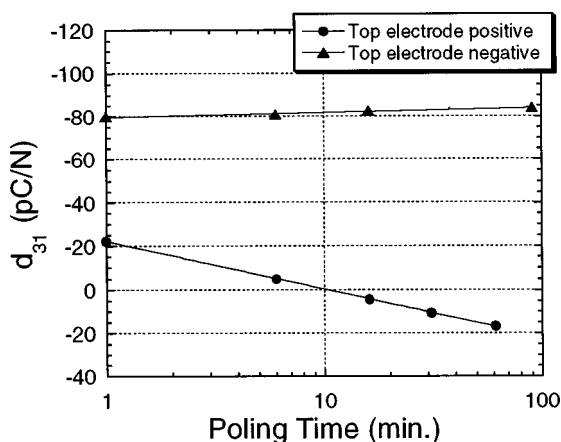


FIG. 3. Change of the d_{31} coefficient of a 3.3- μm -thick 50/50 sputtered film with poling time. The data show a strong sensitivity to poling direction. As-deposited values of d_{31} were measured at about -70 pC/N.

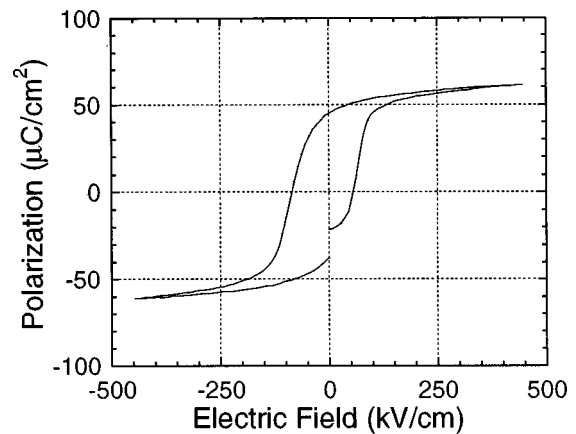


FIG. 4. Polarization hysteresis loop for a $\sim 3\text{-}\mu\text{m}$ -thick 50/50 rf sputtered PZT film. The plot shows the average remanent polarization of the film is 41 $\mu\text{C}/\text{cm}^2$ and the average coercive field is 70 kV/cm. The internal bias field is calculated from the offset on the field axis to be 15 kV/cm.

changed by approximately 180° . To show that the degree of poling did, in fact, increase logarithmically with time, all of the d_{31} data are shown with negative values in the graph; zero marks the point at which the phase of the response changed.

The data presented in Fig. 3 illustrate a number of striking results. The first is the large value (-70 pC/N) of the d_{31} coefficient in the as-deposited films. d_{31} increased with poling to values which approached -85 pC/N. Those numbers are themselves encouraging because they represent some of the largest d_{31} values reported for polycrystalline PZT films. Furthermore, there is significant asymmetry in the d_{31} coefficient as a function of the poling direction. When poled with the top electrode negative, the d_{31} increased by about 20% for poling times of 60 min. In contrast, poling the sample in the opposite direction changed the d_{31} coefficient by a factor of 2.

The large as-deposited d_{31} and the strong asymmetry in the poling behavior are probably related to an internal electric field in the film. The existence of internal bias fields have been well documented for PZT ceramics⁹ and thin films¹⁰ and their presence is usually manifested as a shift in the polarization hysteresis loop or an asymmetry in the current-voltage ($I-V$) curve. In thin films, such internal fields have been reported to result in preferred polarization directions and asymmetry in the piezoelectric response as a function of poling direction.^{11,12} The $P-E$ loop for the 50/50 film is given in Fig. 4. The $P-E$ hysteresis loop is shifted 15 kV/cm along the field axis, which is assumed to be equal to the film's internal field. It is expected that the bias field poles the material as it cools from its deposition temperature (600°C) which leads to a large as-deposited polarization and an appreciable piezoelectric effect. The subsequent application of a poling field in excess of, and in a direction parallel to, the internal bias yields only minimal gains in the d_{31} coefficient. The application of a field in a direction antiparallel to the internal field however, results in appreciable changes of the as-deposited polarization and therefore, the film's d_{31} coefficient. There is also the possibility that the preferred polarization direction is the result of a strain gradient in the film,

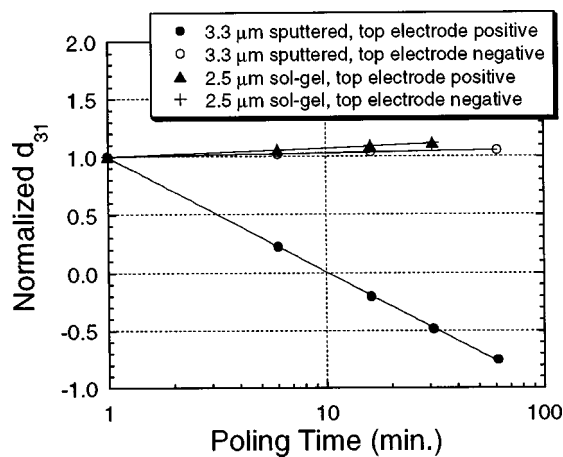


FIG. 5. Normalized d_{31} coefficients as a function of poling time. Data for both a 2.5 μm sol-gel film and a 3.3 μm sputtered film are shown. Note that the response of the sol-gel film is nearly symmetrical with respect to poling direction, so that the two curves for the sol-gel films are superimposed.

though given the distance between the film and the neutral axis of the film/substrate system, a large strain gradient seems unlikely. For simplicity therefore, the mechanism responsible for the shift in the hysteresis loop will be described as an internal field.

The effect of the preferred polarization direction is illustrated most clearly in Fig. 5, which plots the response of both the 2.5 μm 52/48 sol-gel film and the 50/50 sputtered film as a function of poling time. The strong contrast between the poling behavior of the two types of films is believed to result from the relative magnitude of the film's internal bias fields.

The internal bias of the sputtered film was calculated to be about 15 kV/cm, which is an order of magnitude larger than the ~ 1 –2 kV/cm internal bias in the sol-gel films. The large internal field in the sputtered films poles the material almost completely as the material is cooled through T_c . The sputtered films therefore, display only a small increase in the magnitude of d_{31} when poled in a direction parallel to the internal bias and show large changes when poled antiparallel to the preferred direction. In contrast, the internal fields of the sol-gel films are much lower (than the sputtered films). The net polarization produced in either direction is therefore comparable and the response produced is symmetric.

B. Aging behavior of the transverse (d_{31}) piezoelectric coefficient

The aging rates of the transverse piezoelectric coefficients for both sol-gel and sputtered PZT films were measured using the wafer flexure technique. The d_{31} coefficients were monitored at regular intervals after poling and their decay plotted versus the logarithm of time.

Experiments were conducted with sol-gel films poled in either direction at room temperature with fields equal to three times their coercive field strength. Poling times for the experiments conducted were either 1 or 2 min. Figure 6 gives the aging data from the experiments conducted with the top electrode made negative (tests with the top electrode positive were also conducted and the response was similar to that shown). The rates for all experiments (including those con-

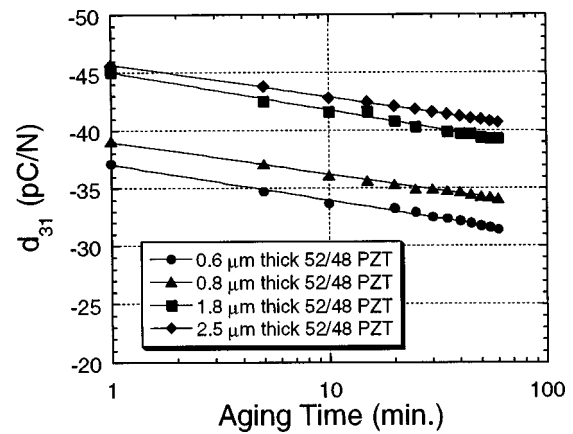


FIG. 6. Aging of the d_{31} coefficient for four sol-gel films ranging in thickness from 0.6 to 2.5 μm . Samples were all poled with three times the coercive field for 1 min with the top electrode negative.

ducted with the top electrode positive) are tabulated from the slopes of the fitted logarithmic curves and are given in Table II.

Similar experiments were conducted on a 4 in. rf sputtered 50/50 PZT film. The film investigated was 3.0 μm thick with an as-deposited d_{31} coefficient of about -45 pC/N. Test capacitors were poled with an electric field of 150 kV/cm, which was approximately equal to two times the coercive field strength. The aging rate was evaluated as a function of poling time and direction with the data taken from different test capacitors on the same film.

Figure 7 is a plot of the decay of the transverse piezoelectric coefficient for the sputtered film poled with a field of ± 150 kV/cm for 1 min at room temperature. The plot shows a strong asymmetry in the film's aging rate, with the sample poled at -150 kV/cm (top electrode negative) measured at 2% per decade while the sample poled in the opposite direction decayed at 26% per decade. When the samples were poled for 15 min, the data showed an aging rate of 4% per decade when poled with the top electrode negative and an aging rate of 20% per decade when poled with the top electrode positive.

The aging data collected from both the sol-gel and rf sputtered films make an interesting contrast to data reported for bulk ceramics. In bulk materials, the decay of the dielectric and piezoelectric constants and the evolution of constricted P - E loops are attributed to ferroelastic stress relief and domain stabilization.¹³ Because extrinsic contributions

TABLE II. Aging rates (percent per decade) of the d_{31} coefficient of 52/48 sol-gel PZT thin films.

Film thickness (μm)	Poling time: 1 min Top electrode (+)	Poling time: 1 min Top electrode (-)	Poling time: 2 min Top electrode (+)
0.6	8%	8%	7%
0.8	7%	7%	5%
1.8	7%	7%	5%
2.5	6%	7%	4%

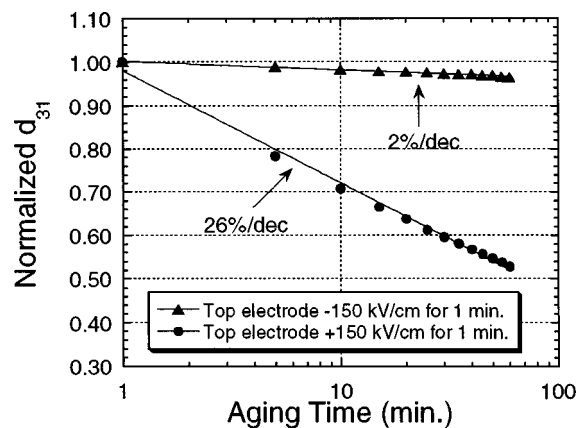


FIG. 7. Aging rate of the d_{31} coefficient of a 3.0- μm -thick 50/50 rf sputtered PZT film. The film had been poled for 1 min with a field of ± 150 kV/cm.

to the dielectric and piezoelectric characteristics are limited in these films¹⁴ and the decay of the dielectric constant proceeds at only a few percent per decade,^{12,15} the mechanism(s) responsible for the decay of the electromechanical constants has been attributed to the reduction of the film's remanent polarization.¹²

In this work, the aging data collected show a correlation with the presence of an internal bias field. The rf sputtered films ($E_{\text{bias}} = 15\text{--}20$ kV/cm) show accelerated aging when the polarization vectors are misaligned with the internal field. Removal of the poling field results in the rapid reorientation of switched domains (i.e., the film begins to switch back to the original orientation) and a rapid decrease of the film's d_{31} coefficient. In contrast to the rf sputtered films, the net internal fields of the sol-gel films ($E_{\text{bias}} = 1\text{--}2$ kV/cm) are smaller, and as a result their response is independent of poling direction. This behavior is in agreement with that reported by Kholkin *et al.*,¹² although the asymmetries observed here for the sputtered films are appreciably larger.

The symmetric aging response of the sol-gel films suggests that depolarization does not result from a net internal electric field. Earlier work on PZT ceramics has shown that large mechanical stresses can result in significant amounts of depolarization^{16,17} however, data presented elsewhere¹⁴ show that the effects of mechanical stress are less pronounced in PZT films. In addition, the limited extrinsic contributions in these PZT films suggest that depolarization results from the backswitching of aligned domains and not non- 180° reorientation or domain wall pinning. Because 180° switching is not a stress relief mechanism, mechanical depolarization cannot be responsible for the aging behavior of thin films. Rather, it is expected that the origins of the accelerated aging rates are related to interfacial or defect-related effects comparable to those responsible for the polarization degradation of ferroelectric non-volatile memory devices.¹⁸

Extensive work has been conducted on degradation mechanisms in films, with both lead and oxygen vacancies identified as potential sources of the problem(s).¹⁸ It is expected that the high volatility of lead oxide at the elevated crystallization temperatures (typically 600–700 °C) results in large concentrations of charged defects in a shallow layer at

the film's surface.¹⁹ There are several possible consequences of this. First, the defective material could form a discrete semiconducting layer at the film surface. Earlier work has suggested that a low- ϵ_r region at one of the film's surfaces results in the reduced dielectric constant of thin (submicron thickness) PZT films.²⁰ A similar region may be responsible for the spontaneous depolarization of the material. In particular, it is suggested that when subjected to *large* poling fields, charge is injected through this layer and domain reversal is possible. After the voltage is removed however, a depolarization field is created which cannot be compensated effectively by the defective layer. In the absence of an external voltage, the limited conductivity of the lead deficient layer prevents additional charge from being transported to compensate the depolarization field. As a result the material depoles, which leads to the accelerated decay of the film's piezoelectric coefficient.

A second possibility is that $V_{\text{pb}}'' - V_{\text{O}}''$ defect dipoles in the near surface regime align with respect to the ferroelectric dipoles on cooling through the transition. Since the domain structure is initially random, there is little net internal bias. If the field associated with these dipoles is not too high, then the material could be poled. However, at room temperature it is unlikely that all of the defects would be reoriented (especially for short poling times). Thus, after poling they would act to drive the film back to its original random domain configuration, which would result in accelerated piezoelectric aging.

There are data presented both here and elsewhere¹² which suggest that the aging rates of the piezoelectric coefficients can be decreased with increased poling times (Table II). The beneficial effects of poling time can be explained within the framework of imprint phenomena which attributes the voltage offset of the P - E loop (i.e., the imprint) to the alignment of defect dipoles with the film's polarization vector.²¹ With increased poling times the defects (predominantly oxygen vacancies) which are responsible for imprint have time to migrate through the film. The migration and reorientation of defect dipoles stabilize the film's domain structure, which prevents depolarization and reduces the aging rate.

The asymmetric aging rates of the d_{31} coefficient of the rf sputtered films are comparable to behavior which has been reported by Maria for epitaxial lead magnesium niobate-lead titanate films.²² The source of the aging behavior in those films was attributed to the presence of a large internal bias which shifted the P - E loops to one side of the origin, i.e., both coercive fields had the same sign. Maria speculated that energetic bombardment, either through implantation or ion peening, was responsible for a displacement of the oxygen sublattice. The shift of the oxygen atoms led to a preferred polarization direction and thus produced the large internal field (and the asymmetry in the aging rates) in the as-deposited films. A similar mechanism could explain why the sputtered films in this work showed asymmetric aging rates while the sol-gel films (which never see bombardment) did not.

IV. CONCLUSIONS

The wafer flexure method was used to characterize the d_{31} coefficients and monitor their aging rates for a number of 52/48 sol-gel and 50/50 rf sputtered PZT films. Piezoelectric characterization indicated an increase of d_{31} with poling time (at room temperature) to maximum values of about -50 pC/N for the $2.5\text{-}\mu\text{m}$ -thick sol-gel film and -85 pC/N for $\sim 3\text{-}\mu\text{m}$ -thick rf sputtered film. Aging results showed that the d_{31} coefficient decreased in a linear fashion with the logarithm of time. The aging rates measured for the sol-gel films were found to be between 4% and 10% per decade with the thickest films tested ($2.5\ \mu\text{m}$) displaying the smallest rates. Similar experiments were conducted on rf sputtered PZT films. In contrast to the aging behavior of the sol-gel films, the aging rates of the sputtered samples showed a strong anisotropy of the decay rate. Rates were measured at as much as 26% per decade when the sample was poled against the as-deposited polarization and as little as 2% per decade when poled in the preferential direction.

The aging rates of PZT films are large when compared to the few percent per decade reported for bulk ceramics. The mechanism responsible for the piezoelectric aging of the PZT films is believed to be depolarization of the material. The rf magnetron sputtered films display large asymmetries in their aging response which is probably the result of a large internal field present in the film. When poled in a direction parallel to the internal bias, the film's polarization is stable and the aging rates are modest. If however, the films are poled antiparallel to the internal field, the remanent polarization is unstable and the aging rates are accelerated. In contrast to the sputtered films, the aging rates of the sol-gel samples were independent of poling direction. The symmetry of aging rate indicated that the net internal fields in the sol-gel films, which were about an order of magnitude less than those in the rf sputtered films, were not the predominant depolarization mechanism in the material. The origin of the

aging response in the sol-gel samples was attributed to charged defects or a defective layer which resulted in the backswitching of domains.

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