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Sol–gel derived $Pb(Zr,Ti)O_3$ thin films: Residual stress and electrical properties

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Abstract

$Pb(Zr,Ti)O_3$ compositions are under investigation for applications that include integrated capacitors, piezoelectric sensors, and actuators. Sol–gel synthesis and spin coating are popular routes to the formation of high quality, dense, crack free, insulating films. However, the electrical properties of the films are often different than those measured for bulk specimens of the same composition. $Pb(Zr_{0.53}Ti_{0.47})O_3$ films were deposited from a 2-methoxyethanol based sol–gel system onto $Pt/Ti/SiO_2//Si$ substrates via spin-casting. Multiple layers were sequentially deposited and heat-treated to 650 °C with the use of a PbO overcoat to ensure complete perovskite phase formation. Film thickness was varied from 0.19 to 0.5 μm to study the effect of thickness and residual stress on the dielectric and piezoelectric properties of the polarizable and deformable material. Ex-situ wafer curvature measurements, combined with cross-sectional scanning electron microscopy, allowed for the determination of residual stresses in the thin films calculated by the Stoney equation. The macroscopic boundary conditions were then related to the measured properties of interest, namely dielectric constant, tan δ, and piezoelectric strain coefficient. Measured dielectric constants varied from ∼750 to ∼1000, while d_{33} values ranged from 30 to 44 pm/V, as determined by single-beam heterodyne laser interferometry measurements.
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1. Introduction

Materials in the $PbZrO_3$–$PbTiO_3$ (PZT) system have been studied for over 50 years for use in devices as varied as transducers and capacitors, and more recently as non-volatile memory elements, sensors, actuators, and electro-optic modulators.[1,2] Initial applications of PZT required bulk material or tape-cast sheets. However, with the rise of integrated circuits based on semiconductor technology, the push for thin films, directly bonded to silicon-based substrates, has grown dramatically. Unfortunately, a common observation during the development of PZT technology was that thin films, whether deposited by sputtering, CVD, PLD, or chemical-solution deposition processes, did not have the same properties as their bulk counterparts.[3–7] These observations have since led to increased activity in the field in an attempt to elucidate the fundamental differences between bulk and thin film ferroelectric perovskites. Potential mechanisms for the observed differences in PZT materials include: thickness, grain size, interface, crystal orientation, and residual stress.[8–12] Results relating to many of these potential mechanisms have been reported in the literature, but a clear understanding is still lacking, and the performance level of thin film PZT has not yet reached bulk values. The work presented here focuses on the effect of residual tensile stress (developed during film processing) on the measured dielectric and piezoelectric properties of films of three distinct thicknesses.

2. Experimental procedure

$Pb(Zr_{0.53}Ti_{0.47})O_3$ thin films were deposited via spin-coating from a 2-methoxyethanol based sol. The solution

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chemistry used throughout this work followed the synthetic route developed by Budd et al.[7] and later refined by Lakeman et al.[13] for the fabrication of Pb-based perovskite thin films and powders. Standard Schlenk glassware with a flowing dry N_2 atmosphere was used to preserve an inert atmosphere throughout all chemical manipulations. Lead acetate trihydrate, $Pb(CH_3COO)_2 \cdot 3H_2O$ (Aldrich Chemical Company), was dehydrated under vacuum at 80 °C for 12 h. A 5 mol % excess of the resulting anhydrous white powder was mixed with a large excess of 2-methoxyethanol (Aldrich Chemical Company) and refluxed at 100 °C for 1 h before distillation under flowing N_2. Two thermal distillations (140 °C) plus two vacuum distillations (∼10 Torr, 65 °C), followed by redilution with 2-methoxyethanol in each step, were used to ensure complete reaction and removal of any by-products. Separately, Ti-isopropoxide and Zr *n*-propoxide (Aldrich Chemical Company) were mixed with excess 2-methoxyethanol in an approximately 1:10 molar ratio and refluxed at 100 °C for one hour under flowing N_2. An opaque yellow solution was obtained after three successive thermal distillations (140 °C). The Zr/Ti precursor was combined with the Pb-precursor in 2-methoxyethanol and refluxed for 1 h. Two thermal distillations and two vacuum distillations were carried out to complete the reaction and remove any remaining reaction by-products to yield a stock solution. This stock solution was then diluted with 2-methoxyethanol and partially hydrolyzed and aged (>24 h) to give a 0.25 M, $R_w = 0.5$ solution suitable for spin-coating. Additionally, a PbO overcoat was prepared and used following the work of Tani et al.[14] to control Pb-loss often experienced during thermal processing.

Prior to spin coating, single-side polished platinized silicon substrates ($Pt/Ti/SiO_2//Si$) were prepared by dc sputtering in Ar onto as received, 375 μm thick, Si(1 0 0) wafers with 5000 Å of thermally grown oxide (Silicon Quest International). Substrates were rinsed with 2-methoxyethanol prior to deposition to remove surface contaminants. A dry N_2 spray was also used to remove any surface particles. A standard photolithography spinner (Headway Research Inc.) was used to deposit all films. Spin-coating conditions were optimized to produce uniform layers over 3 in. diameter substrates with a minimal number of defects. Solutions were deposited through a 0.2 μm filter onto a substrate, initially spinning at 300 rpm. After the surface was saturated with solution, the spin speed was increased to 3000 rpm for the remainder of the 60 s deposition time. A two-step hot-plate treatment was then used at 120 and 300 °C for 1 min each. The temperatures were determined by thermogravimetric analysis (TGA) of a PZT bulk gel for the drying and pyrolysis stages.[15] The spin/hot-plate process was repeated four times, with a subsequent PbO overcoat applied before firing in a pre-heated box furnace at 650 °C for 30 min. This sequence of spin casting and heat treatment was repeated several times to build up thicker perovskite films. All films were identified to be single-phase perovskite by X-ray diffraction (XRD, Philips X'Pert MRD, Cu K_α-radiation). Furthermore, the presence of any possible minor phases, such as pyrochlore or a defect fluorite, often manifested as a nanocrystalline matrix, were not observed by scanning electron microscopy (SEM, Hitachi S-4700).[13]

The macroscopic residual stress in the thin films was determined by wafer-curvature measurements using a KLA-Tencor FLX-2908 laser reflectance system. An accurate fit for the radius of curvature of the substrate was determined using a line scan consisting of 100 points. The radius of curvature of the platinized silicon substrate was used as the reference point for all subsequent measurements. A change in radius of curvature after film deposition can then be used to calculate the stress in the film via the Stoney equation,

$$\sigma = \left(\frac{E}{1-\upsilon}\right)_S \frac{t_S^2}{6t_f}\left(\frac{1}{R} - \frac{1}{R_0}\right)$$

where, $(E/1-\upsilon)_s$ and t_s are the biaxial elastic modulus and thickness of the substrate, R_0 is the reference radius of curvature, and R is the final radius of curvature (in this case, after film processing).[16] Film thickness (t_f) was measured via cross-sectional scanning electron microscopy. The above equation is based on beam bending mechanics and assumes that the layer thickness is much less than that of the substrate. In this work, all films were more than two orders of magnitude thinner than the substrate thickness of ∼375 μm, satisfying the thin-film assumption. With the thickness ratio satisfied, the Stoney equation allows for the calculation of residual stress in any film (on a substrate with known elastic properties) without any prior knowledge of its own elastic behavior. This is particularly useful for sol–gel derived coatings where properties change during heat treatment.

Pt counter electrodes, 1.2 mm in diameter and 2000 Å thick, were sputtered onto the top surface of the films without any observable change in measured stress for the integrated film. The electrodes were connected to fine copper wire (0.025 mm diameter) by a silver-containing epoxy, and the entire assembly was mounted on a rigid 3 in. × 3 in. × 0.375 in. Al block. Dielectric measurements were made with a HP 4284A impedance bridge at 50 mV ac and 1.0 kHz. Piezoelectric properties were determined by driving the specimens at a small ac voltage over a range of dc bias fields. The 100 mV, 1.0 kHz applied ac signal was supplied by a lock-in amplifier (Stanford Research Systems, Model SR 830). As the samples were driven, out-of-plane displacements were measured using a heterodyne interferometric system (with a 0.24 mm diameter spot size) developed previously by Lian and Sottos.[17]

3. Results and discussion

Heat-treated PZT films were dense and macro-crack free for thicknesses of 0.19, 0.35, and 0.50 μm. A representative scanning electron photomicrograph is given in Fig. 1 for the 0.19 μm film in both plan and cross-sectional views. As the film is well bonded to the substrate, and can only expand or contract perpendicular to the substrate surface, residual biax-

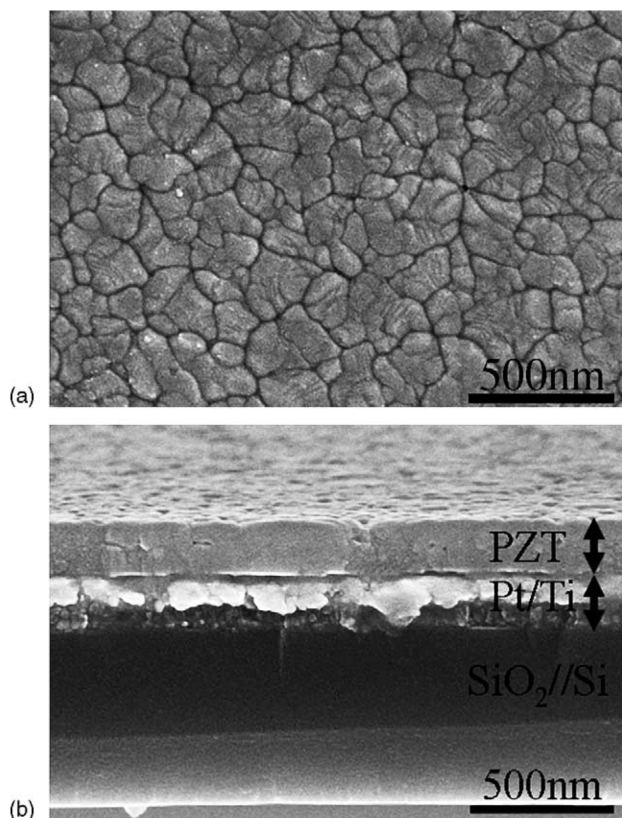

Fig. 1. Scanning electron photomicrographs of a 0.19 μm thick PZT film on $Pt/Ti/SiO_2//Si$ in (a) plan view and (b) cross-section.

ial stresses build up in the film due to constrained shrinkage during drying, pyrolysis, crystallization, and thermal expansion mismatch between the film and substrate on cooling.[15,18] Residual stress measurements carried out on these films (with the $Pt/Ti/SiO_2//Si$ substrate used as a reference) yielded unusually large tensile stresses ranging from 1590, 850, to 650 MPa with measured tensile stress decreasing with increasing thickness. Fig. 2 illustrates the apparent change in calculated residual stress, with increasing film thickness, determined in this study. In all cases, calculated values of residual stress values were inordinately high. Strains ranging from 0.9 to 2.2% were estimated using a Young's modulus of 70 GPa.[2] The result is clearly unlikely for ceramics where the strain-to-failure is usually ∼0.1%. Therefore, the calculated stress must have an additional component other than from the PZT film. This may stem from changes in the sputtered Pt/Ti layer after repeated heat treatments. Work in progress is directed at investigating this effect by etching the PZT film from the substrate and re-measuring the radius of curvature.

SEM and XRD indicated that morphology and phase purity was consistent throughout the sample set. However, dielectric and piezoelectric behavior show a correlation with residual stress (Fig. 3). As calculated tensile stress decreased (from left to right in Fig. 3), calculated values of dielectric constant increased from ∼750 to ∼1000. Tangent δ values were between 0.01 and 0.02, indicating low-loss properties for the films, comparable with bulk values of similar composition. The piezoelectric coefficients reported here are significantly less (d_{33} = 30–45 pm/V) than previously measured for identical samples (d_{33} = 200–400 pm/V).[19] We now correct these values. Substrate bending during actuation was found to artificially enhance the d_{33} coefficients of the PZT film. Kholkin et al. also observed this phenomena when using a single-beam interferometer.[20] The use of a single-beam interferometer in this study, along with a non-rigid adhesive layer (Crystalbond™ 509 (Aremco Products, Inc. Valley Cottage, NY) was originally used to bond the specimen to the Al block) resulted in a change in wafer curvature during actuation, resulting in larger than expected out-of-plane displacements and calculated d_{33} values. We report now corrected d_{33} values from rigidly bonded samples (without substrate bending effects). These values (ranging from 30 to 45 pm/V) are an order-of-magnitude less than bulk values for the same composition.[2]

The trend in d_{33} values for the current specimens can be correlated with stress and film thickness. One plausible

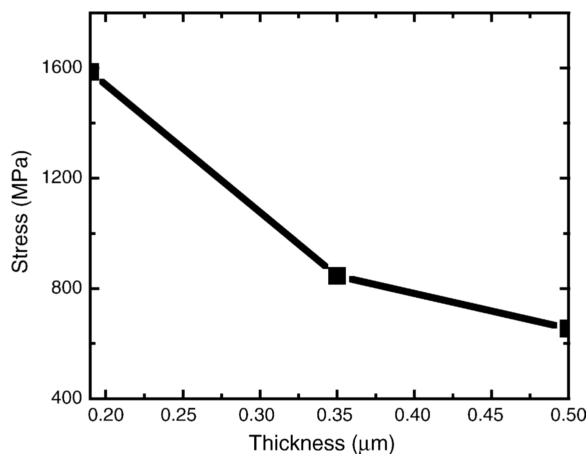

Fig. 2. Measured residual tensile stress in PZT as a function of film thickness.

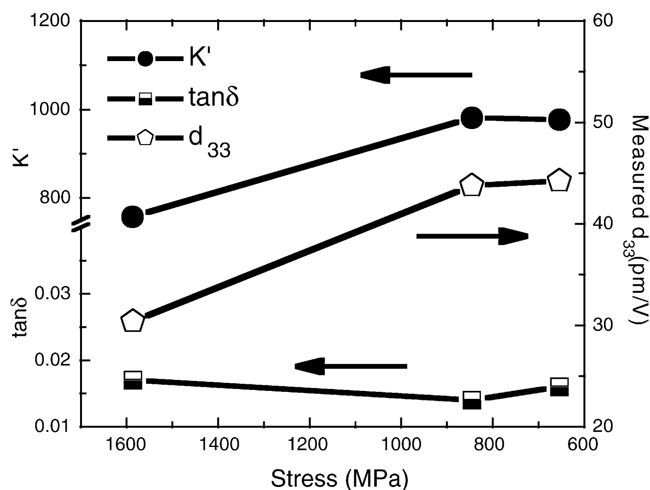

Fig. 3. Dielectric constant, tan δ, and piezoelectric strain coefficient, as a function of residual stress.

explanation for changes in properties is an interface-layer effect.[8] The presence of a low dielectric constant layer in series with the active piezoelectric layer dilutes the observed behavior. While observations of interface layers have been published in the past, this interpretation may not be the entire story. The dilution layer would hold true for a film that could be of arbitrary thickness, while all other conditions (such as stress, crystallite size and orientation) were held constant. In the present case, residual tensile stress decreased as film thickness increased.

Reports indicate that residual or applied stress can have a significant effect on electrical properties. Shepard Jr., et al. reported that application of tensile stress on the order of ∼150–200 MPa could cause a reduction in the remanent polarization of up to 20% of the original value.[21] Garino and Harrington reported complimentary results were the reduction of residual tensile stress (through wafer bending) by 30% increased the dielectric constant by 2%, the remanent polarization by 11%, and the coercive field by 1.5%.[22] Furthermore, reports indicate that the stress state upon cooling through the Curie temperature can affect the domain configuration, and thus dielectric properties, in tetragonal PZT thin films.[23] A tensile stress on cooling from the cubic state yields a preferred orientation of the *c*-axis in the plane of the substrate, whereas a compressive stress would form the *c*-direction normal to the substrate. The composition in the present study (i.e., 53/47) was on the rhombohedral/tetragonal phase boundary, and preferred orientation of domains could not be substantiated by XRD or SEM.

Current results, which have both residual tensile stress and an inseparable thickness component, indicate that dielectric constant values increased by up to 33% as residual stress was reduced by ∼900 MPa, which was in qualitative agreement with the results of Garino and Harrington.[22] However, the concurrent change in measured d_{33} for thin films with residual stress gives new evidence that residual stress can affect the electromechanical switching behavior of these materials. In fact, the measured dielectric constant scales linearly with the measured d_{33} in these films, indicating a constant g_{33} coefficient regardless of thickness or residual stress. The mechanism behind the observed behavior is under current investigation.

4. Conclusions

A sol–gel method was used to deposit $Pb(Zr_{0.53}Ti_{0.47})O_3$ films with different thicknesses and residual tensile stresses. Scanning electron microscopy was used to confirm film thickness and a lack of cracks while a wafer curvature technique was used to calculate residual tensile stress by the Stoney equation. Dielectric and piezoelectric measurements indicated a correlation with measured residual stress values, and film thickness. Separation of the two variables is a topic of ongoing research. Qualitative interpretation of the results is in agreement with previous literature reports. An additional observation regarding the scaling of dielectric constant and the piezoelectric d_{33} coefficient determined a constant g_{33} coefficient for the films.

Added at the time of press:

Preliminary results indicate that calculated strain levels are closer to 0.1% when the contribution of a Pt/Ti reaction is accounted for during PZT film processing.

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