Thin Solid Films 598 (2016) 230–235

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Adhesion strength of lead zirconate titanate sol-gel thin films

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ARTICLE INFO

Article history:
Received 4 November 2015
Received in revised form 28 November 2015
Accepted 4 December 2015
Available online 8 December 2015

Keywords:
Sol-gel
Thin film adhesion
Laser spallation
PZT
Lead zirconate titanate
Monolayer

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/SiO_2 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/SiO_2 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.

1. 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], although 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 Fig. 1, the most basic version of the laser spallation test pioneered by Vossen and Mittal [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 toward 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

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http://dx.doi.org/10.1016/j.tsf.2015.12.014
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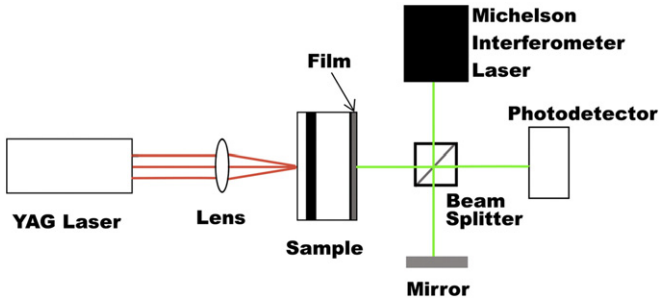

Fig. 1. Schematic of laser spallation test, showing the YAG laser pulse focused on the backside of the specimen and the displacement interferometer focused on the film free surface, opposite.

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 non-linear 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.

2. Materials and sample preparation

Sol-gel films were prepared using a $Pb(Zr_{0.53}Ti_{0.47})O_3$ 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 μm 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 s) directly onto the Si/SiO_2 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 ~6.0 μm using a spin coater. The transparent water glass serves to confine expansion of the absorbing layer upon YAG pulse impact, directing a compressive stress pulse through the substrate thickness. The water-glass 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 SiO_2 layer. The base substrate with exposed SiO_2 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 s, 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 non-fuctionalized Si/SiO_2 substrate, the ODS functionalized specimens do not require a superlayer for inducing interfacial fracture.

3. 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 toward 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

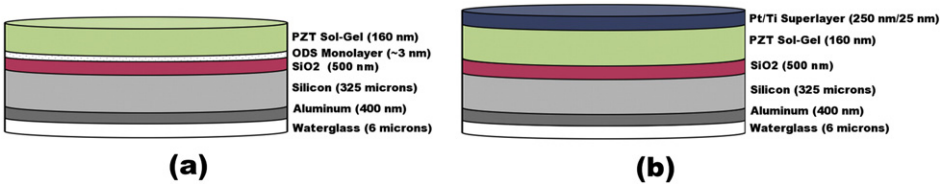

Fig. 2. Schematics showing by layer the PZT sol-gel film adhesion specimens prepared on ODS functionalized substrates (a), with PZT directly on oxidized silicon wafers (b). The high adhesion strength for (b) requires use of a Pt/Ti superlayer for added mass and a hybrid method for calculating interfacial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