Advanced Dielectric, Piezoelectric and Ferroelectric Materials

LEAD STRONTIUM ZIRCONATE TITANATE (PSZT) THIN FILMS FOR TUNABLE DIELECTRIC APPLICATIONS

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ABSTRACT

Lead strontium zirconate titanate (PSZT) solid solutions are investigated for low-process temperature, tunable dielectric applications. PSZT films of three compositions (40%, 50% and 55% Sr) are prepared via a chemical solution deposition route. All films display paraelectric properties at room temperature and dielectric losses below 0.05 under field. Dielectric tunability is demonstrated to increase with annealing temperature. However, even films crystallized at 650°C have tunabilities of at least 24% at 400 kV/cm, with films of the $(Pb_{0.45}Sr_{0.55})(Ti_{0.7}Zr_{0.3})O_3$ composition exhibiting a tunability of 57%. Such dielectric tunability approaches typical values for low-temperature deposited $(Ba,Sr)TiO_3$ films crystallized at 900°C.

INTRODUCTION

The dielectric constant of ferroelectric materials can be varied by the application of an external electric field. Thin films of such tunable dielectric materials are of interest in microelectronic devices used for communication. Recent examples include tunable bandpass filters and phase shifters based on barium strontium titanate (BST) thin films.[1-2] For such applications, it is desirable to choose material compositions with ferroelectric transitions below room temperature such that the device operates in the paraelectric state. Operating tunable dielectrics in the paraelectric regime offers two basic advantages. First, device design is simplified because dielectric tuning is non-hysteretic. Second, dielectric losses are reduced because domain walls are absent.

Currently, most thin film ferroelectric varactors employ solid solution compositions of the $(Ba,Sr)TiO_3$ perovskite family. However, because of its refractory nature, this materials set requires high processing temperature (>800°C) to achieve sufficient grain size and crystallinity for desirable dielectric tunabilities. Because certain substrate materials of interest for frequency agile devices, like high-resistivity silicon, require lower thermal budgets, tunable dielectrics that can be processed at lower temperatures warrant investigation. Recently, Lu and coworkers[3-4] have examined a bismuth-based pyrochlore that can be processed at 750°C. However, because this material is not ferroelectric, it requires a large electric field (2400 kV/cm) to achieve reasonable dielectric tuning (55%). We propose to investigate one of the most common low-process temperature ferroelectrics, $Pb(Zr,Ti)O_3$, as a possible candidate for tunable dielectric applications. Specifically, we choose to modify the *A*-site of PZT with Sr to achieve a room temperature paraelectric state material and examine the effect this has on the thin film's processability, dielectric response, and tunability.

EXPERIMENTAL PROCEDURE

Compositional selection of $(Pb,Sr)(Ti,Zr)O_3$ films was based upon the room temperature quaternary bulk phase diagram,[5] which is shown in Fig. 1. Compositions with near room temperature phase transitions were chosen in an attempt to retain high tunabilities. Three different PSZT compositions were investigated: $(Pb_{0.5}Sr_{0.5})(Ti_{0.5}Zr_{0.5})O_3$, $(Pb_{0.6}Sr_{0.4})$ $(Ti_{0.4}Zr_{0.6})O_3$, and $(Pb_{0.45}Sr_{0.55})(Ti_{0.7}Zr_{0.3})O_3$. These compositions are labeled in the phase diagram of Fig. 1. A $Pb(Zr_{0.52}Ti_{0.48})O_3$ film was also prepared as a standard for comparison.

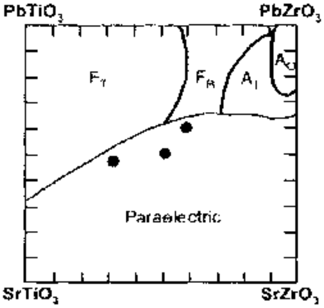

Fig. 1: Room temperature quaternary phase diagram for the $(Pb,Sr)(Ti,Zr)O_3$ system.[5] Black dots represent the three compositions investigated in this paper. Phases fields are notated as F for ferroelectric and A for antiferroelectric; crystal structure is notated by subscripts: T for tetragonal, O for orthorhombic, and R for rhombohedral.

Films were prepared using a chemical solution deposition approach. To prepare the solution, titanium isopropoxide and zirconium propoxide (70 wt% in 1-propanol) precursors were reacted in proper stoichiometric ratio in a low-humidity (<20%) environment. Acetic acid was added in a 4:1 molar ratio with the transition metal cations. After 10 minutes of continuous stirring, a 3:1 molar ratio of acetylacetone was added to chelate the metal cations. At this point the solution could be removed from the dry environment. The solution was diluted to ~0.4 M with acetic acid. Next, strontium acetate was added. The solution was heated to 90°C to facilitate dissolution; the strontium precursor took ~35 min to completely dissolve. Finally lead acetate tri-hydrate was added to give a 10 mol% excess *A*-site stoichiometry to account for probable lead loss during film crystallization. Because Pb was the only volatile constituent, film stoichiometry was assumed to reflect the Sr:Ti:Zr ratio in the prepared solution. The solution was then further diluted with acetic acid to achieve a 0.3 M concentration. Solutions exhibited limited stability with visible precipitation within 2-3 days. Solution stability could be extended to approximately one week if the solution was refrigerated at 0°C.

Films were prepared by spin-coating the solutions on platinized silicon substrates at 3000 rpm for 30 seconds. Films were dried on a hotplate at 325°C for 5 min. This process was repeated for three layers. The PSZT films were then crystallized in a tube furnace at a range of temperatures (600°C-800°C) for 30 min. Final film thickness was ~320 nm.

The crystalline structure of the PSZT films was verified by x-ray diffraction using a Bruker AXS D-5000 with an area detector. Atomic force microscopy was employed to image surface morphology; images were collected in tapping mode. Dielectric properties were probed with an HP4192a impedance analyzer. Besides examining the dielectric tunability, measurements were made as a function of temperature to confirm the Curie point shift. All dielectric measurements were made at 10 kHz with a 0.05 V oscillating voltage. Dielectric tunability is calculated as $(\kappa_{max} - \kappa_{min})/(\kappa_{max})*100\%$ where κ is the dielectric constant.

RESULTS AND DISCUSSION

X-ray diffraction data for three different PSZT compositions fired at 650°C is presented in Fig. 2. These samples have a phase pure perovskite structure with no indication of pyrochlore crystallites. Fig. 3 provides a sampling of the surface morphology for these films; an image of a PZT film prepared at the same temperature (650°C) is included for comparison. Whereas the PZT film exhibits a uniform morphology indicative of columnar grains nucleating at the substrate, the PSZT films contain surface nucleated grains forming rosette structures.[7] Currently, it is unclear whether variations in solution chemistry and/or film processing conditions could improve the uniformity of this microstructure or whether the observed surface nucleation is a direct result of strontium lowering the activation energy for nucleation in this system.

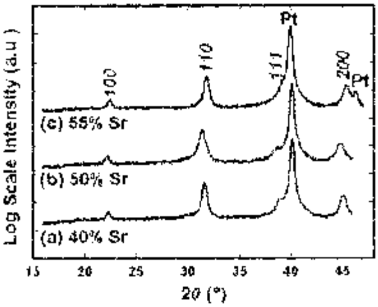

Fig. 2: X-ray diffraction data for chemical solution deposited PSZT films of varying composition annealed at 650°C. Perovskite peaks are labeled by reflection while Pt peaks are observed from the substrate.

(a) $(Pb_{0.6}Sr_{0.4})(Ti_{0.7}Zr_{0.3})O_3$
(b) $(Pb_{0.5}Sr_{0.5})(Ti_{0.7}Zr_{0.3})O_3$
(c) $(Pb_{0.45}Sr_{0.55})(Ti_{0.7}Zr_{0.3})O_3$

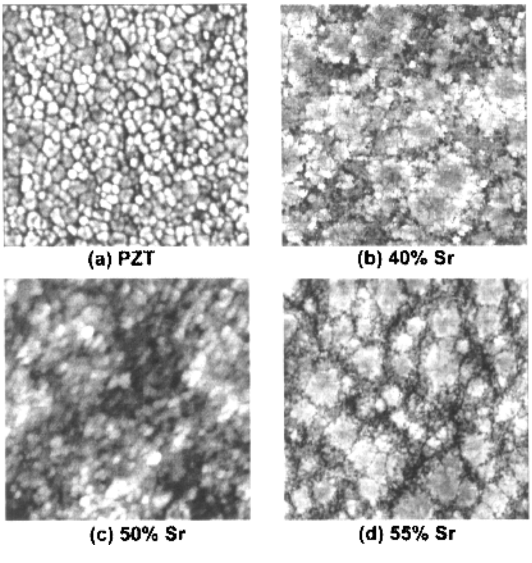

Fig. 3: Atomic force microscopy images of chemical solution deposited PSZT films crystallized at 650°C. Images are 2 μm x 2 μm:

(a) $Pb(Zr_{0.52}Ti_{0.48})O_3$
(b) $(Pb_{0.6}Sr_{0.4})(Ti_{0.7}Zr_{0.3})O_3$
(c) $(Pb_{0.5}Sr_{0.5})(Ti_{0.7}Zr_{0.3})O_3$
(d) $(Pb_{0.45}Sr_{0.55})(Ti_{0.7}Zr_{0.3})O_3$

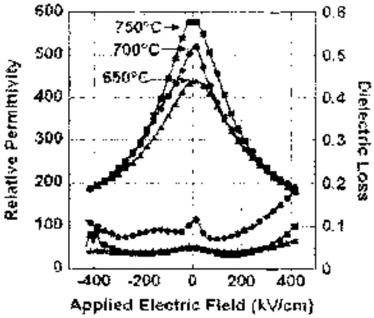

Fig. 4: Room temperature dielectric tunability at 10 kHz sampling frequency for three $(Pb_{0.45}Sr_{0.55})(Ti_{\text{[illegible]}}Zr_{\text{[illegible]}})O_3$ thin films crystalized at varying temperatures.

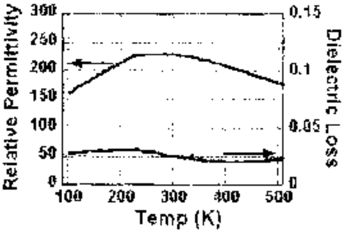

Fig. 5: Measurement of dielectric properties as a function of temperature for a $(Pb_{0.5}Sr_{0.5})(Ti_{0.5}Zr_{0.5})O_3$ thin film collected at 10 kHz.

Various annealing temperatures were investigated to determine the effect on dielectric tunability. As expected, tunability increased with increasing annealing temperature—a result of improved crystallinity and larger grain size. An example of this behavior is presented in Fig. 4 for the 55% Sr PSZT film fired at 650°C, 700°C, and 750°C. For this film, dielectric tunability increases from 57% at 650°C to 67% at 750°C.

The shape of the curves presented in Fig. 4 indicates material in a paraelectric state at room temperature—dielectric tuning with negligible hysteresis and peak permittivity at zero bias. To further confirm that the Curie point has been shifted to below room temperature, dielectric measurements were collected as a function of temperature. An example of temperature dependent dielectric data is presented in Fig. 5 for a PSZT film of the 50% Sr composition. The phase transition for this film appears to occur over a broad temperature range, common for most ferroelectric thin films. However the transition regime is clearly centered at or slightly below room temperature (~298 K)– approximately 350°C lower than unmodified PZT of the same composition. Thus, we verify that the addition of strontium has created a material in the paraelectric state at room temperature.

Table I: Summary of dielectric properties for PZT and PSZT films crystallized at 650°C and measured at room temperature and 10 kHz. Dielectric tunability is taken at 400 kV/cm

Composition	Maximum κ	Average tanδ	Dielectric Tunability
$Pb(Zr_{\text{[illegible]}}Ti_{\text{[illegible]}})O_3$	1450	0.022	60%
$(Pb_{\text{[illegible]}}Sr_{\text{[illegible]}})(Ti_{\text{[illegible]}}Zr_{\text{[illegible]}})O_3$	220	0.023	24%
$(Pb_{\text{[illegible]}}Sr_{\text{[illegible]}})(Ti_{\text{[illegible]}}Zr_{\text{[illegible]}})O_3$	220	0.033	39%
$(Pb_{0.45}Sr_{0.55})(Ti_{\text{[illegible]}}Zr_{\text{[illegible]}})O_3$	440	0.047	57%

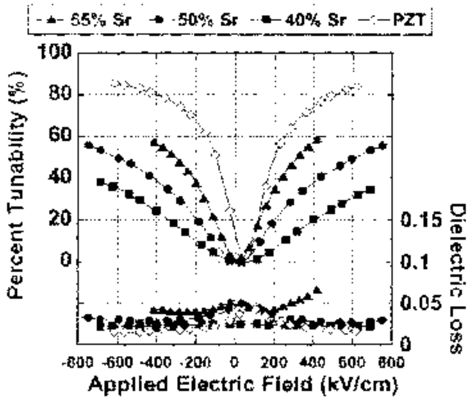

Fig. 6: Plot of dielectric tunability and dielectric loss under applied DC field for PSZT and PZT thin films crystallized at 650°C. Measurements taken at 10 kHz and room temperature.

Finally, in Fig. 6 dielectric tunability data is presented for all three PSZT compositions with pure PZT as a reference. Table I summarizes the dielectric properties of these films. All films presented in this plot are crystallized at 650°C—a relatively low temperature compared to typical BST thin film varactors (800°C – 900°C).[1] Of the investigated compositions, the 55% Sr system appears the most tunable with 57% tunability at 400 kV/cm. Typical polycrystalline BST films prepared at ~900°C have tunabilities of ~65% at 400 kV/cm.[2] Values for dielectric loss also appear promising in this system, largely remaining below 0.05. Further improvements in dielectric loss could be expected from Pb content optimization and acceptor doping.

CONCLUSIONS

Phase pure PSZT films have been prepared via a chemical solution route on platinized silicon substrates. The structure and dielectric response of these films is compared to a similarly prepared PZT film. In contrast to the uniform microstructure of the PZT film, PSZT films have an inhomogeneous structure with features resembling surface-nucleated rosettes. Despite this microstructure, these films exhibit relatively low dielectric losses (<0.05) and reasonable dielectric constants (ranging from 210 to 440 when crystallized at 650°C). Of the compositions investigated, the $(Pb_{0.45}Sr_{0.55})(Ti_{0.5}Zr_{0.5})O_3$ film exhibits the highest dielectric tunability (57% at 400kV/cm) when crystallized at 650°C. This tunability approaches typical values reported for BST thin films prepared at 900°C (~65% at 400kV/cm) but is significantly lower than the pure PZT film (80% at 400kV/cm).

REFERENCES

[1] J. Nath *et al.* An Electronically Tunable Microstrip Bandpass Filter Using Thin-Film Barium Strontium Titanate (BST) Varactors, *IEEE Transactions on Microwave Theory and Techniques*, **53**, 2707 (2005).

[2] J. L. Serraiocco, P. J. Hansen, T. R. Taylor, J. S. Speck, and R. A. York, Compact Distributed Phase Shifters at X-band Using BST. *Int. Ferroelec.*, **56**, 1087-1095 (2003).

J. Lu, S. Stemmer. Low-loss, Tunable Bismuth Zinc Niobate Films Deposited by RF Magnetron Sputtering, *Appl. Phys. Let.*, **83**, 2411-3 (2003).

J. Lu, *et al.* Low-loss tunable capacitors fabricated directly on gold bottom electrodes, *Appl. Phys. Let.*, **88**, 112905 (2006).

T. Ikeda, A Few Quarternary Systems of Perovskite Type $A^{2+}B^{4+}O_3$ Solid Solutions, *J. Phys. Soc. Jap.*, **14**, 1286-94 (1959).

B. A. Tuttle *et al.* Microstructural Evolution of $Pb(Zr,Ti)O_3$ Thin-Films Prepared by Hybrid Metalloorganic Decomposition, *J. Mater. Res.*, **7**, 1876-1882 (1992).

D. Ghosh *et al.* Tunable High-Quality-Factor Interdigitated $(Ba,Sr)TiO_3$ Capacitors Fabricated on Low-cost Substrates with Copper Metallization, *Thin Solid Films*, **496**, 669-673 (2006).