Multivariant Measurement for Thin Film Adhesion as a Function of Temperature and Thin Film Thickness

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ABSTRACT

The next generation of electronic components will require new low-k dielectrics or other novel thin films in the sub-micron level to be integrated into their construction. In developing these new materials, it is important to assess the adhesion reliability between film and substrate in a fast, practical and reproducible fashion. This study is to develop a high-throughput multivariant (combinatorial) approach to the edge delamination test to map the interfacial failure of the film as a function of both temperature and film thickness in a single step to provide the information of adhesion reliability. A simulation result and an initial experimental observation are presented to demonstrate the feasibility of the approach. This approach provides a vehicle for combinatorial assessment of adhesion that can speed the pace of material innovations.

INTRODUCTION

The application of a multivariant (combinatorial) approach, which originally aimed at speeding synthesis and screening of large composition libraries for drugs and functional materials, has also enabled researchers to quickly evaluate how variables influence chemical and physical properties of materials and rapidly screen for optimal material properties [e.g., 1-3]. In this study, a simulation combining fracture mechanics and three-dimensional finite element analyses was developed to evaluate the feasibility of the combinatorial approach outlined below.

During the cooling of a bi-layered material (film/substrate) system with an initial interfacial crack at a stress-free edge, a further crack extension (debonding) along the interface occurs at a critical temperature due to the stress concentration near the crack tip (Fig. 1). The edge delamination test is based on this debonding mechanism using the thermal stresses generated by the mismatch of the coefficients of thermal expansion during the cooling to cause separation of the film from the substrate. By repeating the test for numerous samples of different film thicknesses, a failure map (Fig.2) as a function of temperature and film thickness can be constructed. This failure map provides a tool to assess the reliability limit of the coating as a function
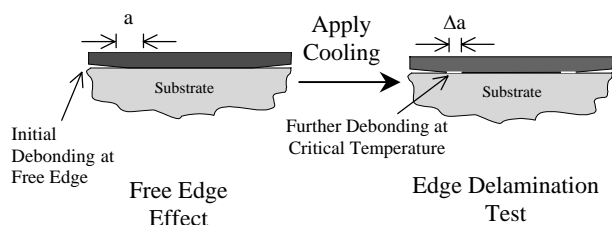

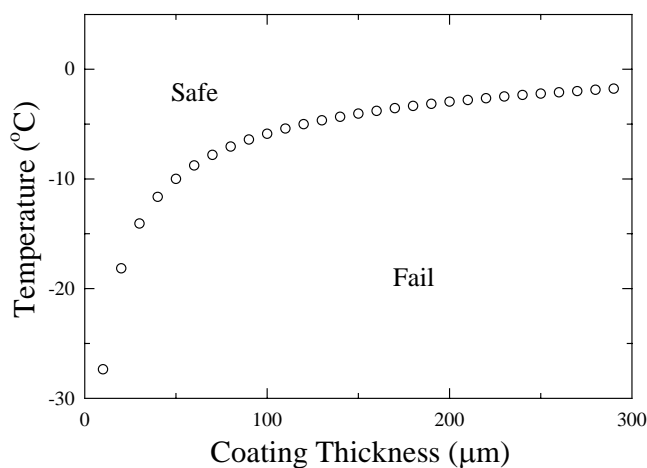Fig. 1 A two-dimensional schematic of the free edge effect and edge-delamination test.

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

of multiple independent variables. For industry, to construct a comparable failure map to screen numerous new formulations and specialty materials is time-consuming. We propose to combine the important variables (temperature and thickness) in a single experiment to map the interfacial failure of the film.

A simulation, based on a three-dimensional finite element modeling and fracture mechanics, has been carried out to demonstrate feasibility and design the experimental protocol for the combinatorial edge delamination test for thin film adhesion measurement. A preliminary test result from using polymethyl methacrylate (PMMA) as the test film and commercial epoxy as the overcoating indicates this approach is very promising. For detailed information with respect to the concept of the combinatorial delamination test and experimental procedures, readers may refer to our forthcoming publications [4,5].

COMBINATORIAL EDGE DELAMINATION TEST

In the proposed combinatorial approach, 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 top of the thin test film. The bi-layer film is cut into a square grid pattern to form an array of individual edge delamination samples on the substrate (Fig. 3). The cut penetrates some distance into the substrate as well. The edges are at 90° to the interface of the film/substrate. Due to the existence of residual biaxial stresses during the solidification of the film and the stress-free edges after cutting 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   [6-9]. 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. 3). 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. 2. This map of reliability can be used to determine the critical bond energy of the thin film in the sub-micron thickness range. The approach is expected to provide accurate results because of its larger sampling space.

One assumption in this combinatorial approach is that the bonding strength between the test film and the overcoating layer is much higher than the bond between the test film and substrate. Also, 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. Consequently, one may use this approach to obtain the adhesion for the thin film in the sub-micron range if the internal stress-temperature relation of the overcoating layer is known. (In this study, the adhesion means the debonding energy or the fracture toughness). 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 a good adhesion exists between the overcoating and the test film.
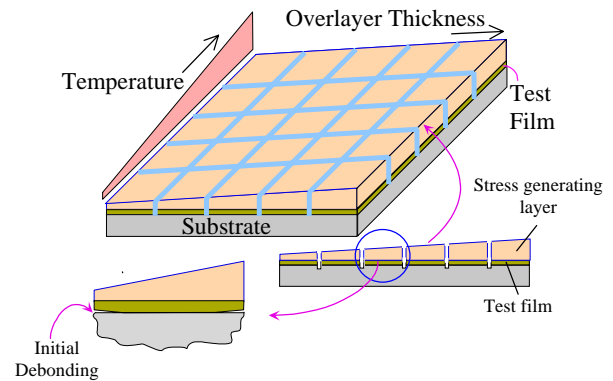

Fig. 3 A schematic of the combinatorial approach to the modified edge lift-off test: the multivariant specimen with constant film thickness, overcoating layer thickness and temperature gradients.

RESULTS AND DISCUSSION

A three-dimensional model of the combinatorial edge delamination specimen was constructed using a commercial code, Abaqus[1] [10], for simulating the proposed combinatorial approach. 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

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[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.

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 adhesion between the film and the substrate is assumed to be temperature independent. A simulation of the interfacial debonding of a combinatorial specimen having 6x6 individual edge delamination samples was carried out, as shown in Fig. 4. The film thickness varied from 20 μm to 200 μm. The temperature gradient was from -40 $^{\circ}$C to -100 $^{\circ}$C. The cutting depth was 100 μm and the cut width was 30 μm. For illustration purposes, the normal stress contours at the interface of the film/substrate are displayed in the figure (the specimen has been flipped over). The gradient of the film thickness is in x_1 direction. The applied temperature gradient is in x_2 direction. Each edge delamination sample provides four independent data points at the four corners, mapping the interfacial failure as a function of temperature and thickness. The darker color at the corner of each sample indicates the stress state at the interface has exceeded the interfacial strength, which is a preset parameter in the simulation. By tracing the far field darker colors, a locus of failure (failure map) as a function of film thickness and temperature can be constructed.
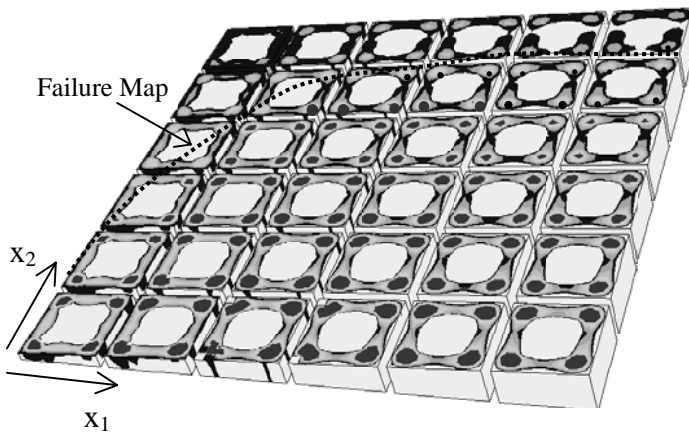

Fig. 4 The finite element simulation of interfacial debonding of a combinatorial specimen having 6x6 individual edge delamination samples.

A combinatorial specimen was prepared using silicon as the substrate, PMMA as the test film and commercial epoxy as the overcoating layer. The test film, PMMA, with nominal thickness 20 nm (the standard uncertainty is 5 nm) was spin-coated from the chloroform solution onto the substrate. The film thickness was determined by an UV (Ultraviolet)-vis reflectance interferometer. The overcoating layer thickness varied from 40 μm to 220 μm (Fig. 5 (a); the standard uncertainty is 5 μm). The contrast in the photograph of the figure is due to the reflected light. By using a diamond saw, the whole specimen was subsequently cut into numerous individual square samples (edge delamination samples) having dimensions of (3.2 x 3.2) mm^2 (the standard uncertainty is (0.3 x 0.3) mm^2). One edge of the specimen, then, was dipped into the liquid nitrogen (Fig. 5(b)) for 15 minutes to form a temperature gradient from -180 $^{\circ}$C to -120 $^{\circ}$C (the standard uncertainty is 2 $^{\circ}$C). Finally, interfacial debonding for those samples having critical stresses can be observed by eye (Fig. 5(c)).

CONCLUSIONS

A three-dimensional finite element modeling with fracture mechanics has been carried out to demonstrate the feasibility for the combinatorial edge delamination test for thin film adhesion measurement. By combining variables that are important and readily controllable in practice (temperature and overcoating layer thickness), the effect of stress concentration on the debonding of the film from substrate is spatially varied in one experiment. Consequently, the failure map as a function of both temperature and overcoating layer thickness can be constructed in a single step. Subsequently, the value of the adhesion of the film to substrate can be deduced from the failure map if the internal stress-temperature relation of the overcoating layer is known. This combinatorial approach 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. An initial test result qualitatively indicates the proposed combinatorial edge delamination test for thin film adhesion is very promising.
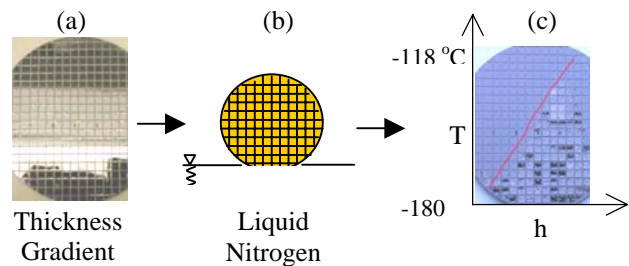

Fig. 5 The initial test result of the combinatorial edge delamination test for PMMA adhesion to silicon substrate.

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