RESIDUAL STRESS EFFECTS ON FERROELECTRIC THIN FILM PATTERNING, PROPERTIES AND PERFORMANCE

N.R. Sottos*, T. Berfield*, R. Ong**, and D.A. Payne**
* *Theoretical and Applied Mechanics, University of Illinois Urbana-Champaign, Urbana IL 61801*
** *Materials Science and Engineering, University of Illinois Urbana-Champaign, Urbana IL 61801*

Summary In this paper, we investigate the influence of processing, interfacial adhesion and residual stresses on ferroelectric thin film performance. Residual stress development is characterized for pattered PZT sol-gel films on functionalized substrates and for fully crystallized PZT films of varying thickness. For sol-gel films, residual stress plays a beneficial role in the patterning process, while for fully crystallized PZT films, residual stress is found to decrease electromechanical performance.

PROCESSING AND MEDIATED PATTERNING OF PZT SOL-GEL THIN FILMS

An additive method of patterning was investigated that enables integration of thin film electroceramics on a chip, rather than as a discrete component added into the circuit and system. Patterned oxide thin-film devices are typically formed by uniform film deposition followed by a somewhat complicated post-deposition ion-beam or chemical etching in a controlled environment, i.e., a subtractive method. In recent work, a unique additive approach has been developed that allows for selective deposition of electroceramic thin layers without conventional photolithography and post-deposition etching [1,2]. In this soft lithographic method, substrate surfaces are selectively functionalized with hydrophobic self-assembled monolayers (SAM) to modify the adhesion of subsequently deposited solution-derived electroceramic materials. The selective functionalization is achieved through microcontact printing (μ-CP) of self-assembled monolayers of the chemical octadecyltrichlorosilane (ODS) on a substrate of interest. Subsequent sol-gel deposition of ceramic oxides on the functionalized substrates, followed by lift-off from the monolayer, yields high quality, patterned oxide thin layers on the unfunctionalized regions, exclusively.

The results of a prototypical selective deposition of PZT, before and after oxide lift-off, are shown in Fig. 1. The ODS molecular monolayer or "ink" was applied to a flexible stamp surface molded with the desired pattern from a master (Fig. 1a). The stamp was then placed in contact with a substrate to achieve selective transfer of the ink pattern. Upon removal of the stamp, selective transfer of monolayer was achieved. Mediated deposition of PZT sol-gel layers above the ODS-modified surfaces was accomplished by spin coating deposition of the sol-gel precursor to the patterned substrate. Low temperature (120-140°C) heat treatment was necessary to achieve selective decohesion above the modified regions (Figs. 1b). The resulting patterned film was then dried and heat-treated further to obtain a dense, patterned layer (Fig. 1c). Shrinkage during heat treatment and the resulting residual stress development in the film led to the desired film cracking for lift-off, enabling the mediated patterning process.

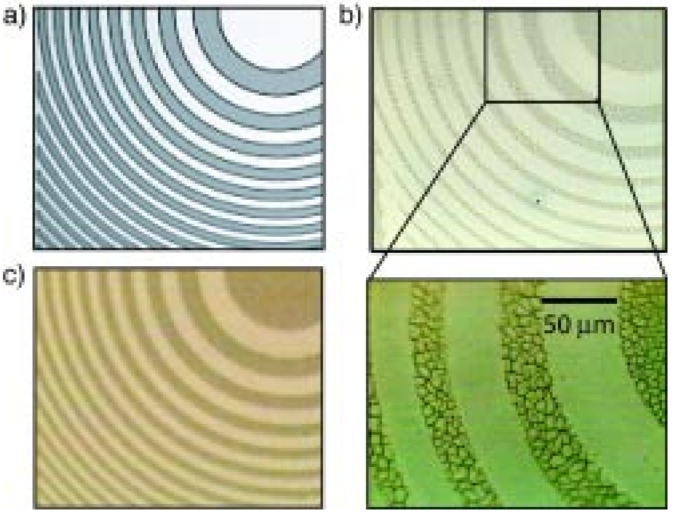

Fig. 1. Mediated deposition of PZT thin film: a) Master mold, b) selective cracking and decohesion over transferred SAM pattern, c) final patterned PZT film, light regions are PZT, dark regions are the Si substrate [1,2].

SHRINKAGE AND RESIDUAL STRESS DEVELOPMENT

Significant residual stresses develop in sol-gel processing of electroceramic thin films during the transformation of the metalorganic gel to the metal oxide (*i.e.*, ceramic) on heat treatment. Intrinsic residual stress is induced by shrinkage and constrained densification during drying and depends on the relative rates of evaporation, viscous deformation and flow of liquid through the pores of the gel. Extrinsic thermal stresses are induced upon cooling due to the mismatch between the developing thermoelastic properties of the film with those of the substrate. Residual stress impacts the mechanical integrity and reliability of the film. The interfacial bond between the film and the substrate must be capable of withstanding the force produced by the integrated stress throughout the film. Stress cracking, buckling and poor adhesion are commonly observed when the stress level exceeds a critical value. The mechanism of monolayer-mediated patterning (Fig. 1) is closely coupled to that of stress release by film decohesion above the functionalized regions of the substrate.

Residual stress development was monitored by in-situ laser reflectance measurements of wafer curvature using a KLA-Tencor FLX-2908 laser reflectance system. This apparatus enables accurate measurement of wafer curvature by carrying out a line scan with up to 100 points fitting the radius of curvature. The stress in the films was calculated from the change in radius of curvature using the Stoney equation [4]. Use of the Stoney equation enabled calculation of stress in the thin film from the substrate elastic properties without the need to know film properties.

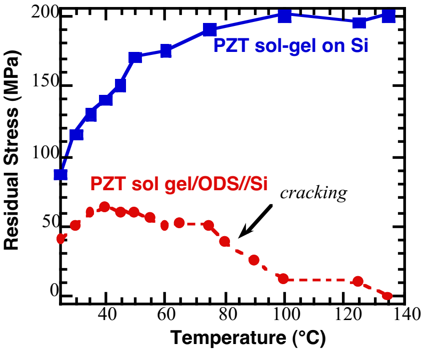

Fig. 2. Residual stress development of PZT sol-gel layers on different ODS-mediated substrates compared with a film on bare Si.

Residual stress development was first investigated during heat treatment and subsequent lift-off of the amorphous sol-gel films. For films deposited on bare substrate (*i.e.,* no ODS layer), constrained shrinkage resulting from adhesion to the supporting substrate led to a coherent (crack-free) film of 50 nm in thickness with biaxial stresses of ~200 MPa (Fig. 2). For ODS-mediated sol-gel films, however, precise *in situ* wafer curvature measurements captured the evolution and release of stresses during de-cohesion of the sol-gel layer. The resultant stresses in the mediated film never exceeded 75 MPa due to the onset of cracking and subsequent decohesion. The relationship between residual stress and interfacial fracture clearly controlled the desired patterning process.

The residual stress of fully crystallized PZT films was then measured after firing in a pre-heated box furnace at 650ºC for 30 minutes. $Pb(Zr_{0.53}Ti_{0.47})O_3$ films ranging in thickness from 190 nm to 500 nm were investigated. Thickness of films was varied by adjusting the number of sol-gel layers (in this case 4, 8, and 12) deposited onto platinized silicon substrates. The measured thickness and residual stress data for each film are listed in Table 1.

Table 1. Measured film properties for different number of sol-gel layer build-ups.

Sample	Thickness (μm)	Residual Stress (MPa)	Dielectric Constant, K'	tan δ
4 Layer	0.19	1500	800	.03
8 Layer	0.35	900	1100	.02
12 Layer	0.50	650	1200	.02

EFFECT OF RESIDUAL STRESS ON ELECTROMECHANICAL PERFORMANCE

Both the dielectric properties and the field-induced strains were measured for the films listed in Table 1. Top electrodes of platinum, 1.2 mm in diameter and 2000Å thick, were sputtered onto the films with no observable change in the measured film stress. The electrodes were jumped using fine copper wire and silver epoxy, and the entire wafer was mounted to a 3"x3" aluminum block. Electrical characterization was carried out on an HP 4284A with an AC signal of 5mV at 1.0 kHz. The dielectric constant (Table 1.) decreased significantly with decreasing film thickness. The field-induced strains of films under varying residual stress states were measured using an interferometric technique developed by Lian and Sottos [3]. Strain-field loops are plotted in Fig. 3 for PZT films of varying thickness and residual state. The strain field response also decreased dramatically with increasing residual stress (decreasing thickness). Hence, residual stress development during processing of fully crystallized ferroelectric thin films is found to have a significant negative impact on electromechanical properties and performance. The tensile residual stress creates an in plane clamping effect on the domains in the film, hindering polarization switching. While residual stress has a desirable effect on film patterning by inducing selective decohesion, it can have an undesirable impact on the electromechanical performance of the final patterned device.

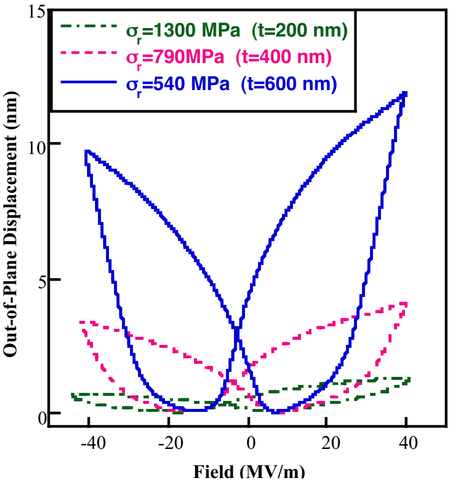

Fig. 3. Effect of residual stress (and film thickness) on field-displacement loops for fully crystallized PZT thin films.

References

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