PZT Films with Reduced and Exaggerated Zr:Ti Gradients

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Abstract:

Lead zirconate titanate ($PbZr_{0.52}Ti_{0.48}O_3$, abbreviated PZT) thin films have shown great promise in many applications, including energy harvesting devices, nonvolatile memory, and miniaturized sensors and actuators, due to their piezoelectric and ferroelectric properties. Efforts to prepare PZT thin films via standard sol-gel deposition result in a compositional gradient, as a Ti-rich phase nucleates first [1]. This compositional gradient adversely affects the piezoelectric properties of the film. In this study, several PZT films were prepared with varying degrees of this gradient, and the effect of the gradient on the electrical properties of the material was examined. The films were prepared using a standard sol-gel deposition process, a "gradient-free" sol-gel process introduced by Calame and Muralt [1], and a "gradient-enhanced" process. The relative permittivity and piezoelectric coefficient $e_{31,f}$ were characterized for each of these films. The gradient-free films show the best piezoelectric coefficient ($e_{31,f}$ = -14 C/m^2 on silicon (Si) substrates), while the gradient-enhanced films show poor piezoelectric properties ($e_{31,f}$ = -7.5 C/m^2 on Si). These results confirm that the gradient-free process produces PZT films with superior piezoelectric properties.

Introduction:

A piezoelectric material is a material which produces a charge when it is strained and will deform under an applied electric field. Applications for these materials include mobile communications and microscale sensors and actuators [2]. Lead zirconate titanate (PZT) is the piezoelectric material of choice due to its high effective transverse piezoelectric coefficient ($e_{31,f}$), which relates the strain in the plane of the film to the polarization developed perpendicular to the film [2]. This coefficient is dependent on composition and reaches a maximum value at the composition $PbZr_{0.52}Ti_{0.48}O_3$ [3].

Unfortunately, standard sol-gel processing produces a compositional gradient throughout the film thickness, as a Ti-rich phase will nucleate first during annealing [3]. This gradient can be reduced by using precursor solutions of varying Zr:Ti compositional ratio to construct a gradient in the opposite direction to counteract the one which will form during annealing [1]. In this project, we deposited PZT films on silicon and magnesium oxide substrates using the standard sol-gel process, the reduced-gradient sol-gel process, and an exaggerated-gradient sol-gel process, and compared the piezoelectric properties of each film.

Experimental Procedure:

PZT films of approximately 1 μm in thickness were deposited on platinized Si and magnesium oxide (MgO) substrates using a sol-gel process. Four PZT precursor solutions of varying Zr:Ti ratio were prepared based on the 2-methoxyethanol route [4].

Films with a reduced and exaggerated Zr:Ti gradient were produced following the procedure described by Muralt [1]. First, a lead titanate ($PbTiO_3$) seed layer was used to promote <100> texturing on Si substrates. Then, the four PZT precursor solutions were spun onto the substrate, starting with the Zr-rich solution for a reduced gradient film and the Ti-rich solution for an exaggerated gradient. Each layer was dried and pyrolyzed on hot plates. The films were annealed every four layers. The "standard-process" films were deposited using one 52:48 Zr:Ti solution, dried, pyrolyzed, and annealed every layer under the same conditions.

The crystalline texture of each PZT film was determined using x-ray diffraction. Polarization-electric field hysteresis loops were also obtained. The transverse piezoelectric coefficient $e_{31,f}$ of each film was measured using the wafer flexure technique [5].

Strain gauges were glued to the film, and then the film was glued to a Si wafer to which a pressure wave was applied. Samples were poled at three to five times their coercive voltages for 15-20 minutes. A lock-in amplifier was used to measure the charge produced and strain in the film in phase with the pressure wave.

Results and Conclusions:

Figure 1 shows the x-ray diffraction patterns of a sample (a) with a $PbTiO_3$ seed layer and (b) without. The intensity of the <110> peak is diminished in the sample with a seed layer, indicating that the seed layer enhanced the <100> orientation of the film.

Polarization-electric field hysteresis curves of select films are shown in Figure 2. The coercive field, or the field at which the polarization switches direction, increases as the concentration gradient is increased. This could be due to impaired domain wall movement caused by non-uniformity in the film.

The measured $e_{31,f}$ and relative permittivity are reported in Table 1. The $e_{31,f}$ coefficient has been shown to increase as the Zr:Ti gradient is reduced. Therefore, reducing the gradient is crucial for applications which take advantage of the piezoelectric properties of PZT, such as energy harvesting.

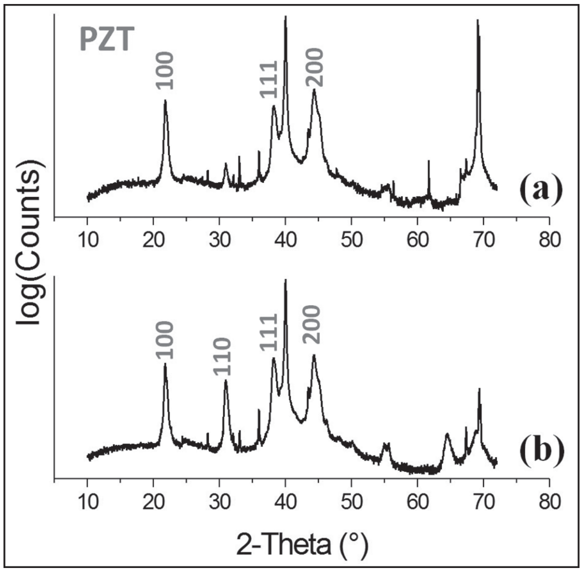

Figure 1: XRD pattern of PZT films on Si substrates (a) with and (b) without a $PbTiO_3$ seed layer.

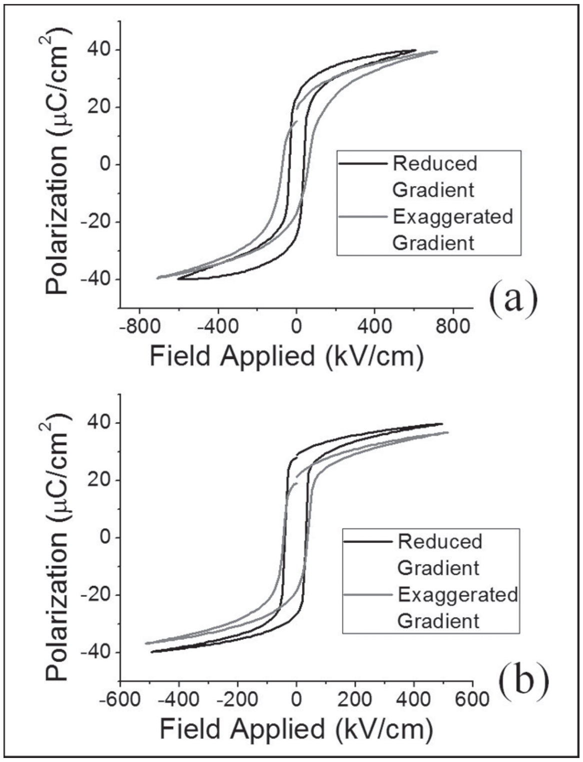

Figure 2: Polarization-electric field hysteresis curves for reduced and exaggerated gradient films on (a) Si and (b) MgO substrates.

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	Si Substrates		MgO Substrates	
	$e_{31,f}$ (C/m²)	Relative Permittivity	$e_{31,f}$ (C/m²)	Relative Permittivity
Exaggerated Gradient	-7.5 ± 0.7	870 ± 30	-5.2 ± 0.5	680 ± 15
Standard Process	-9.9 ± 0.9	950 ± 40	-12.3 ± 1.1	450 ± 30
Reduced Gradient	-14.0 ±1.2	1350 ± 10	-12.5 ± 1.1	580 ± 60

Table 1: $e_{31,f}$ and permittivity values for all three film types on Si and MgO substrates.