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MEASUREMENT AND CALCULATION OF PZT THIN FILM LONGITUDINAL PIEZOELECTRIC COEFFICIENTS*

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MEASUREMENT AND CALCULATION OF PZT THIN FILM LONGITUDINAL PIEZOELECTRIC COEFFICIENTS

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The ferroelectric and piezoelectric properties of 2000 Å thick chemical solution deposited $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ (PZT) thin films were investigated. Several Zr/Ti ratios were studied: 30/70, 50/50 and 65/35, which correspond to tetragonal, near-morphotropic, and rhombohedral symmetries. In all samples, a {111}-texture is predominant. Longitudinal piezoelectric coefficients and their dc field dependence were measured using the contact AFM method. The expected trend of a maximum piezoelectric coefficient at or near to the MPB was not observed. The composition dependence was small, with the maximum d_{33} occurring in the tetragonal material. To explain the results, crystallographic texture and film thickness effects are suggested.

Using a modified phenomenological approach, derived electrostrictive coefficients, and experimental data, d_{33} values were calculated. Qualitative agreement was observed between the measured and calculated coefficients. Justifications of modifications to the calculations are discussed.

Keywords: Piezoelectric; AFM; PZT; composition; calculation, electrostriction

INTRODUCTION

When the piezoelectric coefficients of thin film PZTs are reliably measured, values 30 to 75% smaller than those expected in the same bulk compositions are commonly observed.¹⁻⁴ Understanding this property difference is important with regards to the following issues; (i) incorporation of PZT thin films into reliable electromechanical devices, and (ii) understanding the fundamentals of domain walls by studying their behavior under the influences of boundary conditions associated with the thin film geometry.

Although the compositional dependence of d_{33} across the PZT phase diagram has been reported by several authors, simultaneous assessment of the results does not lead to a consistent conclusion regarding the importance or

influence of the morphotropic composition.⁵⁻⁸ A consistent difficulty, especially in sub-micron films, is encountered when attempting to guarantee that the film stoichiometry, (i.e., A/B ratio), orientation, and microstructure are of sufficient consistency that meaningful comparisons can be drawn.

We present here the initial results of our investigations of PZT thin films directed towards understanding these issues. PZT thin films were deposited by chemical solution deposition with compositions providing tetragonal, near-morphotropic, and rhombohedral symmetries. Insofar as possible, efforts were made to insure electrical and structural properties of consistent quality and character such that conclusions and relationships could be known. All films are consistently {111}-oriented and have dense microstructures with $\sim 0.1 \mu\text{m}$ grain diameters.

Structural characteristics were measured by x-ray diffraction and topographic scanning probe microscopy. Electrical properties including polarization hysteresis and the field dependence of the permittivity and loss were measured using an RT66A and an HP 4192A. Finally, the longitudinal piezoelectric coefficients were measured using a Park Scientific Scanning Probe Microscope. Recent modifications to the SPM-based technique were performed such that previously encountered difficulties including capacitive coupling between the sample and tip, and unambiguous field application (as caused by insufficient supply of switching current to the capacitor) were overcome. Detailed discussions of these modifications are available in the references.⁹ It is noted, however, that full qualification of this SPM-based method has not been completed. Influences from surface microstructure gradients, tip-sample interaction, and wafer bending are still being investigated. In general, however, data comparison between the samples in this study, and the voltage dependence of individual samples appear reliable.

RESULTS AND DISCUSSION

Standard structural and electrical characterization was performed to make an initial assessment of the electrical properties. Interpretation of this data is straight forward, thus useful for the purpose of establishing a baseline by which the film quality and characteristics are initially judged. Fig. 1 shows the polarization hysteresis traces for the three film types used in this report.

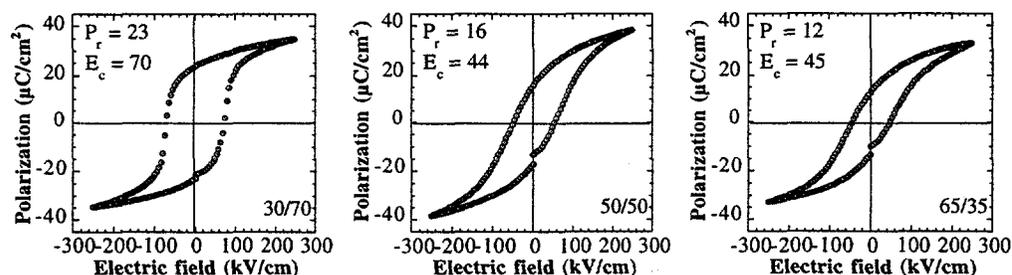


Fig 1: Polarization hysteresis plots for the three film compositions used in this study

As shown in the figures, the tetragonal material exhibits the largest polarization hysteresis values and the most rectangular loop shape. As is commonly observed, when compositions tend towards rhombohedral

symmetry, the loop shape becomes more slanted, remanent polarization and coercive field values are reduced, and classically saturating loops are more difficult to obtain. Figure 2 gives the field dependence of the permittivity for the same set of film compositions, while Fig. 3 shows the the dielectric loss.

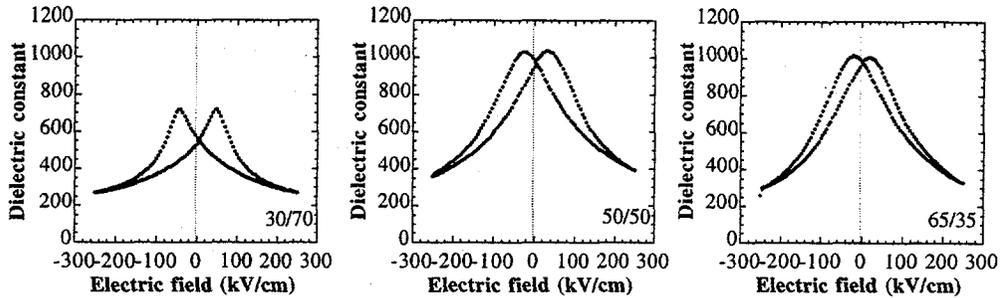


Fig. 2: Small-signal permittivity field-dependence (1 kHz) for the three film compositions

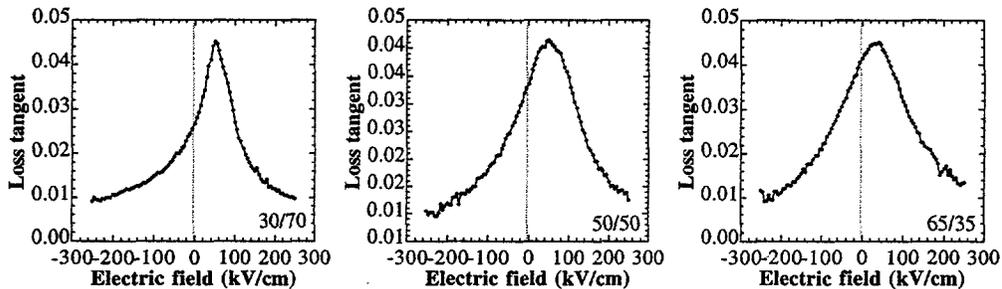


Fig. 3: Field dependence of the loss tangent (1 kHz) for the three film compositions studied. The measurements were taken for one field-sweep direction only

The smaller permittivity values are consistent with expectations of the tetragonal films, as well as the more distinct saturation and larger coercive field values.

The loss tangent values for all compositions are similar, however, the peak breadth for the tetragonal composition is most narrow. This suggests that the tetragonal symmetry, in combination with the {111} orientation, provide for the most abrupt domain switching. Working with the assumption that for films of this thickness (i.e., 2000 Å) non-180° domain wall motion is strongly limited, it is reasonable to assume that the strong loss tangent field dependence results primarily from 180° domain wall motion. An important implication is that the small-signal permittivity measurements must contain an appreciable extrinsic component. Furthermore, it is important to remember that the contribution of this component to the piezoelectric response is negligibly small.^{10,11}

Finally, the SPM-technique was applied to characterize the longitudinal piezoelectric coefficient and its electric field dependence. Fig 4 gives the piezoelectric data plotted in the form of a hysteresis loop.

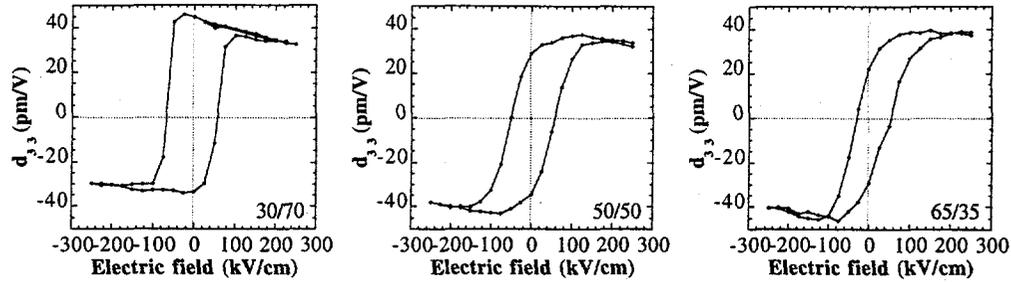


Fig. 4: d_{33} "hysteresis loops" measured for the three compositions studied

As expected, the d_{33} loops bear a strong resemblance to the polarization hysteresis in loop shape, coercive field value, and magnitude. The coercive fields found by the piezoelectric measurements are slightly different than the results from polarization hysteresis. It is likely that this difference results from differences in the specific measurement parameters. Polarization hysteresis is a large ac signal excitation driven at ~ 1 Hz, while this piezoelectric measurement involves a small signal ac excitation at 1kHz superimposed upon a quasi-static dc bias.

The remanent values for the tetragonal composition are largest, while those for the rhombohedral composition are the smallest. This is in sharp contrast to ceramic materials in which a maximum is expected for the morphotropic composition. It is well known that the reason for the maxima at the MPB is the number of domain variants. Fourteen possible polar vector orientations are available, thus efficient poling and domain switching is possible.¹¹ In the case of thin films where the ability to switch non-180° domains may be limited,^{1,3,12,13} and the microstructure is highly textured, a maxima should not be expected at this composition. Therefore, without access to the extrinsic contribution of the electromechanical response present in ceramics, a different compositional dependence to the properties is likely.

To further explore this possibility, the piezoelectric coefficients of the samples were estimated using a modified phenomenological approach. The estimation begins with the phenomenological equation:

$$d_{ij} = 2Q_{ijkl}\epsilon_o\epsilon_{ij}P_s$$

As written, this equation only applies to the case of a single-domain single crystal, however, several modifications can be made making application to other more practical situations possible. These include (i) calculation of an effective electrostrictive coefficient for a textured thin film under the influence of a residual biaxial strain¹⁴ (see Table 1), and (ii) Substitution of the measured polarization for the spontaneous polarization. The importance of a corrected electrostrictive coefficient is clear, while the substitution of the measured polarization for the spontaneous polarization is required to reflect that real samples do not switch within an arbitrarily small voltage range, or to absolute completion at a well defined electric field. This substitution effectively considers the material as a series of discrete crystals with a "field-variable" spontaneous polarization equivalent to the component of the polarization vector in the direction of the applied field at a given field value.

Table 1: Calculated effective electrostrictive coefficients

composition	30/70	50/50	65/35
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$Q_{33}^{eff} \langle 111 \rangle \text{ m}^4/\text{cm}^2$	3.1	2.6	2.5
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A final issue regarding this treatment is the extrinsic contribution of 180° domain wall motion to the measured permittivity, which must not be introduced into the calculated piezoelectric coefficients. Ideally, only the dielectric constant associated with the lattice polarizability would be included, however, determination of this quantity is particularly difficult. One possibility uses the dielectric constant measured at large electric field values, where the film is ideally approaching a single domain state. Since these films do not switch completely at a well-defined electric field, choosing this permittivity value can be somewhat arbitrary. For this calculation, the "intrinsic" dielectric constants were estimated by constructing a linear fit to the highest-field dielectric constants (from the 200 kV/cm to 250 kV/cm range) and extrapolating back to zero field. The results are given in Fig. 5. A second possibility would be to use dP/dE values from the saturation portion of the polarization hysteresis curves. Derivatives of these curves however, yield unreasonably large permittivities. Our hysteresis curves are obtained at very low frequencies, thus may contain polarization contributions from several sources, all of which may not be associated to the switchable ferroelectric polarization (especially at the high field portions of most interest). As such these dielectric constant calculations appear unreasonably inflated. Figs 5 a and b give the calculated results for "intrinsic" dielectric constant and piezoelectric coefficients.

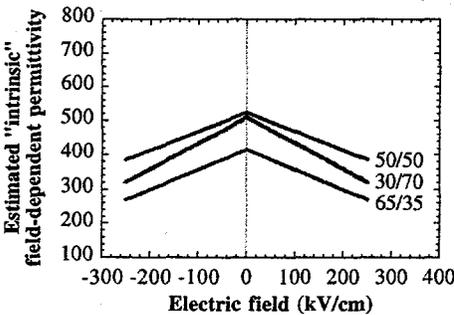


Fig 5a: Estimated "intrinsic" permittivities for the three PZT compositions studied

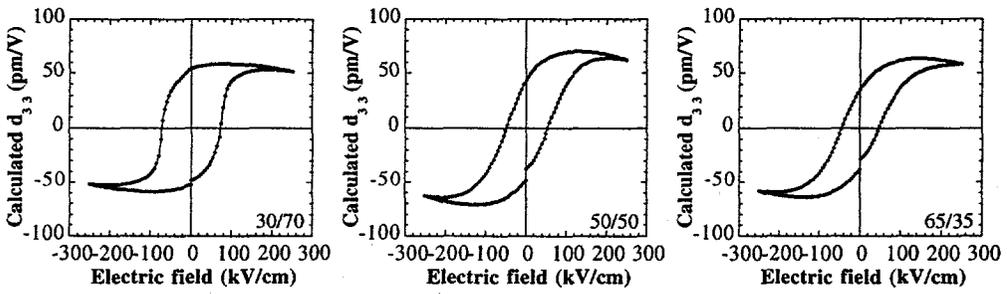


Fig 5b: estimated field-dependent "intrinsic" permittivity and field-dependent longitudinal piezoelectric coefficients.

Comparison of the calculated results and the measured values reveals reasonable quantitative agreement - the functional forms are consistent for all three compositions. Additional efforts are, however, required for a good

quantitative fit. We expect that corrections to the absolute values will necessitate a more rigorous determination of the field-dependent intrinsic dielectric constant and additional corrections to the SPM-based piezoelectric measurement. The high-field polarization values also appear to contain a conduction component, which may be in part responsible for the differences. Measurements of polarization hysteresis at higher frequencies may provide the ability to separate the measured polarization components.

CONCLUSIONS

The dielectric and piezoelectric coefficients of PZT thin films having tetragonal, near-morphotropic, and rhombohedral symmetries were measured. Using a modified phenomenological approach, the "predicted" piezoelectric coefficients were estimated from measured field-dependent permittivity and polarization data. Effective electrostrictive coefficients, which took crystallographic texture and a residual biaxial tensile strain into account, were used in this calculation. Reasonable qualitative agreement was observed between the measured and calculated results.

The expected maxima for piezoelectric coefficients of bulk ceramics was not observed in these thin films; tetragonal compositions showed the largest remanent piezoelectric response. When the high-field values were measured, all compositions showed very similar behavior. The remanent calculated values revealed the same trend however the high field values for the near-morphotropic composition were largest. We believe these values are artificially inflated by field-induced conduction loss. The importance of loop shape is also demonstrated by this study. Clearly, the slanted loop shape of the morphotropic and rhombohedral samples results in a smaller zero-field response, although the structures can potentially supply much stronger actuation. This indicates that oriented thin film samples intended for use as actuators should be optimized for square polarization hysteresis.

These results suggest that the optimal thin film PZT piezoelectric composition may not occur at the morphotropic phase boundary. In very thin films, if the intrinsic piezoelectric response predominates, and a strong {111} crystallographic texture is present, tetragonal material may provide the most desirable electromechanical properties.

Finally, the agreement between measured and calculated piezoelectric coefficients suggests that the derived effective electrostrictive coefficients are reasonable, and potentially useful for further assessment and modeling of PZT thin films.

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