COMBINATORIAL EDGE DELAMINATION TEST FOR THIN FILM ADHESION --- CONCEPT, PROCEDURE, RESULTS

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ABSTRACT

A high-throughput combinatorial approach to edge delamination test is proposed to map the failure of adhesion as a function of both temperature and film thickness in a single step. In this approach, a single specimen of a thin film bonded to a substrate with orthogonal thickness and temperature gradients is subdivided into separate samples. This approach can be adopted to measure the adhesion for films with thickness in the sub-micron range by the addition of an overlayer. Requirements for valid testing results from a mechanistic viewpoint are analyzed using three-dimensional computational fracture mechanics. An initial test result is presented to demonstrate the feasibility of the approach.

Keywords: Combinatorial approach, adhesion, interfacial debonding, thin film, edge delamination, fracture mechanics, finite element

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INTRODUCTION

The objective of this study is to develop a combinatorial (or multivariant) approach based on edge delamination to investigate the adhesion between a thin film and a substrate. This technique is expected to provide information about the interface integrity and is not a substitute for a fundamental adhesion measurement (in this study, the adhesion means the debonding energy or the fracture toughness) [1-3]. More importantly, the proposed combinatorial approach can also be extended to measure the adhesion for films with thickness in the sub-micron range, where the measurement of the adhesion for such thin films is very difficult. The application of a combinatorial approach, which originally aimed at speeding synthesis and screening of large composition libraries for drugs and functional materials, has enabled researchers to quickly evaluate how variables influence chemical and physical properties of materials and rapidly screen for optimal material properties [4-7]. In this study, a three-dimensional finite element analysis was developed to evaluate the feasibility of the combinatorial approach outlined below.

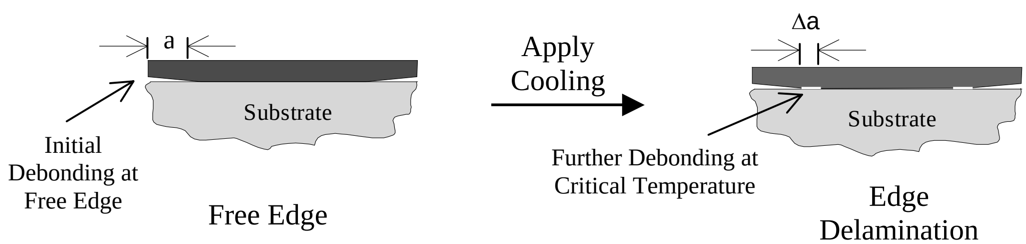

Fig. 1 A schematic of the free edge effect and edge-delamination test.

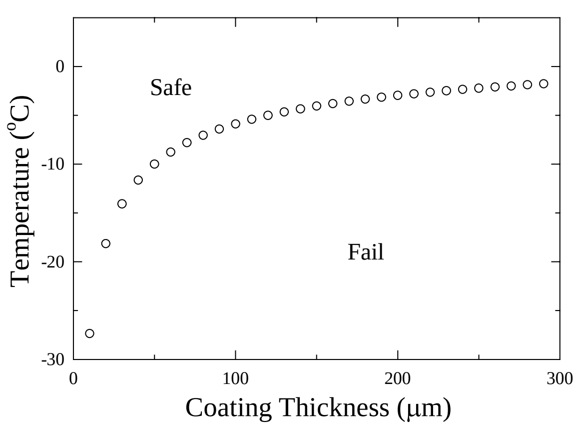

Fig. 2 A schematic of the failure map of a film on a substrate as a function of temperature and coat thickness.

During the cooling of a bi-material film/substrate system with an initial interfacial crack at a stress-free edge (Fig. 1), a further crack extension (debonding) along the interface will occur at a critical temperature due to the stress concentration near the crack tip. The edge delamination test is based on this debonding mechanism using the thermal stress generated during the cooling to cause separation of the film from the substrate. Accordingly, the adhesion (or adhesive strength) between the film coating and the substrate can be deduced (e.g., [8]). By repeating the test for numerous samples with different film thicknesses, a failure map as a function of temperature and film thickness can be constructed [9]. This failure map provides a tool to assess the reliability limit of the coating as a function of multiple independent variables. For industry, to construct a comparable failure map to screen numerous new formulations and specialty materials is time-consuming. In this study, we propose to combine the important variables (temperature and thickness) in a single experiment to map the interfacial failure of the film. Subsequently, the value of the adhesion of the film to substrate can be deduced from the failure map if the internal stress-temperature relationship of the film is known. Essential details in the test design and requirements for valid testing results will be described in the next section of the paper. Numerical results and discussion, as well as an initial test result will be presented in the following sections, and some conclusions will be drawn based on the results. For more information on the combinatorial delamination test and experimental procedure, readers may refer to our forthcoming publications [7,10,11].

COMBINATORIAL EDGE DELAMINATION TEST

In the proposed experiment, a film is coated onto a relatively rigid substrate in such a way that the film has a thickness gradient in one direction (Fig. 3a). The film is scribed in a form of a square grid pattern to form an array of individual edge delamination samples on the substrate (Fig. 3b). The cut penetrates some distance into the substrate also. The edges are at 90^{o} to the interface of the film/substrate. The depth (d) and width (w) of the cut are the design parameters that need to be optimized and will be discussed later (Fig. 3c). Due to the existence of residual biaxial stresses during the solidification of the film and the stress-free edges after dicing in a bi-material system, stress concentrations arise at the interface near the free edges. These stress concentrations are sufficient to create small initial interfacial flaws at the film/substrate boundary. This is the well-known free-edge effect that is unique to bi-material systems [12-15]. Coupled with an interface having finite adhesion strength, these initial flaws are the nucleation sites for interfacial debonding after a further loading. To introduce the further loading, the specimen is cooled with a temperature gradient applied in the direction orthogonal to the thickness gradient (Fig. 3a). Interfacial debonding events will be observed for those samples having critical stresses that depend on the combination of local temperature and film thickness. Consequently, a failure map as a function of temperature and film thickness can be constructed with one step, as shown in Fig. 3a. In principle, if the adhesion of a film to a substrate is independent of temperature, the adhesion

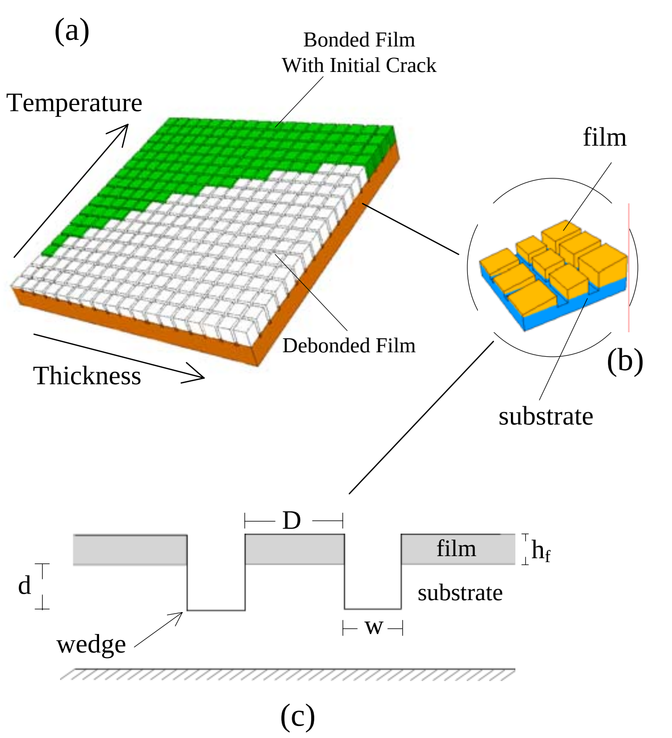

Fig. 3 A schematic of the combinatorial approach to the edge delamination test: the multivariant specimen with film thickness and temperature gradients, and final failure map (a); a square pattern array of individual edge delamination samples on the substrate (b); the cutting depth, d, and width, w (c).

can be deduced from this failure map as long as the thermo-mechanical property (the stress-temperature relation) of the test film is well characterized [9,16]. Sometimes, especially for large film thickness, the residual stresses (or internal energy) resulting from the solidification of the test film on a substrate (the film preparation step) could be large enough to cause premature failure of the film or interface before further cooling in the edge delamination test [9]. Conversely, it could be the case that a film has such a strong bond with the substrate that the stress concentration generated during the cooling process is insufficient to induce debonding. In either case, by adjusting the film thickness and the upper and lower limits of temperature, one can ensure that the debonding condition will be met.

To measure the adhesion for films with thickness in sub-micron region, instead of coating a test film with a thickness gradient (Fig. 3a), a test film with a very small constant thickness is coated onto the substrate. Then, an overcoating layer (stress-generating layer) with a thickness gradient is deposited on the top of the thin test film (Fig. 4). The rest of the experimental procedures are identical with the original one. The thickness of the overcoating layer needs to be much larger than that of the test film such that the debonding energy contributed from the test film during the thermal cooling can be neglected, and only the overcoating layer serves as the stress-generating layer. One assumption in this modified approach is that the bonding strength between the test thin film and the overcoating layer is much higher than the bond between the test film and substrate. In this case, the stress-temperature relation of overcoating is only needed to calculate the adhesion. Consequently, one may use this modified combinatorial approach to obtain the critical bond energy for the thin film in the sub-micron range. It is worthwhile to note that once a well-characterized overcoating layer has been chosen, it can be used as a standard overcoating layer for different test films as long as good adhesion exists between the overcoating and the test film.

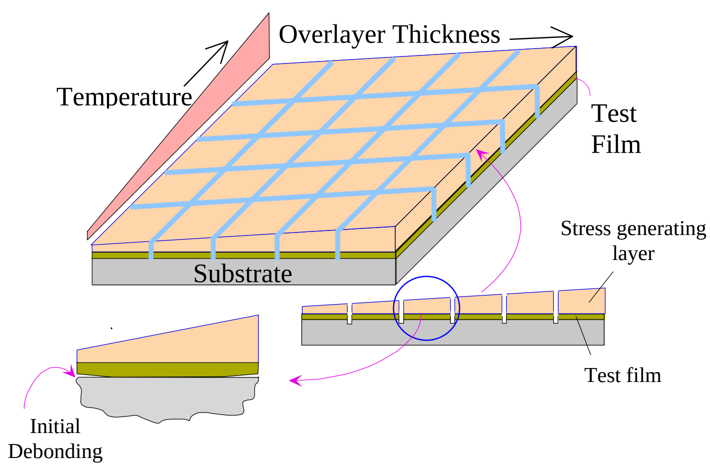

Fig. 4 A schematic of the combinatorial approach to the modified edge delamination test: the multivariant specimen with constant film thickness, overcoating layer thickness and temperature gradients.

For the test results to be valid in this combinatorial edge delamination test, the stress state at the crack tip in each individual square sample must be independent of interfacial crack length. This requirement arises because the initial interfacial crack length in each sample cannot be well controlled. A second condition for validity of the test is that there must be no stress interaction among the separate edge delamination samples within one combinatorial specimen. Thus, two issues that must be determined to ensure valid test results are: the minimum initial crack length such that the stress states are independent of crack length (Fig. 1a), and the required cutting depth and width (“d” and “w” in Fig. 3c) so that the stress interaction among separate edge delamination samples is negligible. A three-dimensional stress analysis (finite element method) and computational fracture mechanics were used to provide answers to these two important questions.

RESULTS AND DISCUSSION

The commercial finite element program, Abaqus[1] [17], was used to calculate the stress distribution in an edge delamination sample. A fully three-dimensional model of the combinatorial edge delamination specimen was constructed for the finite element analyses (FEA). For clarity, some of the FEA results and schematics are presented as two-dimensional configurations in this paper (e.g., Fig. 1). The film and substrate were assumed to be linearly elastic. The ratio of the film stiffness to the substrate stiffness was assumed to be 1/100 to reflect the relative rigidity of the substrate. This ratio also represents a typical organic overcoating on silicon substrate. The Poisson's ratios of the film and the substrate were assumed to be the same. The ratio of the coefficient of thermal expansion (CTE) of the film to the substrate was assumed to be 10. An initial crack was introduced along film/substrate interfaces to mimic the initial flaws; the length of this initial crack was varied to determine the region where the crack-tip stress is independent of crack length. The adhesion between the film and the substrate is assumed to be temperature independent.

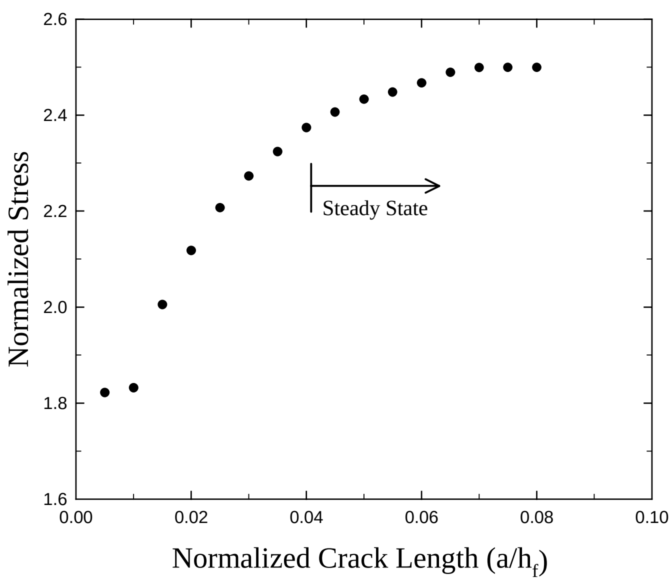

Fig. 5 The variation of the stress normal to the interface at the crack tip with the initial crack length. The stress is normalized by the applied stress.

Fig. 5 shows the variation of the stress normal to the interface at the corner of the sample as a function of the initial crack length. This normal stress is the driving force for interfacial debonding. The corner is where two interfacial cracks meet in the edge delamination sample, so the stress concentration is somewhat higher, and the cracks tend to propagate from the corner inward. The results in the figure indicate that the stress at the corner achieves nearly a steady state if the crack length is larger than 4 % of the film thickness. Thus, once the initial crack lengths of the individual edge delamination samples in the proposed combinatorial specimen are more than 4 % of the film thickness, the stress states would be only a function of temperature and film thickness. This requirement is not a significant barrier for using the proposed combinatorial approach since the initial debonding caused by the free-edge effect

[1] Certain commercial computer code is identified in this paper in order to specify adequately the analysis procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology (NIST) nor does it imply that they are necessarily the best available for the purpose.

after dicing is typically longer than 4 % of the film thickness. Chemical etching could also be used to obtain a suitable initial crack length if necessary.

Once the dicing penetrates into the substrate to form the array of individual edge delamination samples, it would create a wedge near 90^o as shown in Fig. 3c. This wedge will induce a stress concentration during the thermal cooling process due to the existence of a geometric discontinuity. The stress concentration could interfere with the stress state at the film/substrate interface. Also, the stress concentration at different wedges can interact with one another if the cutting width (Fig. 3c) is not large enough. This interaction could also translate into the interface and compound the stress states at the interface. Therefore, in order to make the stress-state at the interface in each sample independent, the geometry parameters (w and d in Fig. 3c) have to be optimized.

Fig. 6 shows the variation of the normal stress (σ) at the corner with cutting width (w) as a function of cutting depth (d). The results clearly demonstrate that when the cutting depth is greater than or equal to 50 % of the film thickness, the normal stress at the corner is independent of cutting width. Experimentally, one would like to have the cutting width as small as possible in order to accumulate many samples on a single combinatorial specimen. Therefore, the results suggest that the cutting depth is a critical geometric parameter, which should be greater than half of the film thickness. In the figure, the deviation of the normal stress from a steady state (for d/h_f = 0.1 or 0.3) implies that there is some influence on the stress state at the interface when the adjacent samples are close together. The difference in the magnitude of the steady-state stress is evidence of the effect of the stress concentration from the cutting wedge on the interfacial stress state.

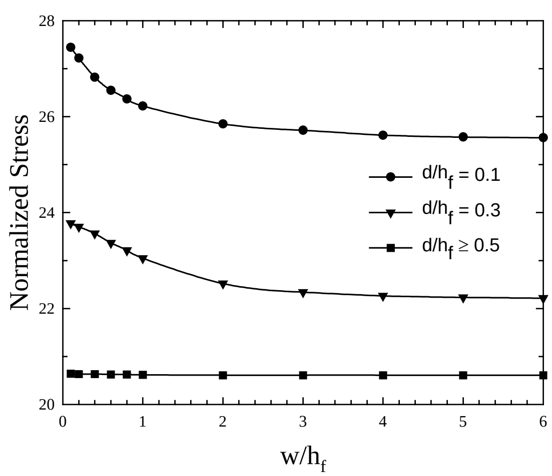

Fig. 6 The variation of the normal stress at the corner with the cutting width (w) as a function of the cutting depth (d).

Based on these results for the geometric requirements, we prepared a combinatorial specimen using silicon as the substrate, PMMA as the test film and commercial epoxy as the overcoating layer. The test film thickness was 10 nm. The overcoating layer thickness varied from 40 μm to 220 μm (Fig. 7 (a), the standard uncertainty is 5 μm). The contrast in the photograph of the figure is due to the reflected light. Next, one side of the specimen, was dipped into the liquid nitrogen (Fig. 7(b)) for 15 min to form a temperature gradient from -

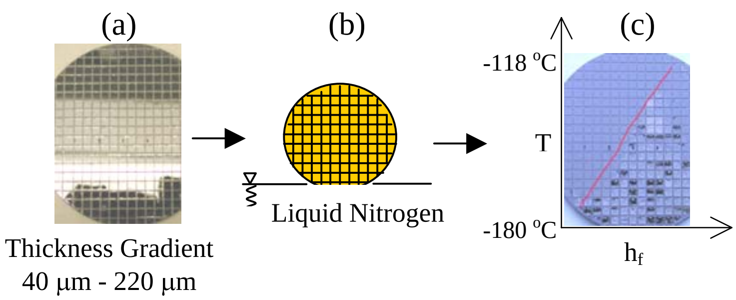

Fig. 7 The initial test result of the combinatorial edge delamination test for PMMA adhesion to silicon substrate.

180 ^{o}C to -120 ^{o}C (the standard uncertainty is 2 ^{o}C). Finally, interfacial debonding for those edge delamination samples having critical stresses can be observed by eye (Fig. 7(c)).

CONCLUSIONS

A three-dimensional finite element modeling with fracture mechanics has been carried out to demonstrate the feasibility and design the experimental protocol for the combinatorial edge delamination test for thin film adhesion measurement. By combining variables that are important and readily controllable in practice (temperature and film thickness), the effect of stress concentration on the debonding of the film from the substrate is spatially varied in one experiment. Consequently, the failure map of the adhesion as a function of both film thickness and temperature can be constructed in a single step. This map of adhesion reliability can be used to determine the critical bond energy of the thin film in sub-micron thickness range. The approach is expected to provide accurate results because of its larger sampling space. Necessary geometry parameters affecting debonding at the film/substrate interface are defined, and the validity of this combinatorial approach is successfully demonstrated in this study. An initial test result indicates this approach is very promising.

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