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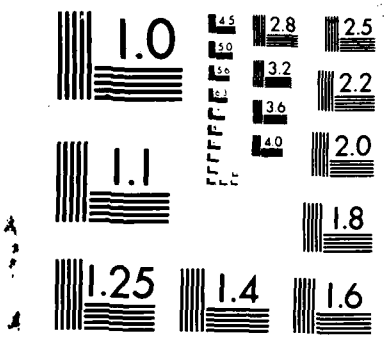

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by

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Prepared for publication in J. Vac. Sci. Technol.

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30 June 1986

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A1

The popularity of polyimides in, for example, packaging and dielectrics in electronic devices, stem from their favorable physical properties (eg. thermal stability, moisture resistance) and their ease of application (spin coating). Investigation of the nature of the bonding between the polymer and metal substrates has, however, been restricted in the past to metal clusters and metal films deposited on cured polymer surfaces or polyimide model compounds [1,2].

The formation of ultra thin polymer films on a bulk metal surface has been achieved by the controlled vapour deposition of the polymer precursors (4,4 -Oxydianiline (ODA) and 1,2,3,5 Benezenetetracarboxylic Anhydride (PMDA)) on a polycrystalline silver substrate and the subsequent thermal polymerization of the codeposited layer. The production of sufficiently thin organic films made the substrate-film interfacial region suitable for analysis using X-ray photoelectron spectroscopy (XPS).

A summary of the integrated intensity ratios of the XPS spectra for separate depositions of PMDA and ODA and a resultant polyimide film (from initial codeposition) on the clean silver surface is shown in Figure 1. The assignment of peaks (with respect to binding energies) was made with reference to calibration spectra of bulk material, thick films [3] and theoretical considerations [4]. Film thicknesses were estimated from the attenuation of the Ag 3d photoemission signal and can only be considered as approximate [3].

In PMDA, a split in the C1s carbonyl (C2) and the O1s bands of the 4Å film as compared to the thicker film indicated a chemical interaction with the substrate. There appears to be loss of a carbonyl group upon initial deposition. This, coupled with angular resolved XPS measurements

indicating a "standing-up" configuration of the molecule suggests a bonding scheme to the substrate via the C atom on the phenyl ring and/or the O on the carboxyl group and the release of one carbonyl group as CO.

The ODA spectra also indicated evidence of fragmentation upon initial deposition. A large split in the O1s peak of the 3Å film together with the appearance of a third peak in the C1s suggests a variation in the chemical environment with a probable bonding to the substrate through the ether oxygen. The total intensity ratios show a doubling of the oxygen content. In terms of splitting of the molecule and the changes apparent in the overall spectra this is consistent with a loss of aniline C_7H_6N.

The general picture for PMDA and ODA deposition is the production of a mixed film of dissociated (chemisorbed to the substrate) and undissociated (physisorbed) species. This is most evident in the thinner films where the ratio of these is comparable.

Codeposition produces spectra which are similar to those of the expected intermediate polyamic acid [5]. Heating removes water (imidization) and forms the thermally stable (~450 C) polyimide. The integrated carbon intensities suggest an increase in the ODA carbons (C3) and this would be expected for a film with a high branching ratio and terminal ODA groups. The totals indicate an excess of aromatic carbon and coupled with the stoichiometric ratios found for oxygen and nitrogen evince a polymer-metal interface consisting of partially fragmented PMDA and ODA.

The formation of the polymer was dependent on the method of deposition. Sequential evaporation or thin codepositions (< 30A) lead to the formation of some polyamic acid but negligible imidization. This supports our conclusion of an interface containing fragmented and chemically bonded constituents and thus a model for the overall adhesion as one of polyimide chemically bonded via fragmented PMDA and ODA to the substrate.

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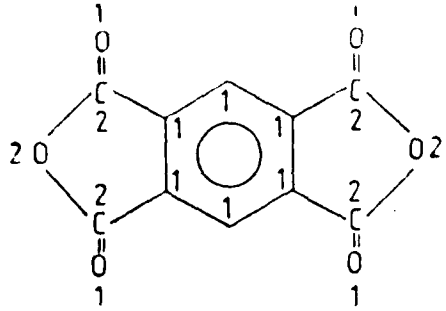
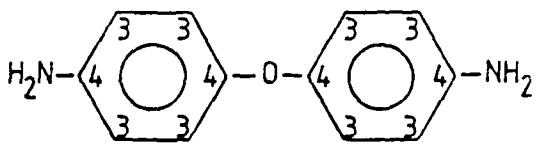
Figure Caption

Various Integrated Intensity Ratios for Precursors and Polymer.



1,2,3,5 Benzenetetracarboxylic
Anhydride
PMDA

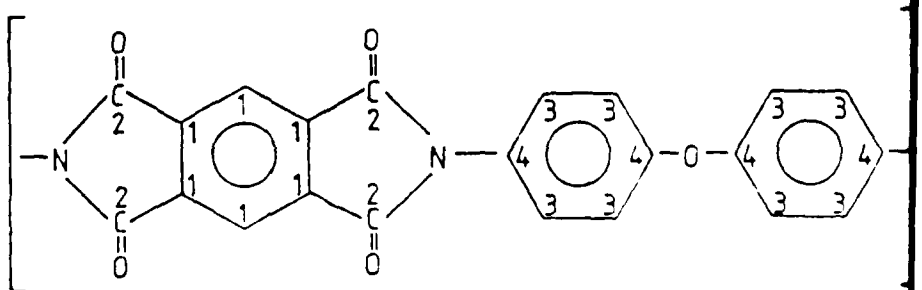
	C1s			O1s			Total		
	C(1)	:	C(2)	O(1)	:	O(2)	C(1)	:ΣO	C(2) :ΣO
Stoichm.	6	:	4	2	:	4	6	: 6	4 : 6
4Å	5.8+0.3	:	3	2	:	2.8	6.1	: 5	3 : 5
16 Å	6.1	:	4	2	:	4.3	6.1	: 6	3.9 : 6



4,4' Oxydianiline
ODA

	Total			
	C	: O	:	N
Stoichm.	12	: 1	:	2
3Å	12	: 2.3	:	1.8
17Å	12	: 1.4	:	1.9

Polyimide (PI)



	C1s				Total			
	C(2)	: C(1,4)	: C(3)	C(2) :ΣO	ΣC	: ΣO	: ΣN	
Stoichm.	4	: 10	: 8	4 : 5	22	: 5	: 2	
11Å	4	: 9.5	: 9.6	2.9 : 5	24.8	: 4.9	: 2	

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