CRACK INITIATION IN ULTRA THIN PATTERNED FILMS

Nancy R. Sottos[1], S. Kandula[2], and P.H. Geubelle[2]
[1] Department of Theoretical and Applied Mechanics, University of Illinois, Urbana, IL 61801, USA
[2] Department of Aerospace engineering, University of Illinois, Urbana, IL 61801 USA

ABSTRACT

We present an investigation of the unique cracking problems associated with patterned thin film devices fabricated via soft lithographic methods. Decohesion and fracture of the patterned films is dominated by two key properties: interfacial failure strength and processing induced stresses/shrinkage. We utilize several experimental methods for characterizing these properties and their relationship to cracking in patterned films. Thin film interfacial strength is measured using a laser induced pulsed loading technique. Laser pulse absorption generates a high amplitude, short duration stress waves from the substrate side of the sample, providing a loading force that does not damage or otherwise affect the test film before the failure event occurs. The rapid, high strain-rate loading minimizes inelastic deformation in the films, providing an intrinsic estimate of the interfacial strength. Processing induced residual stress in the films is determined by *in situ* laser reflectance measurements of wafer curvature. A dynamic edge delamination test is underdevelopment to obtain the fracture toughness of the interface. The link to meaningful fracture parameters is achieved with the aid of appropriate analytical and numerical tools to support the experiments.

1 INTRODUCTION

Commercial interest in micro- and nano-electronic, optical, and mechanical devices has created new opportunities and challenges for fabrication of complex, 2-D and 3-D patterned thin film devices. Micro- and nano-fabrication techniques have largely been driven by the needs of the microelectronic industry, and subtractive patterning of thin films using photolithographic processes has long been the industry standard. While subtractive techniques are well suited for creating 2-D features on flat, rigid substrates, many new applications require alternative approaches to patterning that can accommodate integration of functional materials, pattern relatively large areas or be extended to 3-D (*e.g.* for photonics or micro/nanofluidic applications). Conventional photolithographic fabrication methods also require photoresists, developers and other chemicals that are incompatible with materials such as plastics that would otherwise be desirable for some device applications.

The introduction of soft lithographic techniques has provided one promising avenue for fabricating thin film devices to meet the challenging demands of new applications [1-5]. These methods have been used to create complex 2-D and 3-D structures with feature sizes ranging from hundreds of microns to tens of nanometers for a broad set of applications which include plastic (flexible) electronics, optical components, microelectrode arrays, microfluidic devices, and sensors [4-8]. Soft lithography encompasses a group of techniques that use a flexible elastomeric stamp to facilitate pattern transfer. The surface characteristics ("hills and valleys") of a master mold are imprinted into an elastomeric stamp through the curing of a liquid prepolymer (typically PDMS). Soft lithographic techniques can be used with a variety of materials and surface chemistries and circumvent the diffraction limitations of projection photolithography [2].

Of these techniques, micro-contact printing (μ-CP) is perhaps the most widely used. The μ-CP technique, shown schematically in Fig. 1, involves the application of a molecular "ink" to the flexible stamp surface. The stamp is then placed in contact with a substrate to achieve selective transfer of the ink pattern. Microcontact printing differs from other printing methods [9], in that the ink is a self-assembled monolayer (SAM). Self-assembly, a common trait of biological processes, is the spontaneous aggregation and organization of subunits (e.g. molecules) into a stable, well-defined structure via noncovalent interactions. SAMs are organized molecular films

that assemble into dense, continuous layers (Fig. 1c). These ultra-thin films, often less than 2 nm thick, are surprisingly robust both chemically and thermally. The SAMs provide chemical protection of the substrate and serve as either an etch resist (Fig. 1d) or template in selective deposition (Fig. 1e) to control surface reactions. Hence, SAMs take part in both subtractive and additive routes to the patterning of wide range of materials. The resulting patterned films can cover relatively large areas, limited only by the size of the stamps.

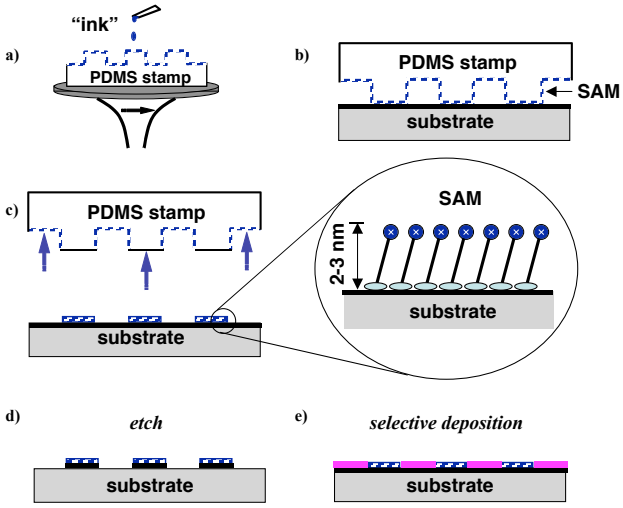

Fig. 1. Schematic of procedures for μ-CP: (a) application of molecular ink to the elastomeric stamp, (b) contact transfer of self-assembled monolayer (SAM) to substrate, (c) substrate with patterned SAM, (d) etching using SAM pattern as a resist, (e) selective deposition using SAM pattern as a template.

The most common defect in the films is cracking, the size and density of which depends strongly on the processing conditions and the surface properties. When the printed film is part of the final device, cracking is highly undesirable. Zaumseil *et al.* [5] reported cracking defects in nanopatterned Au films when the printing process is not carefully controlled. In contrast, controlled cracking on a mediated substrate can be a desirable mechanism for achieving the final pattern [8,10]. Although the mechanics of thin films have been widely investigated [*e.g.* 11-14], the emphasis has been on reliability issues associated with the microelectronic industry and films processed by conventional photolithographic methods. The advent of device fabrication via soft lithography has introduced several new challenges with respect to understanding film cracking.

2. ROLE OF INTERFACIAL ADHESION AND RESIDUAL STRESS

Successful patterning requires either the complete elimination of crack defects or highly controlled cracking to form the desired pattern (Fig. 2). Evans and Hutchinson [12] identified a dimensionless cracking number, l, to understand film fracture and aid in the design of thin film systems. When l is smaller than a critical value l_c, insufficient strain energy is available to cause decohesion. The value of l depends on the biaxial residual stress in the film σ_o , the film thickness h_f, Young's modulus of the film E_f, and the interface fracture energy Γ_i,:

$$\lambda = h_f \sigma_o^2 / E_f \, \Gamma_i \,. \qquad (1)$$

Hence, prediction of patterned film fracture relies on accurate characterization of the interfacial fracture energy and the processing induced stresses. In general, the film stress can be determined by *in situ* laser reflectance measurements of wafer curvature or x-ray diffraction studies (XRD). Measurement of Γ_i, however, presents a more significant challenge, particular for ultra thin films (<100 nm). The total interfacial fracture energy encompasses the intrinsic work of adhesion (the energy required to rupture bonds and create new surface) and any extra work associated with inelastic deformation within the adjoining materials (*e.g.* plastic strains, asperity contact).

Quantitative experimental techniques for measuring interfacial fracture energy of ultra thin films and monolayers are sparse because of the difficulties associated with introducing well-defined interface precracks and applying precise loads. As a result, many researchers working on patterning processes use a qualitative "scotch tape" test to assess adhesion. In this simple test, a piece of tape is applied to the film and then pulled off. Depending on whether the film remains on or lifts off the substrate, the bond is considered either strong or weak. Given the important role of interfacial adhesion in understanding the fracture mechanics of these thin film systems, more precise measurement techniques and sophisticated methods of analysis are warranted.

Many methods for the measurement of thin film adhesion have appeared in the literature, of which the most common are the scratch, peel, pull, blister and indentation tests. All these tests subject the interface to high stress levels that result in significant plastic deformation [13,15]. The stress fields are difficult to analyze and the resulting measurements tend to be qualitative and not well correlated to the fracture energy. Zuk *et al.* [16] used an alternative version of the peel test known as the superlayer delamination test to study the interface fracture energy between micromolded epoxy films and SAMs on Au/Ti/Si substrates. The superlayer test requires fairly complex sample preparation and is limited to films in which the adhesion to the substrate is weaker than to the superlayer. Inelastic dissipation induced in the films during the test makes correlation between the surface chemistry, the work of adhesion and the fracture energy difficult.

3. DETERMINATION OF THIN FILM INTERFACIAL PROPERTIES

In contrast to the adhesion tests described above, laser spallation techniques [17-19] dynamically load the interface in a precise, non-contacting manner using laser-generated stress waves. Because of the rapid loading, inelastic deformations are much smaller than in quasi-static tests. This technique has been used to measure the tensile strength of a wide range of thin film/substrate interfaces [20]. More recently, Wang *et al*. carried out a systematic parametric study of tensile spallation and extended the method to mixed-mode loading of thin film interfaces [21-25].

The basics of stress wave generation in the tensile loading spallation experiment are summarized in Fig. 2. The sample consists of a transparent confining layer, a thin energy-absorbing layer, the substrate and the testing film. An infrared, Nd:YAG pulse (λ=1064 nm) with a variable energy content between 1 and 110 mJ, and a width of about 5 ns is incident on a metallic absorbing layer sandwiched between the confining layer and the substrate. The energy-absorbing layer is chosen to be much thicker (typically ~0.4 μm) than the critical penetration depth of laser light at this wavelength. A compressive longitudinal stress wave with a shape similar to that of the laser pulse is emitted from the absorbing layer. The wave that propagates towards the film-substrate interface is then reflected from the free film surface into a tensile wave, which then loads the testing interface in tension. The laser energy is increased until a longitudinal wave is generated with amplitude sufficient to fail the film/substrate interface. Interferometric measurements of out-of-plane displacement are made at the surface of the testing film. From displacement measurements at the free surface, u, the stress history at the interface is inferred using standard wave mechanics and the maximum stress acting on the interface is calculated. For a small film thickness h_f (smaller than the wave speed times

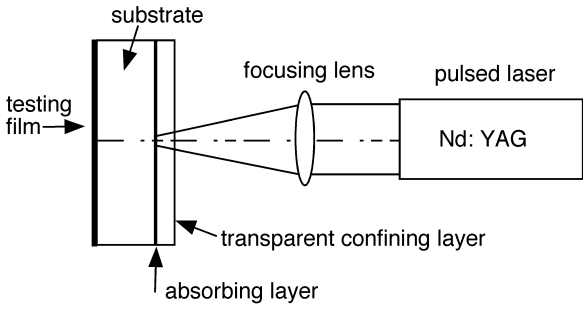

Fig. 2. Schematic of the tensile laser spallation technique.

the rise time of the stress pulse), the laser-induced stress in the substrate, $\sigma_{s,}$ and along the film substrate interface, σ_i are given by

$$\sigma_s = -\frac{1}{2}(\rho c)_s \frac{\partial u}{\partial t} \quad ; \quad \sigma_i = -(\rho h)_f \frac{\partial^2 u}{\partial t^2} \tag{2}$$

where ρ is the density and c is the wave speed [21,22].

Wang et al. investigated the spallation behavior of Al thin films as a function of film thickness, substrate thickness, confining layer thickness, laser energy and various parameters governing the source [21,22]. Two different substrate materials, single crystal Si (100) and fused silica, were studied. For both fused silica and Si substrate samples, the interface stress increased with laser power, film thickness, confining layer thickness, but decreased with substrate thickness due to geometric attenuation caused by the finite size of the YAG beam. One of the most significant achievements of this tensile spallation parametric study was the identification of laser-induced weak shock formation in the fused silica substrate. Due to the nonlinear strain softening of fused silica, a laser-induced Gaussian stress pulse evolved into a shock after traveling a characteristic distance. Shock development was highly beneficial for realizing significant loading at the thin film interface [22,24].

In the current work, the interfacial adhesive strength for patterned film/substrate interfaces are measured using the laser spallation technique. The use of a non-contact, dynamic loading technique provides several key advantages for testing these ultra thin films. Due to the relative fragility of the films, physical or mechanical contact with the surface is impractical. In addition, the stress wave is launched from the substrate side of the sample, providing a loading force that does not damage or otherwise affect the test film before the failure event occurs. Finally, the rapid, high strain-rate loading minimizes inelastic deformation in the films, providing a more intrinsic estimate of the interfacial strength.

Adhesive strength measurements are made on samples in which the monolayer and/or film covers a portion of the substrate larger than the diameter of the focused beam of the pulsed laser (~1 mm). Testing of the larger area films mitigates the effects of edges and corners and facilitate measurement of residual stress in the films. The residual stress for all of the film/substrate combinations are measured by wafer curvature measurement using a scanning laser reflectance system. The system measures deflection of the rigid substrate through repeated 100 point scans of the wafer surface at specified temperature or time intervals.

Interfacial strength is determined by incrementally increasing the laser power and testing different spots on the film surface until failure is initiated at the film interface. In practice, failure is confirmed by optical or scanning electron microscopy after a series of tests are completed. To demonstrate the process for ultra thin patterned films, preliminary tensile strength data was obtained for 50 nm thick PZT sol-gel films on silicon substrates with and without a stamped ODS monolayer. These films were prepared and tested in collaboration with the Payne group at the University of Illinois [26]. Half of the substrate surface was functionalized with a continuous area of ODS and then spin-coated

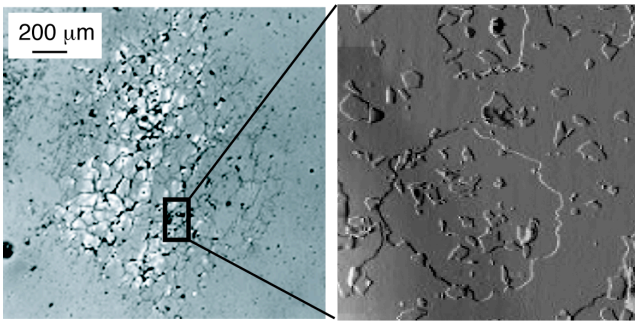

Fig. 3. (a) Optical and (b) AFM deflection images of crack damage for 50 nm thick sol-gel film on an ODS mediated silicon substrate following a tensile spallation test [26].

with an overlying sol-gel film, thereby providing an equivalent sol-gel layer with and without surface mediation. This sample provided two distinct regions for sampling the interface strength: (1) between the sol-gel film and the silicon substrate and (2) between the sol-gel film and the functionalized organic molecular ink (ODS). Using the tensile spallation configuration in Fig. 2, an average interfacial strength of 15 MPa was calculated from interferometric measurements for the sol-gel/ODS mediated Si interface, while the interface strength of the same film on bare Si was greater than 85 MPa. Fig. 3 shows a typical failure of the sol-gel film over the organic ink. Optical microscopy revealed a cracked region in the film with small "specks" dispersed around the test region. Atomic force microscopy confirmed that the specks were fractured pieces of the film. These results demonstrate the ability of the laser-induced pulsed loading technique to quantify interfacial strength for ultra thin films on functionalized substrates.

The ultimate goal of this work is to characterize the interfacial fracture energy (in addition to the interfacial strength) in patterned thin film systems. For this task, a different experimental configuration (Fig. 4) is adopted to initiate interfacial delamination at the edge/corner of patterned film samples. A pulsed laser is used to launch a compressive stress wave in the substrate as described previously for interfacial strength measurements, only in this case the pulse impinges on the edge of the film. The stress concentration associated with the film edge initiates a controlled delamination along the interface at much lower stress levels than required for strength measurement. To support these thin film dynamic failure experiments and extract the fracture energy of the interface, we use a novel combination of finite element and spectral numerical schemes [27-29], which provides an accurate description of the transient stress and displacement in the thin film and especially in the vicinity of the initiating and propagating crack tip.

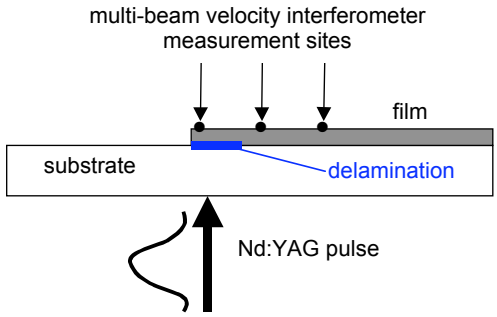

Fig. 4. Experimental configuration to initiate delamination at the edge of a patterned thin film.

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