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Combinatorial approach to the edge delamination test for thin film reliability—adaptability and variability

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Abstract

We have demonstrated the adaptability and variability of a newly developed combinatorial edge delamination test. This was accomplished through studying the effect of substrate surface energy on the adhesion of thin films. In this combinatorial approach, a library (a single specimen) was fabricated with a polymethyl methacrylate (PMMA) film on a silicon substrate. The film has thickness gradient in one direction and the substrate has an orthogonal surface energy gradient. The thickness gradient was produced with a flow coating technique, and the surface energy gradient was controlled by partial oxidation of an alkylsilane layer on a silicon wafer. Applying a constant temperature to the specimen, interfacial debonding events were observed and a distribution of failure was constructed. Our results demonstrate the proposed combinatorial methodology for rapidly and efficiently evaluating the adhesion of general film/substrate systems as a function of many controllable parameters. In addition, this methodology can be used to predict the reliability distributions of the adhesion for practical parameters.

Keywords: Combinatorial methods; Thin film reliability; Adhesion; Surface energy; Contact angle

1. Introduction

Polymers and polymeric composites are used successfully in many applications (e.g., civil infrastructures, aerospace, automotive, electronics, and biomedical engineering). For all of these systems, polymer adhesion plays a major role in an application's success; therefore, the challenge of understanding the mechanisms of adhesion is of primary importance. From previous research, we know that numerous factors such as surface energy, surface roughness, molecular weight of the polymer, curing temperature, time, etc., can affect the adhesion strength. Consequently, it is important for both material designers and manufacturers to quickly evaluate how these factors influence the adhesion and rapidly screen for optimal performance. With this motivation and the concept of combinatorial approach to material science [1], we have developed a combinatorial technique to quickly evaluate critical regions of parameter space. This technique was previously introduced as a combinatorial edge delamination test to map the failure of thin film adhesion to rigid substrates as a function of both temperature and film thickness in a single step [2,3]. As an extension of this work, we demonstrate how this technique can be adapted for various adhesion-controlling parameters such as substrate surface energy. Subsequently, this information is used to predict the reliability distributions of the adhesion for practical parameters such as thickness/temperature combination.

In this work, we investigate the dependence of polymethyl methacrylate (PMMA) film adhesion on the surface energy of a silicon substrate (the adhesion, in this study, corresponds to the fracture toughness or the debonding energy). This material system serves as a model system for our study since its physical and mechanical properties are relatively well characterized.

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Our combinatorial libraries (specimens) consist of PMMA films with film thickness gradients in one direction, and a silicon wafer with a surface energy (or contact angle (θ_c)) gradient orthogonal to the thickness gradient. To evaluate the adhesion of the PMMA/substrate interface within libraries, we subdivide each library into an array of separate edge delamination samples and, then, apply a constant temperature. Subsequently, the adhesion corresponding to each specific contact angle can be deduced from the failure distribution across the library. As we discuss below, the quantitative measurement is dependent upon the characterization of the thermo-mechanical properties (the stress–temperature relation) of the film bonded to the substrate [2]. In addition, the reliability of adhesion (the failure map) between a thin film and a substrate as a function of film thickness and temperature for each specific contact angle can be theoretically constructed. Such reliability information about the interfacial integrity could be practical to product development in addition to fundamental adhesion measurements, especially in electronic applications [4].

2. Combinatorial methodology

In a previously developed combinatorial edge delamination test for thin film adhesion measurement [1], a film with controlled thickness gradient is bonded to a substrate and subdivided into an array of separate edge delamination samples. The specimen is then cooled with a temperature gradient applied in the direction orthogonal to the thickness gradient (Fig. 1a and b). Accordingly, the stress concentration on these edge delamination samples is spatially varied in one experiment. Debonding events will be observed for those samples having critical stresses that depend on the combination of local temperature and film thickness. Consequently, a distribution of failure (failure map, Fig. 1c) as a function of temperature and film thickness can be constructed in one step. An initial test result using a commercial epoxy as the film and a silicon wafer as the substrate demonstrated the success of this approach (Fig. 2).

Instead of the specimen having orthogonal thickness and temperature gradients as in the original method, in the current approach, a thin film with a unidirectional film thickness gradient is deposited on a substrate with an orthogonal surface energy gradient (contact angle gradient). A constant temperature field then is applied to the specimen to evaluate the separate edge delamination samples across the library (the specimen). Due to the thickness gradient, this constant temperature induces a stress concentration gradient at the interface between the film and substrate. Interfacial debonding events are observed for edge delamination samples having the critical combination of local adhesion (varies with surface energy) and local stress (that depends on the local film thickness). By tracing the locus of debonding, a failure distribution as a function of film thickness and surface

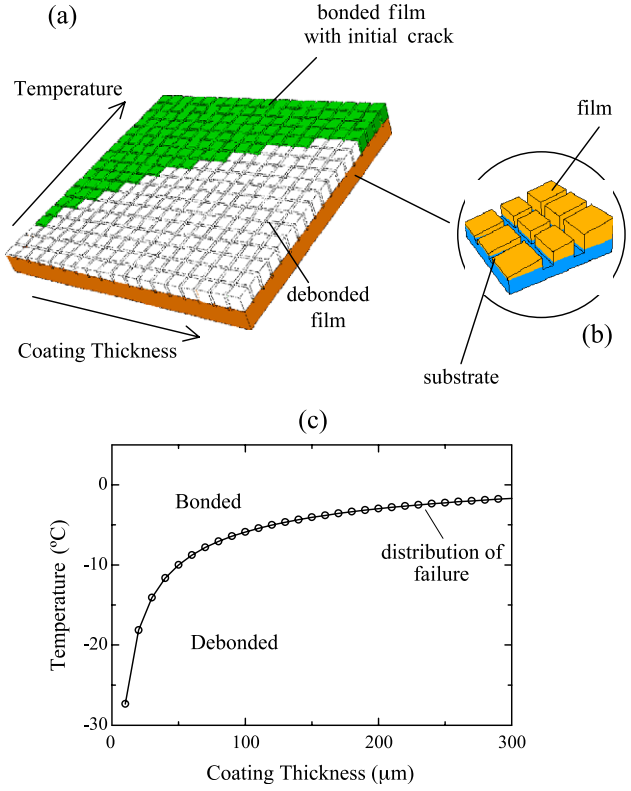

Fig. 1. A schematic of the combinatorial approach to the edge delamination test: the multivariant specimen with film thickness and temperature gradients, and final failure map (a); a square pattern array of individual edge delamination samples on the substrate (b); the distribution of failure (failure map) of a film on a substrate as a function of both temperature and film thickness (c).

energy can be constructed. The surface energy gradient on the substrate was introduced by modifying the contact angle of a self-assembled monolayer (SAM) generated on the substrate [5]. The film thickness gradient was obtained through controlling the speed and blade height of a flow coater [6].

For demonstrating the aforementioned combinatorial approach, we measure the adhesion of PMMA film to an alkylsilane layer on a silicon wafer. In this study, a PMMA (Polysciences, Warrington, PA, USA [7]) thin film is applied to a silicon wafer (Polishing Corporation of American, CA). The molar mass and polydispersity of the PMMA are 100,000 g/mol and 2.26, respectively. A differential scanning calorimeter (DSC) test at a heating rate of 20 °C/min starting from room temperature indicated that the PMMA has a glass transition temperature (T_g) of ca. 105 °C. Critical procedures to the combinatorial library preparation are the substrate cleaning, formation of a self-assembled monolayer and surface energy gradient on the silicon surface, and applying the PMMA film with a thickness gradient orthogonal to the surface energy gradient.

2.1. Substrate cleaning

A polished silicon wafer (100) with a 1- to 2-nm-thick native oxide coating was cut into a rectangle (30 mm×50

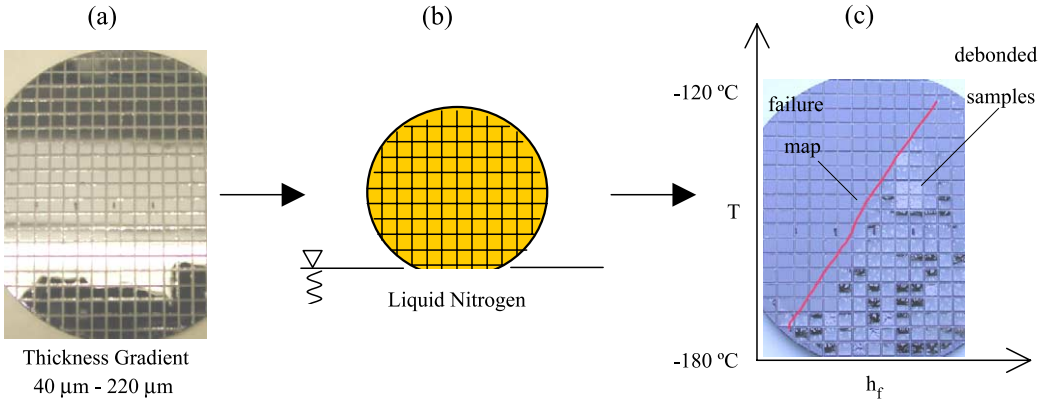

Fig. 2. The initial test result of the combinatorial edge delamination test for the adhesion measurement. The film thickness varied from 40 to 220 μm (a); the contrast in the photograph of the figure is due to the reflected light. One side of the specimen was dipped into the liquid nitrogen for 15 s to form a temperature gradient from −180 to −120 °C (b). Interfacial debonding for those edge delamination samples having critical stresses can be observed by the un-aided eye (c).

mm) and thoroughly cleaned prior to introducing a self-assembly monolayer (SAM) with a surface energy gradient on its surface. The silicone wafer was air-cleaned with nitrogen to remove dust and sequentially ultrasonic-cleaned in acetone, 2-propanol, as well as deionized and ultra-filtered water (with resistance more than 18 MΩ cm^{-1}). The wafer was dried with nitrogen between these ultrasonic-cleaning steps. After the cleaning process, the wafer was placed into a UVO (UV Ozone) cleaner (Model 342 UV Cleaner, Jelight, Irvine, CA) for 15 min to generate a more uniform silicon oxide layer, and rinsed with water and dried with nitrogen. Afterwards, the wafer was etched with buffered HF for 20–30 s to remove the oxide layer and leave an exposed hydrophobic Si–H layer on the surface of the silicon wafer. The wafer was rinsed with water, dried with nitrogen, and placed back into the UVO cleaner for 3 min. At the end, the wafer was washed and dried again before the SAM formation.

2.2. Formation of the SAM and surface energy gradient

Surface modifications on a SAM-covered substrate are possible using photochemical oxidation to obtain a finely tuned or chemically patterned surface [8,9]. In this study, we used reactive alkylsilane and controlled UV exposure density to obtain a SAM with a surface energy gradient on the substrate. As investigated previously, the use of reactive alkylsilane to modify the surface properties of inorganic materials is a widely accepted process [10–14]. In the preparation of the SAM, both a solution method and a vapor method were adopted in this study. In the case of the solution method, a cleaned substrate was submerged into a solution mixture (2.5% in mass fraction), made from 1 g of *n*-octyldimethylchlorosilane (*n*-ODCS, used as received from Gelest, Morrisville, PA) and 39 g of toluene, for 30–40 min. Afterwards, the wafer was rinsed with toluene, and dried with nitrogen before annealing in an oven at 120 °C for more than 1 h. After the annealing step, the coated substrate was washed with toluene and dried again with nitrogen. In the vapor method, the wafer was kept overnight in a vacuum desiccator filled with the silane vapor at room temperature. Then, it was thoroughly rinsed with toluene and dried with nitrogen as usual. Generally, a more uniform layer can be achieved using the vapor method rather than the solution method. A detailed description of the vapor method can be found elsewhere [15–17].

After the SAM formation, the wafer was placed into the UVO with the exposure of the surface limited by a linear optical density gradient filter for 3–5 min for generating a contact angle gradient [18]. Theoretically, the larger the UV dose, the less the surface contact angle (higher the surface energy) will be. In other words, the hydrophobicity of the surface will decrease with the UV exposure intensity. In this study, the resulting contact angle normally ranged continuously from 30° to 80° for a 3-min UVO treatment.

2.3. Coating PMMA and the construction of combinatorial specimen

For applying a PMMA film having a thickness gradient orthogonal to the contact angle gradient of the silicon wafer with a SAM, a flow-coating method [6] using a blade was used. The wafer was fixed onto a robotic stage and the blade edge with an angle of 5° was lowered to ca. 300 μm above the surface. The thickness gradient was obtained through the control of the blade height and the speed at which the blade was drawn over the substrate. In order to get a desired viscosity for the flow coating, a PMMA solution in chloroform (10% mass fraction) was employed. The film thickness was measured after solidification using a UV-Vis reflectance interferometer F20 (Filmetrics, San Diego, CA) with a 0.5-mm-diameter spot size, and corroborated by a Dektak 8 stylus profiler (Veeco, Santa Barbara, CA). Over the range of 10 nm to 100 nm, the thickness measurement using the reflectance agrees with that using the profiler within 4% discrepancy (the standard uncertainty is ±0.05

μm). The wettability of the substrate was evaluated at room temperature by measuring the static contact angle at four to six different positions using a G2 tensiometer (Kruss, Hamburg, Germany) and high purity water as the probe solvent. The standard uncertainty of the contact angle measurement is within $\pm 1^\circ$.

The deposited film was cut, using a fine diamond saw, into a square grid pattern (~4 mm×4 mm) to form an array of about 8×13 (total of 104) individual edge delamination samples of the film on the substrate (Fig. 1b). Each sample provides four independent data points in terms of the adhesion and local stress due to the orthogonal film thickness and contact angle gradients. The cut penetrates some distance (≈ 20 μm) into the substrate and forms 90° edges at the film/substrate interface. The depth and width of the cut are design parameters that need to be optimized and were based on previous studies [2]. Due to the existence of residual biaxial stresses during the solidification of the PMMA film and the stress-free edges after cutting in a bimaterial system (PMMA/silicon), stress concentrations arise at the interface near the free edges. These stress concentrations are sufficient to create small initial interfacial flaws (cracks) at the film/substrate boundary. These initial cracks are by-products of the cutting process such that, unlike conventional fracture experiments, artificial pre-cracks are not needed at the interface for the fracture test. Coupled with an interface having finite adhesion, these initial cracks are the nucleation sites for interfacial debonding after a further loading. The stress state at the crack tip in each individual square sample would be independent of the interfacial crack length, since the length is much smaller than the film thickness [2]. To introduce the further loading, the specimen was quenched into a liquid nitrogen cell for at least 5 s to reach an equilibrium temperature at 77K (−196°). Afterwards, interfacial debonding events were visible with unaided eye for those samples having the critical relationship of stress and contact angle. It is worthwhile to note that the exposed hydrophobic Si–H layer on the surface of a silicon wafer can form covalent bonds with the SAM of *n*-ODCS alkylsilane. While PMMA and SAM form physical bonds that depend on the contact angle; these bonds are much weaker than the covalent bonds. Thus, the interfacial debondings are expected to happen at the PMMA/SAM interface rather than at the silicon/SAM interface.

3. Results and discussion

Fig. 3a shows the variation of the film thickness (h_f) along the *X*-axis of the specimen for the combinatorial edge delamination test, while Fig. 3b displays the variation of the contact angle (θ_c) along the *Y*-axis of the specimen. The film thickness ranges from 3.7 to 9.1 μm over a 30-mm distance, and θ_c ranges from 23° to 68° over a 50-mm distance. Within experimental uncertainties, the results in the figure indicate that both the orthogonal thickness and contact angle gradients have a linear variation within the specimen. After cooling, the specimen having 104 individual edge delamination samples, debonding events were observed for those samples having the critical relationship of stress and adhesion as shown in Fig. 4a. By tracing the locus of far-field debonding, a failure map as a function of film thickness and contact angle was constructed. Fig. 4b gives the quantitative information of the critical relationship between the h_f and θ_c.

During the debonding of a film from a relatively rigid substrate, the contribution to the energy release due to the substrate can be neglected. Moreover, the stress intensity in opening mode (K_I), which is assumed to drive the

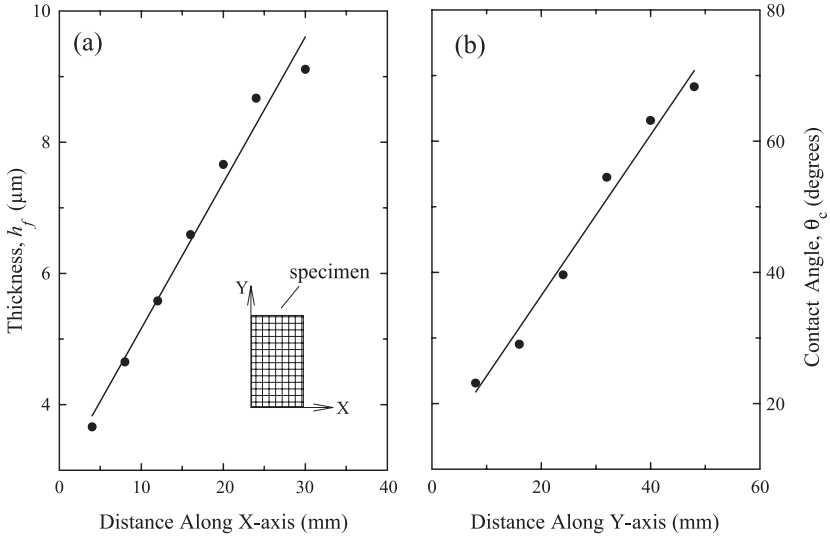

Fig. 3. Variation of the film thickness along the *X*-axis of the combinatorial edge delamination specimen (a); variation of the contact angle along the *Y*-axis (b). The solid lines are the curve-fittings to the experimental measurement (symbols).

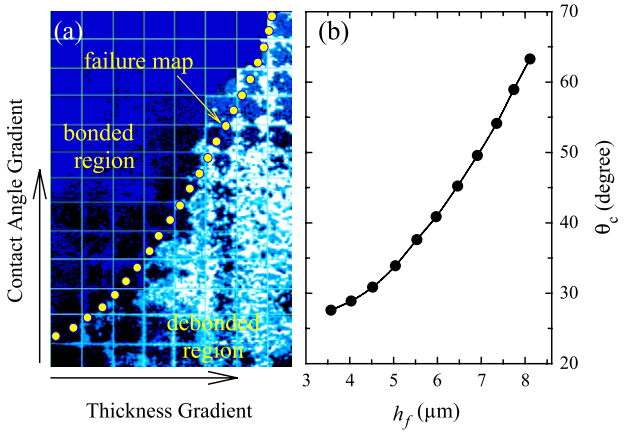

Fig. 4. Debonding events in a typical combinatorial edge delamination specimen having PMMA film bonded to the silicon substrate (a); the variation of contact angle with the film thickness along the failure map (b).

debonding during the cooling, can be expressed in the following form [19]:

$$K_I = \sigma_o \sqrt{\frac{h_f}{2}} \quad (1)$$

where σ_o is the internal biaxial stress that depends on the mismatch of the coefficients of thermal expansion and temperature. Since a constant temperature was applied to the specimen, the K_I can be normalized by a constant σ_o. Combining Eq. (1) and the critical relationship between the h_f and θ_c of Fig. 4b, one can build the relationship between the normalized fracture toughness (K_{IC}, i.e., the stress intensity at a critical condition) and contact angle as shown in Fig. 5a. In this case, the magnitude of K_{IC}/σ_o decreases linearly from 2.02 $\mu m^{1/2}$ to 1.33 $\mu m^{1/2}$ while θ_c increases from 28° to 63° (i.e., the increase of the hydrophobicity of the surface underneath the PMMA film). This result implies that debonding would develop more quickly with the increasing surface hydrophobicity. Furthermore, this result is consistent with extensive literature results showing that the adhesion is directly proportional to the work of adhesion, which is a direct function of contact angle [20]. Similar observations, presented in a study of Pfau et al. [21], also indicate that the hydrophilic PMMA tends to adhere more strongly to the surface with smaller contact angles.

One can quantitatively determine the K_{IC} as a function of θ_c if σ_o is determined from a separate experiment. Fig. 5b displays the stress–temperature relationship of a PMMA film bonded to the silicon substrate; σ_o is calculated through Stoney's formula [22,23] based on in situ curvature (R) measurements of a bimaterial circular plate (built up of the film and substrate, the inset of Fig. 5b) due to a change in temperature (T). Also, shown in the figure, a linear relationship for the temperatures range from 298 (25 °C) to 353 K (80 °C) can be assumed as:

$$\sigma_o = c_1 + c_2 T \quad (2)$$

where c_1 and c_2 are constants of 18.97 MPa and −0.24 MPa/°C, respectively. By extrapolating the results from Eq. (2), one can obtain the σ_o of the PMMA film at 77 K (σ_o=66 MPa). Subsequently, the quantitative information of K_{IC} should be obtained as a function of the contact angle (for example, K_{IC}=0.13 MPa $m^{1/2}$ for θ_c=28°). It can be noted from the Fig. 6b that stress diminishes when the temperature approaches 80 °C due to the rubbery state of the PMMA film at the temperatures close to its T_g (≈105 °C). The difference in stress between the heating and cooling processes near the rubbery state can be attributed to energy losses (hysteresis effect) during the thermal cycling and does not affect our extrapolation of σ_o at low temperatures.

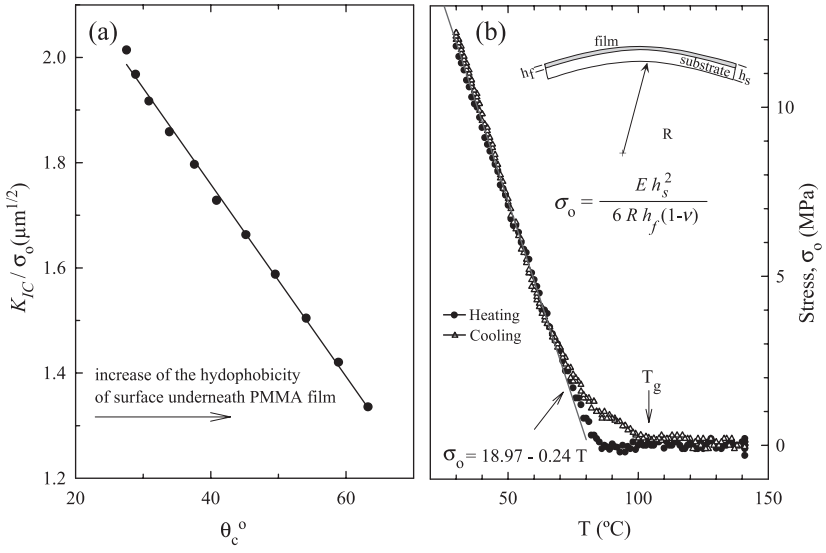

Fig. 5. Variation of the normalized fracture toughness as a function of contact angle (a); the thermal stress–temperature relationship of PMMA film bonded to the silicon substrate during the thermal cycling. The solid line is a curve fitting to the average stress values of cooling and heating at the temperature range from 25 to 70 °C. The inset is the Stoney's formula for the stress calculation based on the curvature (R) measurement. h_s and h_f are the thickness of the substrate and the film, respectively. E and ν are the elastic modulus and Poisson's ratio of the substrate, respectively.

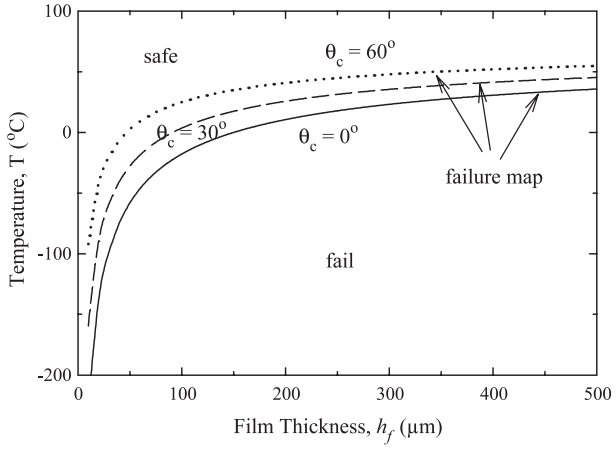

Fig. 6. Failure maps constructed as a function of temperature and film thickness for PMMA film bonded to silane-treated silicon substrate with different contact angles; the K_{IC}=164, 128, and 92 MPa-mm$^{1/2}$ for θ_c=0°, 30°, and 60°, respectively.

In the experiment, surface cracking on the film was not observed after the specimen (film/substrate) was quenched in a liquid nitrogen cell. This is expected, as the value of the biaxial stress (σ_o) induced in the PMMA film at 77 K (66 MPa) is lower than its tensile strength (85 MPa) reported in the literature [24]. In addition, surface analyses on the substrate of debonded samples (shown in Figs. 2 and 4) indicate interfacial debonding occurred between the PMMA film and the silicon substrate, rather than cohesive failure of the film. Using σ_o at 77 K and the data in Fig. 5a, K_{IC} ranges from 0.13 to 0.09 MPa m$^{1/2}$ for the contact angles from 28° to 63°. These values are much smaller than the fracture toughness of the PMMA film (1.6 MPa m$^{1/2}$) reported in the literature [24], thereby confirming our findings on the interfacial debonding process.

By combining Eqs. (1) and (2) of a critical situation, one can construct the adhesion reliability (failure map) as a function of film thickness and temperature from the following equation:

$$K_{IC} = (c_1 + c_2 T)\sqrt{\frac{h_f}{2}} \tag{3}$$

Fig. 6 presents failure maps created using Eq. (3) for the corresponding K_{IC} of each specific contact angle. These determined failure maps, based on the combinatorial measurements of fracture toughness, can be used by customers and manufacturers to quickly screen candidate materials to meet adhesion requirement as a function of practical parameters (temperature and film thickness). The results in Fig. 6 assume that the debonding of film from substrate is an interfacial (adhesive) failure. However, in some cases, the bond strength can be limited by the cohesive strength of the film and the failure maps should be modified accordingly. Moreover, although the mixture of the opening and shearing modes can exist at the interface, the analytical procedures should follow the same steps as proposed for the opening mode failure.

If the mechanical and physical properties of a film and a substrate are given, the stress–temperature relationship of a thin film coated on a relatively rigid substrate can be established using the following equation:

$$\sigma_o = \bar{E}_f(\alpha_s - \alpha_f)(T - T_{ref}) \tag{4}$$

where $\bar{E}_f$=((E_f)/(1−ν_f)) The subscript f represents the film and s represents the substrate. E and α are the elastic modulus and coefficients of thermal expansion, respectively. T_{ref} is the reference temperature at which the film/substrate system is in a stress-free state, and it can be reasonably chosen as the T_g of the film. For the PMMA film, E_f=3.3 GPa, ν_f=0.3, α_f=63×10^{-6}/K, where α_s=3.2×10^{-6}/K for the silicon substrate [24]. By setting T_{ref} equal to 378 K (the T_g of the film), the calculated σ_o at 77 K is 85 MPa. This magnitude is higher than that of the measurement simply because of the assumption on T_{ref} and independence of E_f and α_f in Eq. (4) on the thermal history. While this equation is not complete, it does provide a quick estimation of the stress.

4. Conclusions

Experiments based on a combinatorial approach to the edge delamination test of a film/substrate system have been carried out to demonstrate the feasibility and adaptability of the approach for the adhesion measurement with different variables. By combining the variation of a material parameter (contact angle) and a practical parameter (film thickness) that are important and readily controllable, the effect of the material parameter on the adhesion can be mapped in one experiment. In this implementation, the film thickness parameter provides control of the stress in the film. Therefore, once the stress–temperature relationship of the film/substrate system is known, this map can be used to predict the adhesion reliability as a function of both film thickness and temperature (that are practical in product developments) in a single step for each variation of the material parameter. Moreover, this approach can be used to determine the adhesion of the thin film in the submicron range and is expected to provide accurate results because of its larger sampling space. By combining this study with our previous study on the combinatorial edge delamination test, conceptually, we have completed a framework of the combinatorial metrology. This framework includes the concept, experimental protocol design, simulation of the method, experiment, as well as a study of the adaptability and variability of the methodology—a complete story.

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