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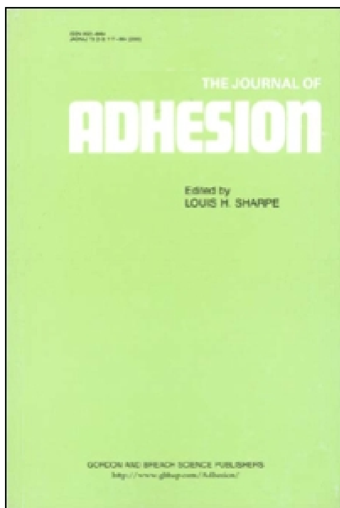

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An XPS Study of the Locus of Failure Between PMDA–ODA Polyimide and SiO_2 Surface

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This study was undertaken to determine the locus of failure between a fully cured (up to 400°C) PMDA–ODA polyimide and SiO_2 surface. We have shown that an interfacial layer is formed between the bulk polyimide and the substrate surface. The chemistry of this 2 nm-thick layer is different from that of the polymer interface surface of the polyimide film and of the bulk polymer. The locus of failure is at the interface of the interfacial layer and the bulk polyimide film.

INTRODUCTION

Adhesion plays a very important role in the semiconductor industry, where polymeric materials are commonly bonded to inorganic substrates. Polyimides are thermally stable organic insulators. These polymers are usually coated onto the inorganic substrates as polyamic-acid solutions by spinning or spraying. The imidization is most often achieved by thermal treatment up to ~400°C. This causes an inherent problem, which is the mismatch of the coefficient of thermal expansion between the polymer and the inorganic substrate. The stresses developed in such a situation may cause

cracking, crazing or delamination that can be accelerated by process solvents, thermal cycling, etc. The adhesion of the polymer to the inorganic substrate plays a dominant role in the overall mechanical stability of a device or package structure during both the processing and the final use.

The knowledge of the locus of failure of an adhesive joint is very important in the understanding of the adhesion phenomenon. This is of particular interest if one is studying improvement of adhesion utilizing adhesion promoters, surface modifications by plasma techniques, etc. If a failure occurs cohesively in either of the bulk materials, the problem is a materials one rather than an adhesive one. If the failure is an interfacial one, or caused by a creation of a weak boundary layer, the adhesion could be improved by surface treatments or by removal of moieties that cause the formation of a weak boundary layer.[1]

This study determined the locus of failure between pyromellitic dianhydride–oxydianiline (PMDA–ODA) polyimide and SiO_2 by using X-ray photoelectron spectroscopy (XPS),[1–4] and investigated the adhesion of the PMDA-ODA film to the SiO_2 surface as a function of cure.

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EXPERIMENTAL

Sample preparation

We prepared samples by spin-coating the PMDA–ODA polyamic acid onto Si wafers, which were first cleaned in buffered hydrofluoric acid and then exposed to an oxygen plasma for further cleaning and creation of a thin SiO_2 layer. The thickness of the polyimide film was 23 μm. Plasma cleaning took place in a Tegal Plasmaline barrel reactor under the following conditions:

Incident Power	200 W
Reflected Power	5 W
Pressure	0.1 Torr
Time	5 min

The polymer samples were cured using the following parameters:

Sample #	Cure temp./°C	Time/min	Ambient
1	200	30	air
2	300	30	air
3	400	30	N_2
4	400	120	N_2

Sample analysis

The adhesion was measured after every cure temperature by using a peel technique that employs a 90-degree peel angle, constant peel speed, and a 1.59-mm peel strip width (Figure 1). The peel strips were first scribed onto the polymer surface using a Tempress scriber. The lines were then cut through the PMDA–ODA film down to the silicon wafer by means of a sharp scalpel. The peel was measured in g/mm using an Instron tester.

We used XPS analysis to analyze both the polymer and the substrate interface sides. The XPS spectra were recorded on a Hewlett–Packard 5950A spectrometer with a monochromatized

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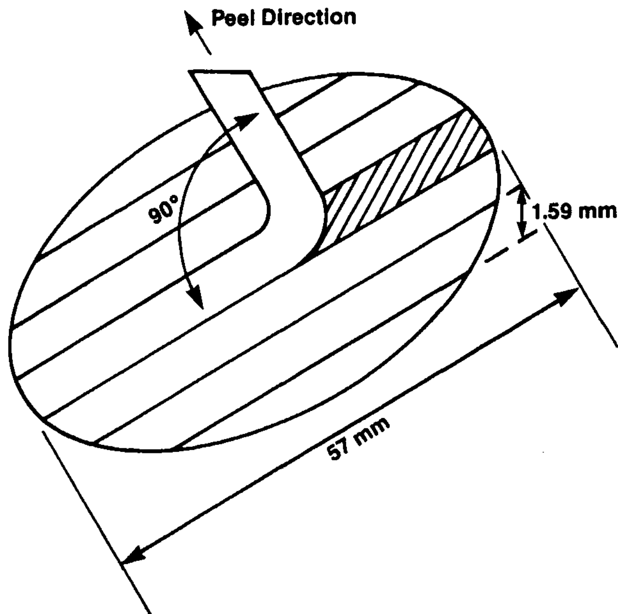

FIGURE 1 Peel sample.

AlK_α radiation source of 1487 eV energy. The X-ray power was set to 800 W. The electrical insulating properties of both the polyimide film and the substrate required us to use an electron-emitting device (flood gun) to reduce the shifts and to avoid distortion of the spectra due to charging. The instrument was calibrated using the Au_{4f} doublet at 83.9 eV and 87.7 eV. The carbon 1s peak at 285.0 eV was used as an internal standard for correction of shifts due to charging.

The XPS spectra were resolved into component peaks using a non-linear least squares curve fitting program.[5] We synthesized the XPS curves by summing Gaussian peaks into a form identical to the experimental data. XPS curve envelopes consisting of overlapping peaks were resolved by fitting a minimum number of Gaussian peaks. The individual components were then plotted and relative areas determined.

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RESULTS AND DISCUSSION

Table I presents the elemental composition of the polymer and the substrate interfaces including fully cured (to 400°C) PMDA–ODA (control) top surface composition as analyzed by XPS.

As is evident from the data presented in Table I, the elemental composition of the polymer interface is comparable to the data collected for the fully imidized PMDA–ODA top surface. The substrate side, however, is different. It is clear that organic material has been left on the SiO_2 surface after the peeling of the polymer film. On samples #3 and #4, the organic content of the substrate surface exhibits a significant increase, which is evidenced by the

TABLE I
Elemental composition of polymer and substrate interface

	Polymer interface			Substrate interface					
Sample #	C%	N%	O%	C%	N%	O%	Si%	C/Si	N/Si
1	76	7	17	13	1	47	39	0.3	0.03
2	77	7	16	19	1	47	32	0.6	0.03
3	76	7	17	41	4	33	22	1.9	0.18
4	76	7	17	41	4	34	24	1.7	0.17
control	78	7	15						

great increase in the relative concentrations of carbon and nitrogen.

When studying the binding energies and the relative concentrations of the different oxidation states of carbon, oxygen, and silicon as a function of cure, we observed no significant differences on the polymer or substrate interfaces. Nitrogen 1s spectra do show some differences, which are tabulated in Table II. The nitrogen 1s data for fully cured PMDA-ODA top surface is included in the table for comparison (control).

The nitrogen 1s spectrum of fully cured PMDA–ODA top surface normally contains two peaks; one at 400.8 eV and another at 399.3 eV. The higher binding energy peak is assigned to imide nitrogens, while the lower binding energy peak is due to isoimide moieties. IR analysis of the fully cured PMDA–ODA film suggests the presence of isoimide moieties in the bulk of the film also.[6] No nitrogen 1s peak at 399.3 eV was observed on the polymer interface. This is rather surprising since the top surface and the bulk evidently have the nitrogen species that would give rise to a N 1s peak at 399.3 eV. The substrate interface data clearly shows the presence of the low binding energy nitrogen 1s peak (samples #3 & #4, cured to 400°C). Samples #1 & #2 do not show this peak; however, the peak may be hidden under noise caused by a small amount of material left behind on the substrate after peeling. For this reason it cannot be said unequivocally that the peak is not there.

Calculating the elemental %-concentrations of the material left on the substrate surface after peeling requires the exclusion of silicon and oxygen intensities due to the substrate surface itself. The amount of SiO_2 is readily available from the silicon 2p XPS data. Elemental silicon 2p is at ~100 eV, while the SiO_2 silicon 2p peak is

TABLE II
Nitrogen 1s XPS data for polymer and substrate interfaces

	Polymer interface		Substrate interface	
Sample #	400.8 eV	399.3 eV	400.8 eV	399.3 eV
1	100%	—	~100%	~0%
2	100%	—	~100%	~0%
3	100%	—	90%	10%
4	100%	—	85%	15%
control	92%	8%		

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TABLE III
Elemental composition of the organic material on the substrate surface

Sample #	C%	N%	O%
1	43	3	53
2	54	3	43
3	69	7	24
4	72	7	21
control	78	7	15

at ~103.7 eV. Table III displays the calculated elemental %-concentrations of the organic material on the substrate surface, including fully cured PMDA–ODA top surface data for comparison (control).

As was stated earlier, the spectra of the first two samples (#1 & #2) are very noisy. Therefore, those results are less precise. It is evident from the data presented in Tables II and III that the material left behind on the substrate surface after peeling is different from the top or interface surfaces of PMDA–ODA film. The low binding energy nitrogen 1s peak observed on the substrate interface may not be due to isoimide moieties. It can represent a degradation product,[7] which has its nitrogen 1s binding energy at the same location as isoimide does. For example —C=N nitrogen 1s is at 398.4 eV and —N=N— at 399.3 eV (ref. to carbon 1s at 284.6 eV with binding energy accuracy of 0.2 eV).[8] A possible degradation product as described by Ehlers *et al.*[7] is carbodiimide via isocyanate formation. The nitrogen 1s peak for carbodiimide may very well be at 399.3 eV. It is unclear why no nitrogens at 399.3 eV are seen in the polymer interface. Perhaps the isoimide moieties or the degradation products are the weak link between this organic layer on the substrate and the bulk polyimide, so that when the failure occurs, the polymer interface is made void of low binding energy nitrogen species.

Table IV displays the peel analysis results, including C/Si and N/Si data.

The adhesion of PMDA–ODA to SiO_2 is a function of curing conditions. The adhesion also correlates with the amount of organic material left on the substrate surface after peeling. While a very small amount of material is left on the substrate surface when

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TABLE IV
Peel analysis results, C/Si and N/Si data from Table I

Sample #	Cure temp/time	Peel g/mm	C/Si	N/Si
1	200°C/30 min	0	0.3	0.03
2	300°C/30 min	0	0.6	0.03
3	400°C/30 min	57	1.9	0.18
4	400°C/120 min	82	1.7	0.17

adhesion is poor, a significantly larger amount is left when adhesion was increased. Note that we did test whether material from fully cured PMDA–ODA could transfer to a SiO_2 surface. As explained earlier, we cleaned two wafers and coated the face of one of them with the polyimide. The polymer film was then fully cured (at 400°C), and that wafer was then placed face down onto the other cleaned wafer. A KBr infra-red crystal was placed on top of them as a weight and the whole assembly put into a nitrogen flow box for two days. Then, the uncoated wafer surface was analyzed using XPS. We found no evidence of the transfer of fully cured PMDA–ODA onto this surface.

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To achieve more evidence that we indeed had a uniform layer or film of organic material on the substrate surface, we proceeded to use a scanning Auger technique to analyze the sample cured to 400°C. Using this technique, we determined the thickness and uniformity of the organic film. However, before this could be done, we needed to know the thickness of the SiO_2. The following empirical formula was used:[9]

$$t = 3.53 + 31.6[\ln(1 + 2.083R)]$$

where t = thickness of SiO_2, and

$$R = I(SiO_2)/I(Si)$$

where I = intensity (of the material).

This formula is independent of the thickness of the organic film since both the oxide and the bulk silicon signal are attenuated the same amount because their binding energies are close together. We used the Si_{KLL} signal for determining the SiO_2 thickness, which we found to be 1.2 nm.

The thickness and uniformity of the organic film could now be

determined using the following equations and criteria:[10]

$$t = \ln(I/I^{\infty})$$

where t = thickness of organic film + SiO_2 film
I = Si peak intensity under organic film
I^{∞} = Si peak intensity after organic film and SiO_2 film are sputtered off

Both Si_{LVV} (low energy peak $\lambda \sim 0.678$ nm, more sensitive to film thickness) and Si_{KLL} (high energy peak $\lambda \sim 3.17$ nm) were used for the determination of the film thickness.

The film is non-uniform if:

$$t_{LVV}/t_{KLL} < 1$$

and uniform if:

$$t_{LVV}/t_{KLL} = 1$$

The results of this study show that $t_{LVV} = 3.5$ nm and that $t_{KLL} = 3.5$ nm; therefore, the film is uniform. This was confirmed by using the scanning Auger microprobe technique to create carbon and silicon maps. On the basis of these maps [size $(200 \times 100)\ \mu m^2$], it is evident that the film is uniform within the resolution of the mapping (~5 mm). The thickness of the organic film was found to be 2.3 nm, (after allowing 1.2 nm for SiO_2).

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SUMMARY

1) No nitrogen 1s peaks at 399.3 eV were found on the polyimide interfaces, while they were found on the substrate interfaces (sample #3 & 4). This suggests that the isoimide or the degradation product may be the weak link, so that the failure occurs at that point leaving the polymer interface void of low binding energy nitrogen moieties.

2) C/Si and N/Si ratios correlate with adhesion (a higher ratio indicates better adhesion).

3) The results suggest a formation of a thin interfacial layer between the SiO_2 surface and the cured polyimide coating. The

failure occurs at the interface of this layer and the bulk polyimide film.

4) The thickness of the uniform interfacial layer was found to be 2.3 nm (samples #3 & 4).

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