Adhesion Strength of Lead Zirconate Titanate Sol-Gel Thin Films

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Abstract

The adhesion strength between a thin film and substrate is often the critical parameter that controls the initiation as well as the mode of film failure. In this work, a laser-based spallation method is used to determine the adhesion strength of "as deposited" lead zirconate titanate (PZT) sol-gel thin films on the two functionally different substrates. For the first case, PZT sol-gel film is deposited onto bare Si/SiO₂ substrates via spin-casting. The extremely high adhesion strength between the film and the substrate necessitated an additional platinum mass superlayer to be deposited on top of the PZT film in order to induce interfacial failure. For the superlayer film system, a hybrid experimental/numerical method is employed for determining the substrate/film interfacial strength, quantified to be in the range of 460-480 MPa. A second substrate variation with lower adhesion strength is also prepared by applying a self-assembled octadecyltrichlorosilane (ODS) monolayer to the Si/SiO₂ substrate prior to the film deposition. For the monolayer-coated substrate case the adhesion strength is observed to be significantly lower (54.7 MPa) when compared to the earlier case.

Keywords: sol-gel; thin film adhesion; laser spallation; PZT; lead zirconate titanate; monolayer

Background

The interfacial strength between a film and substrate is a critical parameter for predicting or preventing failure of sol-gel films. However, adhesion testing for thin films has proven notoriously difficult to perform with a satisfactory degree of quantitative assessment. For films that are extremely thin (*e.g.*, less than 500 nm in thickness) or highly compliant compared to the mechanical properties of the substrate, interfacial adhesion measurements become even more problematic. Commonly used peel tests [1-4] and pull-tests [5-7] can provide a valuable characterization of interfacial strength in theory, but present numerous difficulties in practice for thin film cases. The primary experimental issue with both of these tests is the manner in which the film must be physically gripped or attached to a loading tab. Adhesives can negatively influence test results for thin films by masking the mechanical properties of the film or, worse, chemically reacting with solvents contained within sol-gel films. The bonding process for adhesives can also introduce complications due to contact forces and the curing reaction. Contact forces needed to securely bond the film to the loading mechanism may prematurely initiate interfacial damage or create substantial residual stresses. For epoxy-based adhesives, the curing reaction can produce an exothermic reaction or require a long cure time, either of which can lead to solvent loss within the sol-gel film.

Another possible method to characterize the adhesion strength of thin films is the micro/nano scratch test [8-11]. In standard versions of the scratch test, a sharp indenter tip is driven perpendicularly into the film surface. After penetrating the film, the indenter is pulled along the film surface while the normal and lateral forces are monitored. Under some film failure modes, the adhesion strength can be extracted after a careful analysis of the film scratch track and the load data. Considerations in this analysis involve assumptions of failure type and

compensations for the indenter tip geometry and friction effects [12]. The adhesion assessment provided by the scratch test is only relevant if interfacial failure, *i.e.* film debonding, actually occurs. Film debonding happens only when the interfacial shear strength is lower than the film shear strength [10], which is difficult a criteria to meet for soft films. Despite these difficulties, the scratch test has been applied recently to sol-gel film systems [12,13], though generally limited to sol-gel films much thicker than 1 μm .

As an alternative to peel/pull and scratch tests, the laser induced spallation test offers a non-contact based method for determining film adhesion strength. Shown schematically in Figure 1, the most basic version of the laser spallation test pioneered by Vossen [14] and Gupta, *et al.*, [15-21] requires a short (nanosecond scale) high-energy laser pulse. The laser pulse is directed through a transparent confining layer and onto an absorbing metal layer that covers the backside of the sample substrate, with the film interface of interest coating the opposite side of the substrate. The energy absorbed by the metal layer causes a rapid expansion, launching a compressive stress wave through the thickness of the substrate. The stress wave propagates towards the film-substrate interface and then reflects from the free film surface as a tensile wave, loading the testing interface in tension. Displacements are measured at the free film surface at a point aligned directly with the stress pulsed region using an interferometer, typically a Michelson style. The magnitude of the stress pulse experienced by the film/substrate interface is proportional to the laser power applied and the mass of the film layer. Thus, the threshold for interfacial adhesion strength can be estimated by incrementing the laser power and inspecting the sample surface for failure.

Further enhancements to the laser spallation method include variations that enable adhesion testing for very difficult cases. Specifically, the introduction of nonlinear elastic

substrate materials to generate shock wave profiles for the loading stress pulse [22-23] has allowed adhesion testing of layers with very low mass and thicknesses below 100 nm. Additionally, adhesion tests involving mixed mode loading conditions [24-25] have been developed using unique sample geometries. Kandula, *et al.*, [26] have shown that the interfacial energy between a film and substrate can be measured by carefully designed sample preparation and film patterning. Finally, Kitey, *et al.*, [27] developed a highly useful procedure for characterizing the interfacial strength of especially thin and well-bonded thin films through the use of a superlayer and hybrid experimental/numerical simulation to estimate interfacial stresses. One potential drawback to the inclusion of a superlayer is that this method necessitates that the film interface of interest be the first to fail, *i.e.* before the superlayer/film interface shows damage.

The objective of this work is to quantify the adhesive strength of "green" PZT sol-gel films deposited on both octadecyltrichlorosilane (ODS) functionalized substrates and oxidized silicon (SiO_2/Si) substrates. In the case of the ODS functionalized substrate, poor adhesion is often observed to play a critical role in initiating delamination-driven failure modes such as island cracking. By contrast, PZT sol-gel films in direct contact with a SiO_2/Si substrate typically show extremely good adhesion, necessitating a variation of the hybrid method from [27] to be used within this study to quantify the interfacial strength.

Materials and Sample Preparation

Sol-gel films were prepared using a $\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$ composition stock solution following a recipe originally developed by Budd *et al.* [28], and later refined by Lakeman *et al.* [29]. The stock solution was then diluted to a final concentration with a molarity of 0.25 mol/L

and a 0.5 R_w molar ratio of water to alkoxide, similar to that used in previous work [30].

Substrates used were <100> oriented single crystal silicon wafers with a nominal thickness of 325 μ m and a 500 nm layer of thermally grown silicon dioxide.

For measuring the adhesion between the PZT sol-gel film and the silicon dioxide, the sol-gel solution was spin coated at 3000 rpm (for 45 sec) directly onto the Si/SiO₂ surface. The PZT sol-gel film consisted of four consecutively spin-cast layers of sol-gel, giving a 160 nm total film thickness (measured by profilometry). Preliminary spallation tests on thus prepared specimens resulted in unintended failure of the Si substrate rather than at the interface of interest due to a very high adhesion strength between the film and the bare substrate. The specimen geometry was then modified by depositing two additional layers, 25 nm of Ti followed by 250 nm of Pt, on top of the PZT film. The superlayers increase the mass of the film, thus magnifying the developed interface stress (at much lower substrate stress) due to the increased momentum of the film material during spallation tests. The unexposed side of the silicon wafer was then coated with a 400 nm aluminum energy-absorbing layer by an E-Beam Evaporation System (Temescal), followed by depositing a confining water-glass layer of $\sim 6.0 \mu$ m using a spin-coater. The transparent waterglass serves to confine expansion of the absorbing layer upon YAG pulse impact, directing a compressive stress pulse through the substrate thickness. The waterglass layer was previously determined by [19] to produce a stress profile with sufficient decay time to enable higher tensile loading at the film/substrate interface. The final test specimen layer geometries are shown schematically in Fig. 2b.

Next, separate specimens were prepared with PZT sol-gel films fabricated on top of an octadecyltrichlorosilane (ODS) functionalized SiO₂ layer. The base substrate with exposed SiO₂ was functionalized with an ODS monolayer through a soft lithography stamping process. A

featureless polydimethylsiloxane (PDMS) stamp was inked with a 10 mM solution of ODS in hexane (mixture of isomers) and stamped on top of the silicon dioxide surface. The PDMS stamp was held in place for ~ 60 seconds, facilitating the transfer of the ODS monolayer on to the oxidized wafer. Prior to stamping, the substrate was treated in an ozone-creating UV box to remove organics. Upon ODS functionalization of the substrate surface, the specimen was rinsed with hexane and spin-coated with four layers of PZT sol-gel using the same procedure as described earlier. The resulting PZT sol-gel films were measured to have nearly identical nominal thickness of 160 nm. Finally, the aluminum absorbing layer was coated on the unexposed back surface of the silicon wafer, followed by a 6 μm water-glass layer (See, Fig. 2a). Unlike the nonfunctionalized Si/SiO₂ substrate, the ODS functionalized specimens do not require a superlayer for inducing interfacial fracture.

Experimental Procedure

The substrate/film interfaces were loaded using laser induced stress pulses. An infrared, Nd:YAG laser (1064 nm), capable of emitting a variable energy content up to 150 mJ in a span of about 8 ns, was focused onto the absorbing layer at the back surface of the substrate, as shown in Fig. 1. The pulsed laser ablation of Al layer develops a compressive longitudinal stress pulse (with an initial shape similar to that of the incident laser pulse) which propagates towards the film layers. The mode converted tensile wave upon reflection from the free film surface loads the interface between the PZT sol-gel film and the substrate in tensile mode. The laser fluence is gradually increased until the failure is detected at the interface.

Layer Material	Layer thickness (nm)	Density ρ (kg/m ³)	Elastic Modulus E (GPa)	Poisson's ratio ν
Si	325 x 10 ³	2,330	125.1	0.29
Sol-gel	160	4,270	55.0	0.33
Ti	25	4,510	102.7	0.33
Pt	250	21,450	171.0	0.39

Table 1. The layer material properties used in the wave propagation study

Typically, the stress history at thin film interface can be evaluated by continuously observing the free film surface through a Michelson Interferometer and recording the transient displacement of the film [14-27]. However, direct measurements on top of the PZT films could not be performed due to their low reflectivity. Therefore, an experimental/computational methodology described by Kitey *et al.* [27] is adopted for interface stress evaluations. First, calibration tests are conducted by performing laser spallation experiments on SiO₂ exposed Si substrate samples over a range of laser fluences. The backside of Si substrate was prepared with an identical waterglass confinement layer as described earlier in the sample preparation process. *In situ* interferometric measurements are performed for determining substrate stress history corresponding to the chosen laser fluence. Next, using values in Table 1, the PZT film specimen geometry is modeled and analyzed in a one dimensional wave propagation simulation using the substrate stress history as the loading configuration. The maximum tensile stress, determined from the computed interface stress history, is plotted as a function of laser fluence to generate the interface stress calibration curve. The laser spallation experiments are conducted next on PZT film specimens and the critical laser fluence for failure initiation is determined. The PZT film adhesion strength is extracted from the associated calibration curve using the critical laser fluence.

Calibration Methodology

The out-of-plane displacement history in Si/SiO₂ calibration samples during laser spallation tests is determined by employing a Michelson Interferometer. The optical path difference between coherent laser beams reflected from the calibration sample surface and the reference mirror develops interferometric fringes (Fig. 3a). The variation of fringe intensity, $I(t)$, at the point-of-interest is recorded using a high speed photo-detector (EOT 2000N) and 2 GHz LeCroy Oscilloscope. The variation in fringe intensity is given by,

$$I(t) = \frac{I_{\max} + I_{\min}}{2} + \frac{I_{\max} - I_{\min}}{2} \sin 2\pi N(t) , \quad (1)$$

where $N(t)$ represents fringe order with $I_{\max}$ and $I_{\min}$ being the maximum and minimum intensities of the corresponding fringe, respectively. The out-of-plane displacement history, $u(t)$, is evaluated using $N(t)$ from the Doppler shift as[1],

$$u(t) = \frac{\lambda}{2} N(t) , \quad (2)$$

where λ is the wavelength of the probe beam. For the specimens-in-consideration, the substrate pulse rise time is significantly smaller compared to the wave travel time in the SiO₂ layer.

Therefore, the following thin film equation is used to evaluate substrate stress history [22],

$$\sigma_{\text{sub}}(t) = -\frac{1}{2}(\rho C_d)_{\text{sub}} \frac{\partial u}{\partial t} . \quad (3)$$

The density and the dilatational wave speed are represented by, ρ and C_d , respectively, in the above equation.

Representative interferometric measurements at 37.5 mJ/mm^2 laser fluence from the calibration experiment are illustrated in Fig. 3. The fringes recorded during the experiments (Fig. 3a) are analyzed using Eqs. (1) and (2) to plot the out-of-plane displacement history at the Si/SiO₂ free surface (Fig. 3b). The substrate stress evaluated from the displacement history shows a characteristic linear ramp attaining a peak value of 0.8 GPa.

The interface stresses are then assessed by simulating wave propagation in the PZT test specimens using the calibrated substrate stress associated with the various laser fluences as the transient loading profiles. The multilayer stack of substrate and thin films are modeled to be under plane strain conditions with traction free boundaries. Based on a convergence study, a one-dimensional mesh of element size $h/20$, h being the thinnest layer dimension in the stack, is created to model the specimen geometry. Table 1 shows the constituent layer properties used in the simulations. An explicit time integration scheme is adopted with a forward difference time step scheme. The temporal variation of substrate stress is applied at the free surface of the substrate in the modeled geometry and transient analysis is performed using a time step $\Delta t/5$, where Δt is the smallest of the wave travel times in the stacked layers. A representative stress history at the SiO₂/PZT interface in Si/SiO₂/PZT/Ti/Pt sample is illustrated in Fig. 3d where the simulations are performed by applying the substrate stress history, shown in Fig. 3c. Calibration experiments are performed for the laser fluence varying from 30 mJ/mm^2 to 70 mJ/mm^2 and the resultant substrate stress amplitudes are plotted with laser fluence in Fig. 4a. Corresponding calibration data for the maximum stress developed at the SiO₂/PZT and the PZT/ODS interfaces, obtained from the wave propagation study, are plotted in Fig. 4d.

Results

The interface of the PZT sol-gel film on the ODS monolayer coated substrate was found to just begin to fail at a laser fluence of 59.5 mJ/mm^2 . Using a film density of 4.3 g/cm^3 [31], the interface strength was measured to be 54.7 MPa (S.D. 10.9 MPa). Images of the film surface for increasing laser fluence (interface stress) applied beyond the failure initiation threshold are shown in Figure 5a-d. As higher substrate stress was applied, a larger spallation damage area was consistently observed. For the film deposited on the monolayer coated substrate, interface failure appeared as clusters of film flakes.

For the sol-gel film deposited directly on the substrate, film flaking did not occur during interface failure due to the Pt superlayer, Figure 5e-h. To calculate the interfacial strength between the sol-gel film and the substrate, a hybrid experimental-simulation approach was used. In the experimental testing, interfacial failure was observed to begin at a laser fluence of 63 mJ/mm^2 . Due to the inertial effects of the additional Pt/Ti layer atop the sol-gel film, a given laser fluence develops significantly higher interface stress compared to the case when there is no superlayer. From the substrate stress history and direct measurements of the surface displacement, a numerical simulation was used to determine the interfacial strength. Because the interface strength calculated by the simulation was dependent on the elastic properties of the sol-gel film, a range of physically plausible elastic properties for the PZT sol-gel films was used to estimate the interfacial strength. Assuming film properties of a more compliant polymer sol-gel layer, with density $\rho = 4.3 \text{ g/cm}^3$, Poisson's ratio $\nu = 0.33$, and Elastic Modulus $E = 1.0 \text{ GPa}$, the applied laser fluence and displacement measurements translate to an interfacial strength of 480 MPa (S.D. 54 MPa). Using properties for a stiffer sol-gel film with $E = 55 \text{ GPa}$, the interfacial strength changes to 463 MPa (S.D. 95 MPa). Recent estimations of the modulus for "green" (as

deposited) PZT sol-gel films having a similar composition has found that the stiffness appears to be closer to the lower end of this range ($E \sim 5$ GPa) [32].

Discussion

As expected, the measured adhesion strength of PZT sol-gel films deposited onto ODS functionalized substrates was significantly lower than that found for PZT sol-gel deposited directly on a SiO₂ surface. Immediately after spin-casting, the PZT sol-gel solution undergoes gelation, setting up a nanoporous polymer network containing a substantial volume of solvent [33,34]. Repulsive interactions between the hydrophobic exposed surface CH₃ group for the ODS monolayer and the water contained within the PZT sol-gel likely prevents good adhesive bonding during film gelation. Although the interfacial strength for the ODS coated substrates is low (~ 55 MPa), it does remain strong enough to withstand the initial interface loading due to the gelation and evaporation shrinkage-related stresses that develop immediately upon film deposition. This low, but non-negligible level of adhesion has great significance for patterning applications. Alternative self assembled monolayers that offer a higher degree of hydrophobicity than ODS can often prevent a PZT sol-gel layer from even coating the substrate surface, rather "bouncing off" during spin casting.

It should be noted that the interfacial strength values determined within this study do not account for this residual stress level for the "as deposited" PZT films. Previous works on this particular PZT sol-gel solution concentration have estimated this residual biaxial stress state (parallel to the interface) to be fairly low, generally below 60 MPa [31]. However, for the deposition of multiple PZT sol-gel layers or different stock solution variations, the effects of the

residual stress state can be substantial and, in some cases, large enough to induce interfacial failure via spontaneous spallation upon film deposition.

The observed differences in failure features within Figure 4 for the two different film/substrate specimen types is reasonable given that the total film thickness for the superlayer samples is 2-3 times greater than that for the PZT on ODS variation. Additionally, the metal superlayer likely applies a more uniform interfacial loading profile to the PZT/substrate interface and provides greater integrity to the debonded film region, resulting in a single large "intact" section of PZT film that separates rather than a large number of film flakes.

Conclusions

The adhesion strength for PZT sol-gel thin films deposited via spin coating was greatly influenced by surface functionalization. A non-contact laser spallation technique was used to determine the level of adhesion between PZT films and SiO₂ substrates, with and without functionalized ODS. The interfacial strength for PZT sol-gel films on the ODS monolayer surface was found to be ~ 55 MPa, while the adhesion strength between PZT and SiO₂ was significantly higher (in the range of 460-480 MPa).

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Table 1. The layer material properties used in the wave propagation study

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Figure 1. Schematic of laser spallation test, showing the YAG laser pulse focused on the backside of the specimen and the displacement interferometer focused on the film free surface, opposite.

Figure 2. Schematics showing by layer the PZT sol-gel film adhesion specimens prepared on ODS functionalized substrates (**a**), with PZT directly on oxidized silicon wafers (**b**). The high adhesion strength for (**b**) requires use of a Pt/Ti superlayer for added mass and a hybrid method for calculating interfacial strength.

Figure 3. Interferometric measurements on Si/SiO₂ calibration sample and evaluation of interface stress (a) Variation of fringe intensity recorded from photo-diode at 375 mJ/mm² laser fluence, (b) and (c) illustrate corresponding out-of-plane displacement and substrate stress history, respectively, (d) Associated stress history evaluated from the wave propagation analysis at the Si/PZT film interface in Si/PZT/Ti/Pt stack.

Figure 4. (a) The substrate stress amplitude obtained from calibration experiments vs. laser fluence, (b) Peak interfacial tensile stress experienced between PZT sol-gel films and substrate, as a function of applied laser fluence. Error bars correspond to repeatability (S.D.) of stress with laser fluence.

Figure 5. Interfacial damage resulting from laser-induced spallation testing at increasing laser fluence for PZT sol-gel films deposited on ODS functionalized substrates (**a-d**), and directly on silicon dioxide (**e-h**). Note that while specimens shown in **e-h** contain a superlayer of Pt/Ti on top of the PZT film, the PZT/SiO₂ layer is the interface that fails.

Figure 1

Figure 2

(a)

(b)

Figure 3

Figure 4

Figure 5