An XPS Analysis of Polyimide/Substrate Fracture Surfaces

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Introduction

With the advent of polymer films in microelectronics, the need to accurately measure *in-situ* the mechanical properties and adhesion of polymer films as thin as 2 μm has arisen. The island blister test has recently been shown [1,2] to be particularly applicable to quantitative measurement of the debond energy of thin, well-adhered films. However, in order to understand the physical and chemical phenomena underlying the adhesion of thin films to various substrates, it is necessary to do more than simply measure debond energy. Contributions to the quality of adhesion of a film layer include many effects, such as intrinsic interfacial adhesion strength, plasticity of the film and/or substrate, and mechanical interlocking between film and substrate. In order to acquire chemical bonding information as well as quantitatively determine the locus of failure of the peeled film, surface spectroscopic techniques are used. In particular, the technique of X-ray photoelectron spectroscopy (XPS) has been shown to be very useful to accomplish these tasks.

XPS has been widely used to spectroscopically probe in-situ the formation of the metal-polymer interface formed by vacuum deposition of metal onto a polymer surface [3-6]. However, investigation of the interface formed by deposition of polymer on metal surfaces using this technique is much more difficult. This is primarily due to the difficulty of depositing polymeric films thin enough (approximately 20 Å) such that the interface can be seen through the bulk of the film. Vacuum deposition of polyamic acids and subsequent curing in-situ (analogous to the metal deposition) is difficult due to the relatively high molecular weight of the polyimide precursors. Grunze [7] has developed a technique in which polyimide monomers, e.g. pyromellitic dianhydride (PMDA) and oxydianiline (ODA), are vacuum deposited on a metal substrate inside an XPS chamber and the signal measured as a function of polymer coverage. Using this technique, it has been possible to elucidate the mechanism and angular orientation of the first few layers of PMDA and ODA which are bonded to the metal surface. Heating of the surface allows conversion of the deposited monomers to a polyimide (as deduced from shifts in the XPS signal). Although this technique has proven valuable in elucidating fundamental mechanisms of PMDA and ODA chemistry, the results may not be directly applicable to polyimide films which are formed from already-linked polyamic acids spin-cast from solution (which is the usual method of polyimide application).

One method which allows access to the polymer on metal interface is inspection of fracture surfaces after a polymer film has been peeled from the metal substrate. In principle, this measurement could also be carried out in-situ by peeling the material while it is inside the XPS chamber and inspecting the fracture surfaces without exposing the fracture surfaces to air. Even with this precaution, the measurement is complicated by the fact that the details of mechanical loading may affect where the interfacial failure occurs [8]. In practice, peeling of the material occurs outside the XPS chamber, and the additional variable of possible environmental contamination of the fracture surfaces prior to measurement. In spite of this, due to the difficulty with in-situ measurements of polymer on metal interfaces, ex-situ peel using the island blister test and

subsequent measurement in the XPS spectrometer will be employed in an atte to elucidate bonding mechanisms and locus of failure of these polyimide film

Experimental

Island blister test sites were fabricated using micromachining techniqu as described previously [2]. Detailed information about film/substrate prepar is described below. Gold substrates consisted of island blister silicon wafers coated with a 50 Å thick film of chromium (to act as an adhesion layer) and a 2000 Å thick film of gold, deposited in an electron beam evaporator at a rate o Å/sec. The adhered film was a PMDA-ODA polyimide (DuPont PI-2545), sj cast as its polyamic acid precursor from N-methylpyrrolidone and baked at 15 for 10 minutes. This process was repeated three times until a total thickness o coats of material. The polyimide was then cured at 400 °C in nitrogen for one hour. Aluminum substrates consisted of island blister wafers coated with a 1 thick film of aluminum, deposited in an electron beam evaporator at a rate of : Å/sec. The adhered film was either a PMDA-ODA or BTDA-ODA/MPDA (DuPont PI-2555, hereafter referred to as BTDA-ODA), spin-cast and cured a described above. The PMDA-ODA film was deposited in three coats, and the BTDA-ODA film was deposited in two coats. Silicon dioxide substrates consisted of island blister wafers on which 3000Å of highly p-doped silicon dioxide had been thermally grown. This surface was optimally primed with a 0.5% solution of γ-aminopropyltriethoxysilane in 95% methanol/5% water. T adhered film was either a PMDA-ODA or BTDA-ODA, spin-cast and cured as described above. As above, the PMDA-ODA film was deposited in three coa and the BTDA-ODA film was deposited in two coats.

Test sites fabricated as described above were then peeled using the isla blister test (Figure 1) and the debond energies were measured. After peeling, wafers were transferred as quickly as possible (within three hours) to the XPS spectrometer for measurement. The suspended polyimide film was cut away from over the island and turned over to expose the film side of the fracture surface, leaving the island side of the fracture surface suitably uncovered. Surface analysis was carried out at the Harvard/MIT Joint Spectroscopy Facilit using a Surface Science Instruments SSX-100 ESCA spectrometer under a bas pressure of approximately 10-9 torr. Monochromatic Al Kα radiation (1486.6 eV) was used at a take-off angle with respect to the sample surface of 35° an angle of 35° to the surface were analyzed. A flood gun was used to prevent charging of the non-conducting samples. The gun energy was optimized for th given geometry to yield narrow, intense peaks; for the polyimide samples described below, the gun energy was about 6.0 eV. All spectra were reference to the phenyl carbon peak in polyimide at 285.0 eV (see below). All spectra reported herein are unsmoothed data which were deconvoluted using 100% gaussian peaks with a smoothing factor of better than 2.5. Spectra of both the film sic and island side were taken to deduce the locus of failure and investigate bonding mechanisms. Binding energy shifts due to charging were corrected by assignin the phenyl carbons in both PMDA-ODA and BTDA-ODA to a binding energy o

28 eV. Figure 1 shows a film in the island blister test configuration prior to and after peel, and shows the location of the film side and island side fracture surfaces as defined in this paper.

Results and Discussion

Table 1 summarizes the results of the debond energy measurements which quantify the film/substrate adhesion, and XPS measurements which determine the locus of failure of the film. Locus of failure was defined in one of three ways: interfacial, cohesive, or mixed. In interfacial failure, the film and substrate separated cleanly, with little or no film on the substrate side and little or no substrate on the film side. In cohesive failure, failure occurred either entirely within the film (denoted as PI) or entirely within the substrate (denoted as S). Finally, in mixed failure, the failure crossed and recrossed the bond line, resulting in evidence of substrate material on the film side and film material on the substrate side. Space limitations preclude the inclusion of XPS spectra for all the measured cases. Representative XPS spectra and an illustration of the determination of locus of failure from the spectra will therefore be detailed for only one case, PMDA-ODA polyimide on aluminum. Similar procedures were then used to make the other assignments in Table I.

Figure 2 shows the C1s spectrum of the fracture surfaces (film side and island side) of a PMDA-ODA film peeled from aluminum. The spectra have been deconvolved into a series of 100% gaussian peaks for chemical assignment and identification. In this case some evidence of reaction is signified by new peaks in the C 1s and N 1s spectra (not shown) relative to the standard. The substrate side spectra indicate that there is substantial polyimide remaining on the substrate side which is chemically close to 'bulk' polyimide; however, this polyimide residue is thin enough (< 20-30 Å) that the Al substrate XPS signal can be seen through the residue. In addition, there is no evidence of aluminum on the film side fracture surface. As both fracture surfaces contain the new peak in the C 1s spectrum, the failure has occurred within a thin interphase region of the polymer which appears to have been chemically modified by curing on the oxidized aluminum surface, and that the measured 95 J/m² is the cohesive failure energy of this interphase. While this new peak in the C1s spectrum is consistent in binding energy with an Al-O-C bond, it may also be due to other effects, and therefore cannot be assigned at this time. The debond energy measured for the gold surface was lower than that for aluminum. This is not surprising, as one would expect that there would be no chemical reaction between the polyimide and gold surfaces. Examination of the polyimide/gold spectra indicated essentially interfacial failure. It was also noted that the chromium which was underneath the gold acting as an adhesion layer migrated to the surface during the polyimide cure. The migration of chromium in gold has been observed previously [9], but usually occurs at higher anneal temperatures and/or longer anneal times than a typical polyimide cure.

The effect of environmental degradation on PMDA-ODA/aluminum adhesion was also investigated. Samples were prepared identically to those described above and allowed to age for fifty hours at a temperature of 85 °C and a relative humidity of 80%. It was found that over the time scale of this experiment, there was essentially no change in either the debond energy or the XPS spectrum of the fracture surfaces. The measured debond energy for these aged samples was 93 J/m², identical to the previous measurement within experimental error. It should be noted that this agreement also highlights the reproducibility of the island blister test.

The effect of environmental stress on the adhesion of BTDA-ODA on aluminum was also measured. In previous work [2], a value for the debond energy of unaged BTDA-ODA on aluminum of 460 J/m² was measured. Samples for aging tests were prepared identically to those peeled previously and were aged at 85 °C / 80% relative humidity for 50 hours. Upon peeling, a value of 465 J/m² for the debond energy was obtained, essentially unchanged within the experimental error of the test. Once again, this illustrates two points - the debond energy of BTDA-ODA to aluminum is not affected over these time scales of environmental exposure, and the reproducibility of the island blister test is quite good. The aged BTDA-ODA samples were investigated using XPS. As no degradation of adhesion was observed, these spectra should also provide a good representation of unaged fracture surfaces. XPS analysis shows substantial amounts of both polyimide and aluminum on both fracture surfaces. Thus, a mixed failure is occurring in the peel of BTDA on aluminum. Since failure in this case does not occur in an interphase region wholly within the film (as is the case for PMDA-ODA), the measured debond energy will depend on the specific substrate as well as its chemical and mechanical properties. The mixed-mode cohesive failure in BTDA-ODA/Al demonstrates that substantially better interfacial adhesion is obtainable with this material, at least on aluminum.

The adhesion of PMDA-ODA to silicon dioxide was also investigated using the above analysis techniques. Two effects were studied: the effect of pretreatment of the silicon dioxide surface with a silane adhesion promoter, and the effect of temperature/humidity aging. A 2x2 matrix of experiments was

performed: samples were prepared (fresh, no adhesion promoter), (aged, no adhesion promoter), (fresh, adhesion promoter), (aged, adhesion promoter). Results of the adhesion measurement for the above four cases are also given in Table I. Due to difficulties in measuring the residual stress in these samples (primarily due to residual oxides), the values given in Table I are reported as the slope of the island blister adhesion plot in Pa-J/m [2]. Thus, although comparisons of debond energies between these measurements and other classes of measurements cannot be made, a relative assessment of adhesion quality within this matrix of experiments can be quantitatively made by comparing the adhesion plot slopes given in Table I.

The simpler case of no adhesion promoter will be considered first. The film side C1s spectrum appears to be very close to standard polyimide while the island side shows a combination of polyimide-like carbon as well as a distorted phenyl carbon envelope which may be indicative of either surface contamination or low amounts of polyimide on the surface (i.e., adventitious carbon and polyimide carbon may be present in approximately the same amounts). A very interesting result is shown in the Si 2p spectrum, however. The island side shows the expected strong silicon dioxide signal, but the film side shows evidence of silicon also. Silicon dioxide was the only substrate investigated for which failure of PMDA-ODA was mixed instead of purely adhesive or purely cohesive within the film [10]. Recent work in the fracture mechanics area implies that the brittleness of the substrate may play a major role in the locus of failure of a peeled compliant film [8]. As silicon dioxide is the most brittle substrate investigated here, this hypothesis may explain this mixed cohesive failure mode. The effect of aging for 120 hours at 85 °C/80% relative humidity is quite significant. The measured adhesive strength was zero; the film could be debonded with zero effort from the substrate. Thus, purely interfacial failure is expected and confirmed by XPS analysis.

Adhesion of PMDA-ODA to silicon dioxide with an adhesion promoter primer layer was also investigated. There is a substantial increase in the measured adhesion over the unprimed case. It is not clear whether this effect is due to the sensitivity of the unprimed samples to moisture (and thus degradation occurring between sample preparation and measurement in the unprimed case), change in the residual stress of the film (and thus the debond energy) due to the adhesion promoter, or an actual increase in the debond energy. The effect of aging at 85 °C/80% RH resulted in a drop in the adhesion plot slope of approximately a factor of two. Although this is a significant drop in the measured adhesion, it is far superior to the unprimed case, where adhesion dropped essentially to zero over the same time scale. Thus, the silane adhesion promoter is indeed improving the stability of the polyimide/oxide bond. It should be emphasized that no attempt has been made to optimize the processing of the aminosilane treatment. Hence, these results should not be taken as other than generally indicative of the use of adhesion promoter. XPS analysis showed mixed mode failure at the polymer/substrate interface; however, it is difficult to elucidate the chemical role of the adhesion promoter; traces of adhesion promoter may be present on both fracture surfaces. Detailed examination of the spectra of aged material shows fracture is again moving towards a failure in the interphase within the film (analogously to the PMDA-Al case described above). However, it is not clear whether this effect is due to a change in the mechanics of the peel (due to modification of the mechanical properties of the interphase caused by aging) or a change in the chemical nature of the interphase. With further aging, as the adhesion drops toward zero, hydrolysis of the aminosilane and corresponding adhesive failure may occur. Although it must be confirmed by further experiment, it seems as if aminosilane-primed adhesion to the relatively brittle silicon dioxide surface passes through three stages; mixed-mode cohesive failure (best adhesion), interphase failure within the film (intermediate adhesion), and pure adhesive failure (worst adhesion).

Conclusions

X-ray photoelectron spectroscopy was used in conjunction with the island blister adhesion measurement technique in an attempt to probe the fracture surfaces resulting from the peel of thin polyimide films. By combining debond energies as measured by the island blister test with XPS, detailed information on the failure mechanisms (both chemical, e.g., new bond formation, and mechanical, e.g., effect of brittle substrate) could be obtained. Three substrates of importance in microelectronics, aluminum, gold, and silicon dioxide, were investigated, along with two frequently used polyimides, PMDA-ODA and BTDA-ODA. Further experiments using these techniques could potentially elucidate important information about the relationships between the mechanical properties of thin films and their loci of adhesion failure.

Acknowledgements

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Table I. Measured debond energies (as measured by island blister test) and modes of failure (as determined by XPS) of various polyimide/substrate combinations.

Polyimide	Substrate	Debond energy (J/m²) (±10%)	Failure mode
PMDA	Au	57	interfacial
PMDA	Al, fresh	91	cohesive, in PI
PMDA	Al, aged	93	cohesive, in PI
PMDA	SiOx, fresh	2.0 (*)	mixed
PMDA	SiOx, aged	0 (*)	interfacial
PMDA	SiOx, fresh, AP	46 (*)	mixed
PMDA	SiOx, aged, AP	23 (*)	mixed
BTDA	Al, fresh	460	mixed
BTDA	Al, aged	465	mixed

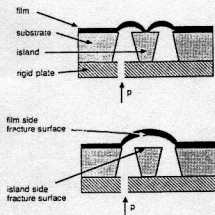(*) slope of adhesion plot, Pa J/m (see text)

Figure 1. Schematic view of island blister configuration, showing before peel (top) and after peel (bottom). Fracture surfaces probed by XPS are indicated in the bottom figure.

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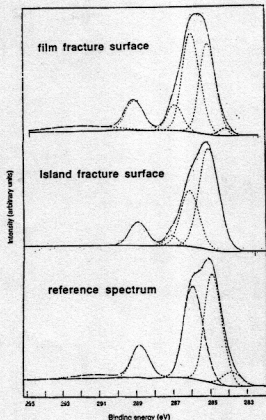
Figure 2. C 1s XPS spectra of PMDA-ODA peeled from aluminum. The top spectrum is the film fracture surface; the center spectrum is the island fracture surface; and the bottom spectrum is a reference spectrum of PMDA-ODA. The spectra have been shifted 6.8, 7.4, and 5.3 eV respectively so as to assign the phenyl carbon peak to 285.0 eV.