Strain Measurement and Mechanical Property Evolution in Sol-Gel PZT Thin Films

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Abstract

Cracking is a notorious issue with sol-gel PZT thin films, and film failure in this manner is difficult to reliably predict due to constantly evolving mechanical properties. In this work, two non-contact experimental methods are used to quantify the stiffness response of PZT sol-gel during thermal loading and the influence of solution additives, such as lactic acid and gycerol. The mechanical properties are determined using a digital image correlation method to measure strain and wafer curvature measurements to estimate bi-axial stress. Results show the transition from a compliant response to more glassy behavior. The importance of this changing stiffness is shown for a specific application of a buckled MEMS actuator and in relation to adhesion based failure modes.

Keywords: Sol-Gel PZT, Strain Measurement, Digital Image Correlation, Bi-Axial Modulus

Introduction

Given their predisposition to cracking, creating perovskite rich lead zirconate titanate (PZT) thin films via a sol-gel deposition method can be quite challenging. Successful fabrication of ferroelectric PZT derived from sol-gel thin films requires ushering the material from room temperature at initial deposition, up to the requisite firing temperature, and back down again to room temperature. During these thermal processing steps, PZT sol-gel films can experience intense in-plane stresses due to a number of both intrinsic and extrinsic sources.

Scherer [1-2] and others [3] have written extensively about the many mechanisms by which stress develops within sol-gel films during thermal processing. Immediately after a spin-coating deposition, the microstructure of sol-gel layer is typically a nanoporous polymeric network filled with the solution solvents. In order of occurrence during PZT sol-gel thin film thermal processing, sources of intrinsic stress include shrinkage and collapse of the polymeric gel network, pyrolysis stages, grain boundary interactions, and phase transformations upon cooling through the Curie temperature. Additional extrinsic stress sources also add to the residual stress of the film, mostly due to mismatches in coefficients of thermal expansion between the sol-gel film and the substrate materials.

Often, the combination of intrinsic and extrinsic stresses is sufficient to induce mechanical failure of the sol-gel film. In many cases, failure manifests itself in the form of cracking. Excessive tensile stresses can lead to periodic fracture and the formation of "islands" of the film layer, while stresses that are compressive in nature can cause blistering, wrinkling, or buckling type failure modes.

Beyond simply knowing the magnitude of the stress on the film layer, the boundary conditions for film loading are also critical for dictating the type of failure the loading threshold for failure initiation. In the case of sol-gel thin films, the constraint supplied by the substrate and the quality of adhesion across the film/substrate interface tend to be the factors that dominate this response. For cases in which the interfacial strength between the film and the substrate is low, delamination (or, spalling) of the film can occur. Conversely, in cases of very high adhesion strength, fracture of the substrate material may actually occur prior to film failure.

To aid in design of thin film systems, a theoretical mechanics analysis was developed by Evans, *et al.* [4], and expanded by Hutchinson and Suo [5], which identifies parameters necessary to outline regimes of expected failure types. This analysis defines a dimensionless cracking number, Z, that is associated with different film-substrate failure

types that are commonly found for bi-axially loaded cases.

This dimensionless cracking number is given as:

$$Z = \frac{\Gamma\left(E_f\right)}{h_c\left(\sigma^2\right)} \qquad (1)$$

where, Γ is the fracture resistance of the particular material in question, E_f is the Young's Modulus of the film, σ is the bi-axial stress state, and h_c is the critical film thickness [5]. By knowing the Z values associated with the different types of failure, one can in theory predict whether a certain style of cracking will occur for a specific material system. However, this prediction is only possible if an accurate characterization of the material properties and interfacial fracture resistance can be made.

Prediction of film failure in sol-gel films presents a series of challenges. Foremost, the mechanical properties of the sol-gel film are not easily obtained. Commonplace material testing methods, such as tensile tests on dog-bone shaped specimens, are highly impractical, if not outright impossible. Nanoindentation tests can offer some insights into the mechanical behavior, but generally give results that are difficult to interpret. For thin, highly compliant films on rigid substrates, separating the mechanical responses of the individual materials is especially problematic for nanoindentation experimentation.

Determining the stiffness response for sol-gel films presents additional complexities due to the chemical and physical (microstructure) changes that occur during thermal processing. These changes cause a corresponding evolution of the elastic properties. With a goal of contributing towards predictions of sol-gel film failure, this work uses a set of non-contact experiments to estimate the transient mechanical properties of PZT sol-gel layers. In particular, the influence of solution additives purported to enhance the mechanical stability of resulting films is investigated.

Materials and Sample Preparation

In this research work, two variations of a "table-top" sol-gel PZT were prepared following the method used by Yi, Wu, and Sayer [6-8]. One variation of the solution, herein referred to as "non-mechanically enhanced", used a stock solution derived identically to that in [6]. The stock solution constituents included only lead acetate, acetic acid, zirconium propoxide, titanium isopropoxide, ethylene glycol and distilled water. Prior to film deposition, the stock solution was diluted slightly with water and propanol in the ratio of 1:1:1 (stock PZT sol-gel solution: H_20: $CH_3CH_2CH_2OH$) by volume.

A second sol-gel solution variation uses the previous stock solution and adds a small concentration of lactic acid and gycerol, following precisely the recipe presented by [8]. The solution variation with these additional chemicals is referred to within this work as the "mechanically enhanced" solution. After preparing this stock solution variation, it was then diluted with water and propanol in the ratio of 1:1:1 (stock PZT sol-gel solution: H_20: $CH_3CH_2CH_2OH$) by volume. The addition of lactic acid and gycerol has two immediately noticeable effects. First, the viscosity of the sol-gel solution increases slightly. Second, the stability (shelf life) of the solution increases.

Specimens were prepared by spin-coat deposition of a single layer of sol-gel solution. Approximately 0.5 mL of sol-gel solution was deposited onto a substrate spinning at 300 rpm (10 sec) before spinning up to 3,000 rpm (60 sec). Substrates for thickness and strain experiments consisted of ~20 mm x 20 mm <100> single crystal silicon pieces, while for wafer curvature measurement tests the substrate consisted of an entire 100 mm diameter wafer.

Ellipsometry Measurements

It is important to emphasize that three separate sets of experiments are performed in this work, each independently of the others. Although the sample preparation and applied heating rate were identical, no one sample can be subjected to all tests (thickness, stress, and strain all measured separately). For the purpose of making estimations of the bi-axial modulus, the assumption is made that mechanical response of specimens of each type is similar and simply a function of the applied thermal loading. Using the results of all three types of tests, the aggregate behavior of sol-gel films is then calculated as a function of temperature.

The thickness of both mechanically enhanced and non-mechanically enhanced sol-gel layers was determined by ellipsometry. Ellipsometry is a laser-based method for measuring film thickness in which the change in angle due to a material's index of refraction is precisely determined over a range of light wavelengths. If the optical properties of the film are unknown, a variable angle test can be performed to back calculate both the index of refraction and the film thickness. The thickness of

both sol-gel PZT film layers across a range of temperature was determined using such a variable angle ellipsometry measurement device (VASE series, J.A. Woollam Co.). The optical properties for sol-gel PZT were determined by fitting data for a Cauchy material model. The Cauchy model assumes that over the visible light spectrum that the index of refraction, n, of the material varies as a function of the light wavelength, λ, as:

$$n(\lambda) = A_n + \frac{B_n}{\lambda^2} \qquad (2)$$

For both sol-gel types, the Cauchy material fitting parameters were calculated over a range of wavelengths from 400-1100 nm, and are shown in Table 1. Using these optical properties, the film thickness of each sol-gel specimen type was calculated as a function of applied temperature. Identical to other tests, specimens were heated at a rate of 10°C per minute using a Linkam THMS 600 hotstage. The results of the film thickness testing are shown in Figure 1.

Table 1. Cauchy material model optical parameters

Temp. (°C)	ME A_n	ME B_n (nm^2)	Non-ME A_n	Non-ME B_n (nm^2)
21	1.642	0.0124	1.649	0.0140
75	1.655	0.0126	1.665	0.0121
125	1.674	0.0137	1.674	0.0134
200	1.704	0.0144	1.693	0.0168
300	1.977	0.0328	1.984	0.0371
400	2.078	0.0451	2.011	0.0469

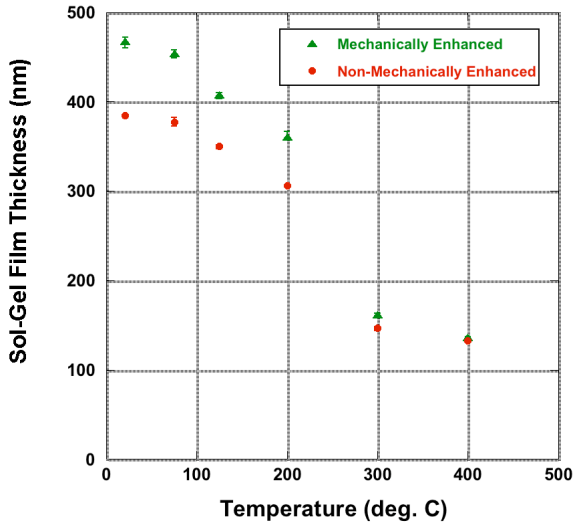

Figure 1. Thickness measured over a range of temperatures via variable angle ellipsometry measurements.

It was found that the more viscous solution (mechanically enhanced variation) initially gave slightly thicker sol-gel films. However, as heating occurred, the final film thicknesses for the two variations became nearly the same.

Wafer Curvature Measurements

For both mechanically enhanced and non-mechanically enhanced solutions deposited onto full 100 mm silicon wafers, wafer curvatures were measured as a function of temperature using a Toho Film Measurement System. In this system, the substrate sits on a heated platen with the film side positioned upwards. Inside the thermal chamber, a scanning laser is used to determine deflection across the surface of the wafer, which is then converted to a radius of curvature.

From wafer curvature measurements, the bi-axial stress state can then be calculated using the Stoney Equation [9]:

$$\sigma_{Bi-axial} = \frac{E_s(t_s)^2}{6t_f(1-\nu_s)}\left(\frac{1}{R}-\frac{1}{R_0}\right) \qquad (3)$$

where, t_s, E_s, and υ_s are the thickness, Young's Modulus, and Poisson's ratio of the substrate, respectively. The initial radius of curvature, R_0, is measured on the bare silicon substrate, prior to any film deposition. The sol-gel film thickness, t_f, in this equation is measured independently as a function of temperature via elliposmetry as discussed previously. No film elastic properties are necessary for the stress calculation, only that of the substrate. If the thin film assumption is met ($t_f << t_s$), then the change in the substrate curvature is directly attributed to load held by the film. This load is assumed to be uniformly held over the film thickness, and equal for in-plane principal directions due to the symmetry (in xy-plane of substrate, $\sigma_x = \sigma_y$). While a stress gradient may exist across the film thickness, it is expected to be minimal.

The results of the bi-axial stress calculations based on wafer curvature measurements are shown in Figure 2. For both sol-gel films types used in this study, the stresses were found to be tensile upon deposition. With specimen heating, the magnitude of the tensile stresses generally increased. When heating the samples above 200°C, the rate of stress increases dramatically, which corresponds to a change in the thermal expansion behavior of the silicon substrate. Surprisingly, the stress magnitude in the 21-125°C remained rather low, despite

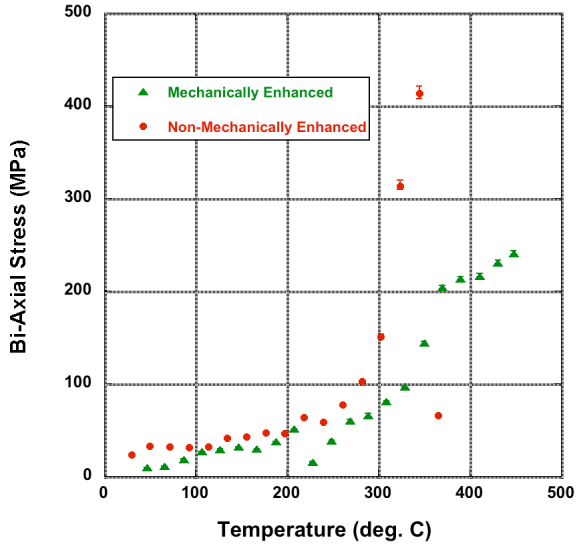

Figure 2. Bi-axial stress calculated via wafer curvature, as a function of temperature.

substantial solvent drive-off and capillary action during densification of the polymer gel network that occurs in this range.

For the non-mechanically enhanced films, the bi-axial stress was found to experience a large drop in the temperature range of 325-350°C. Observations of specimens heating under an optical microscope revealed that cracking of the non-mechanically enhanced films occurred. Dispersed cracks initiated at around ~150°C, and widespread and interconnected above 300°C, Figure 3. Interconnect cracks prevent load transfer, relieving film stress.

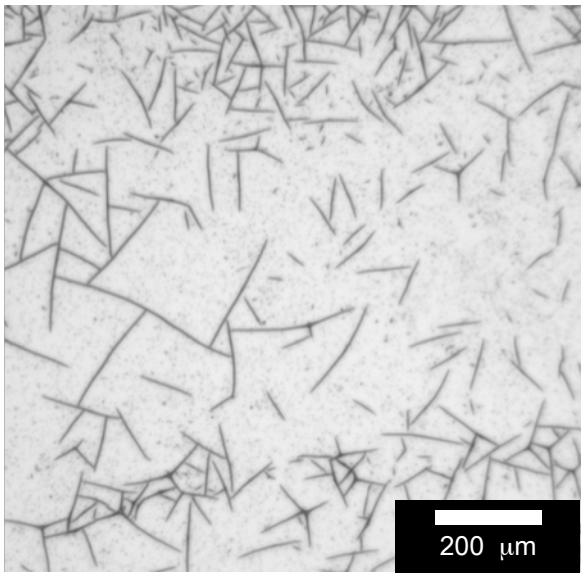

Figure 3. Optical image of the non-mechanically enhanced sol-gel film surface after heating to 325°C.

In-Plane Strain Characterization

In-plane strains are measured for the sol-gel films via digital image correlation (DIC). First developed by Sutton and others [10-12], digital image correlation is a technique that can be used to measure surface deformations at nearly any length scale, provided the surface has an appropriate random speckle pattern at the imaged size scale. DIC is performed by taking images of a specimen surface throughout an applied loading or material deformation. The digital images before and after loading are then run through an algorithm, which computes rigid body motions and deformations of image subsets. The net output of 2D versions of DIC programs is a data file that gives direct calculations of the in-plane displacements and strains for each individual subset of the image. Thus, complex strain fields can be measured optically.

In this work, specimens deposited identically to those used for ellipsometry were used for a DIC-based strain analysis during thermal loading. Prior to heating, the sol-gel film surfaces were airbrushed with an ethanol solution of silica nanoparticles (*c.a.* 200 nm diameter). The nanoparticles and clumps of nanoparticles dispersed on the sol-gel surface provide the requisite pattern for DIC calculations. Importantly, the pattern is not a continuous film, consists of particulate on the order of the film thickness, and remains well-attached to the sol-gel surface during thermal loading.

Strains were measured via DIC by taking images of the sol-gel film surfaces during thermal loading using a Leica DMR microscope (20X long

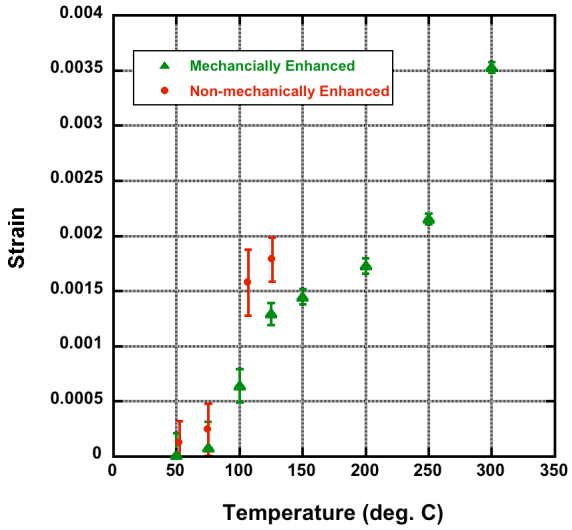

Figure 4. Average biaxial strain for sol-gel thin films as a function of temperature.

working distance objective) and a 2048 x 2048 pixel Reitiga 4000R camera (QImaging). Figure 4 shows the in-plane strains calculated via DIC over the field of view, averaging results from both the "x" and "y" directions (error bars represent range for multiple samples). The non-mechanically enhanced specimens were observed to demonstrate fracture initiation starting around 150°C, after which DIC analysis across the non-contiguous film would be erroneous (though local measurements could be made). The mechanically enhanced specimens showed no cracking throughout the entire thermal testing range. For both sol-gel specimen types, the strains increased quickly during the solvent drive-off stage (100-125°C).

Making the assumption that a symmetric in-plane stress/strain state exists ($\sigma_x = \sigma_y$; $\varepsilon_x = \varepsilon_y$), and that the stress, strain, and thickness behavior of the sol-gel films all act as simply a function of the applied thermal conditions, one can generate an estimate of the instantaneous bi-axial modulus of the films via:

$$\frac{\sigma_{Bi-axial}}{\varepsilon_{Bi-axial}} = \frac{E}{(1-\nu)} \qquad (4)$$

The bi-axial modulus calculation was performed for critical temperature ranges in which different mechanisms appear to dominate the film stress (solvent drive-off, substrate expansion, pyrolysis, etc.), Table 2. The results show a general transition in mechanical response, from very compliant "polymer"-like behavior at low temperature, towards a stiffer "glass"-like response at higher temperatures. This should coincide with the evolution into an amorphous film layer. The non-mechanically enhanced solution also trends upwards at higher temperatures, but fails to remain intact.

Table 2. Bi-axial modulus estimations

Temp. Range (°C)	Mechanically Enhanced	Non-Mechanically Enhanced
21-125°C	8.5 ± 1.4	5.3 ± 0.8
125-200°C	22.6 ± 0.6	12.1 ± 0.5
200-300°C	19.5 ± 0.9	N/A (cracks)

Conclusions

The addition of gycerol and lactic acid appear to add to the mechanical stability of the PZT sol-gel film, producing a slightly higher initial bi-axial modulus and different failure threshold than the sol-gel specimens that did not contain these additives. Both optical parameters and the stiffness response of sol-gel films were seen to evolve with temperature. Bi-axial modulus estimations should help with future material models for predicting sol-gel film failure.

Acknowledgements

This work has been funded in part by the National Science Foundation, Award #1130528 through the CMMI Division. The authors also acknowledge the assistance of the Micro/Nanotechnology Center at the University of Louisville in this effort.

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