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# Amino Organo Alkoxysilanes in Organic Solvents for Promoting Adhesion of Polyimide Films to Silicon Substrates

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In this study of silane adhesion promoters for coupling polyimide films to clean silicon dioxide surfaces the adhesion values obtained with three amino organo trialkoxysilanes and with several solvents for these silanes were compared. When applied from aqueous solution the silanes with primary amino groups gave higher adhesion values, as measured by a peel test, than did one having only a secondary amino group; however, when applied from organic solvents all three were effective. The highest values for all of the solvents tested were obtained with N-(2-aminoethyl)-3-aminopropyltrimethoxysilane. A fundamental discussion is presented to rationalize the differences.

**KEY WORDS** Adhesion; coupling; polyimides; silanes; silicon; solvents.

## INTRODUCTION

Polyimides prepared from pyromellitic dianhydride and 4,4'-oxydianiline (PMDA-ODA) are widely used in the microelectronic industry for insulation layers in device structures; however, due to a difference between the coefficients of thermal expansion of silicon,  $3 \times 10^{-6}/^{\circ}\text{C}$ ,<sup>1</sup> and polyimide,  $40 \times 10^{-6}/^{\circ}\text{C}$ ,<sup>2</sup> curing and thermal

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cycling which are required during product processing lead to the buildup of mechanical stresses which can result in cracking and in delamination of the polyimide from the silicon substrate. The application of coupling agents to silicon dioxide surfaces can not only improve the adhesion of PMDA-ODA polyimides to such surfaces but can also enhance the overall mechanical stability of these systems, thereby resulting in more reliable commercial products.

One of the most widely used coupling agents is 3-aminopropyltriethoxysilane, here denoted as "APS", which is supplied by Union Carbide Corporation as "Organofunctional Silane A-1100".<sup>3</sup> Typically, APS is applied from aqueous solution so that hydrolysis of the triethoxysilane to the triol can occur before the siliceous surface is treated. The silane triol reacts with itself and with the hydroxyl groups of the siliceous surface to form a bonded polymeric silicone film with aminopropyl functionality capable of interacting both chemically and physically with the subsequently applied polymer.<sup>3</sup> Although it is recognized that for optimum physical properties there should be chemical bonding between the coupling agent and the polymer,<sup>4</sup> relatively little work has been performed to show how the chemical structures of coupling agents relate to the strength of adhesion between siliceous surfaces and polyimides. Additionally, although the solution chemistry and functional aspects of the aqueous coupling agent systems have been studied, including the effects of concentration and solution pH,<sup>5</sup> no such fundamental information exists for nonaqueous systems.

In this study three coupling agents and various solvents were investigated to elucidate their roles in improving the bonding of PMDA-ODA to silicon dioxide surfaces, *viz.* in the form of native oxides on highly polished silicon wafers.

## EXPERIMENTAL

### Substrate preparation

Silicon dioxide surfaces were prepared from 82-mm diameter, single crystal, p-type, silicon wafers supplied by Wacker Chemetronics

Company. Cleaned  $\text{SiO}_2$  surfaces free of adsorbed hydrocarbons were obtained by submerging the wafers in 7:1 ammonium fluoride/hydrofluoric acid solution (7 parts of 40%  $\text{NH}_4\text{F}$  and 1 part of 49.5% HF) for 30 minutes. This etching method results in the removal of the mechanically weak boundary layer of  $\text{SiO}_2$  on the wafer surface and in the generation of a clean layer, approximately 22 angstroms thick, of oxide.<sup>6</sup> The cleaning was completed by a thorough rinse with deionized water. Wafers were used immediately after preparation to avoid any adsorption of hydrocarbons or other materials that would render the surface nonwetttable and be weak boundary layers. The wafers received all subsequent processing in a class 1000 clean room environment, since particles on a surface can greatly reduce adhesion to that surface.<sup>7</sup>

In order to facilitate the initiation of a peel of each sample for peel strength testing, about one-sixth of the wafer edge was masked with tape before the freshly prepared coupling agent solution was applied. For aqueous solutions of adhesion promoters vinyl adhesive tape was used. For nonaqueous solutions standard masking tape was used.

#### **Application of adhesion promoter and polyimide**

All preparation and handling of systems prior to final curing were done in the class 1000 environment at  $23^\circ \pm 1^\circ\text{C}$  and relative humidity of  $40 \pm 10\%$ . To prepare adhesion promoter solutions with water as the solvent the promoter was added to water in a Nalgene flask. For the cases where organic solvents were used, Pyrex glassware was employed. The solutions were prepared to contain 0.1% of adhesion promoter by weight, it being known that concentrations of silane adhesion promoters of less than 2% by weight provide optimum strength for the oxide/polymer systems.<sup>8</sup> Each solution was well agitated and allowed to stand for approximately one hour before use.

The application procedure consisted of flooding the wafer surface for 30 seconds and then spinning it at 2000 rpm for 60 seconds. This spinning reduced the layer of adhesion promoter to a thickness of about 100 angstroms (3 to 5 molecular layers). The aforementioned

tape was then removed, and the wafer was baked for 5 minutes in a nitrogen atmosphere.

PMDA-ODA polyamic acid, precursor of the polyimide, was obtained from the DuPont Co. as "RC 5878" and employed as a 20% solution in *N*-methylpyrrolidone. Four coatings were applied and the thickness adjusted by spinning the wafer at 1700 rpm for 30 seconds after each application. The curing procedure employed was that described by Geldermann.<sup>9</sup> Each of the first three coatings was followed by heating at 85°C for 30 minutes. The fourth coating was followed by heating at 85°C (15 minutes), 200°C (30 minutes), 300°C (30 minutes), and 380°C (30 minutes). All curing was done in a strictly-maintained, particle free, nitrogen atmosphere. To ensure reproducibility, all experiments employed the same batch of unaged RC 5878. After complete curing, the polyimide coating thickness was approximately 56 microns. The film thickness was measured using Alpha Step Equipment.<sup>10</sup>

The spinning conditions for both the adhesion promoter and the PMDA-ODA were kept constant throughout the study so as to help achieve the same thicknesses of materials. It is known that the adhesion value obtained in the peel test depends in part on the thickness of the coating.<sup>5</sup>

### **Adhesion peel strength test**

The adhesion strengths in the present study were measured by the peel test, which is found to have the widest application for micron-thick films of polymers.<sup>10</sup> The test was performed with an Instron Material System Tester.

The peel strengths were determined in the following fashion. Each fully-cured polyimide coating was scribed with a sharp scalpel to form strips approximately 6.35 mm wide across the wafer. The scribing effectively cut the polyimide all the way down to the silicon oxide surface. The exact width of each strip was measured. In running the tests at least four strips were pulled from each wafer, and at least three wafers were examined for each experiment; therefore, there were, on the average, about twelve peel strength measurements for each experimental system.

The peels were initiated manually by using tweezers on the areas which had been masked with tape prior to the application of the

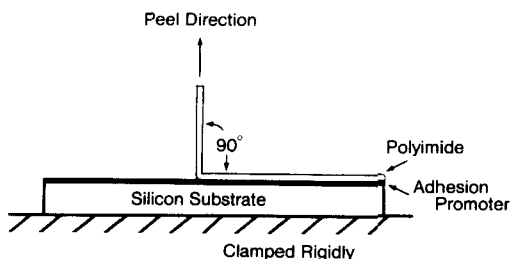


FIGURE 1 Schematic diagram of the peel test.

coupling agent. The measurements with the Instron Tester were then conducted, in laboratory air at room temperature, under identical conditions for each measurement: i.e., a constant peel rate of 10 mm per minute with a peel angle of 90 degrees. Figure 1 shows a schematic diagram of the polyimide strip being peeled from the silicon wafer.

In most cases peeling of at least 2 cm was achieved; however, occasionally the adhesion strength of the system was so great that the test resulted not in the peeling of the polyimide film from the wafer but instead in a breaking of the polyimide strip, indicating that the adhesion between the polyimide and the silicone wafer was greater than or equal to the strength of the polyimide.<sup>11,12</sup> This gave what is often referred to as the "tear value", a figure of significance in that the true adhesion value must be at least that great. Nine of the twenty-one points obtained in the peel tests were tear values, which ranged from 138 to 160 g/mm. These are thought to be representative primarily of the strengths of the polyimide films. The agreement of  $\pm 7.4\%$  from the average value of 149 is considered good for this test. The values of the peel strength were recorded in Newtons. These were then normalized with respect to the width of the strips and expressed as grams per millimeter.

The peel strengths of samples prepared without the use of adhesion promoters were determined and reported by Suryanarayana and Mittal, who used the same equipment and technique that were used in the present study.<sup>5</sup> They obtained values of 20–30 g/mm and ascribed the range to "wafer-to-wafer" variations.

## RESULTS AND DISCUSSION

### Comparison of selected amino organo alkoxysilanes as adhesion promoters

In addition to APS two analogs were also studied to determine the effects of certain structural changes on the coupling of PMDA/ODA to the silicon dioxide surface. One was *N*-(2-aminoethyl)-3-amino-propyltrimethoxysilane, Union Carbide's "Silane Coupling Agent A-1120", here designated "AAPS"; and *N*-methyl-3-aminopropyltrimethoxysilane, here designated "MPS".<sup>13</sup> The APS and AAPS were the standard commercial grades and were not redistilled before use. The structures of the three promoters are shown in Figure 2.

Although AAPS and MPS differ from APS in having methoxy rather than ethoxy groups, it can be assumed that this has no effect on the bonding to the silica surface since hydrolytic removal of the alkoxy groups takes place in the aqueous solution prior to its application to the surface. It is known that methoxysilanes are hydrolyzed more readily than ethoxysilane,<sup>14</sup> so in all of the experiments approximately one hour was allowed for hydrolysis before the adhesion promoter was applied to the substrate surface.

Figure 3 gives a comparison of the adhesion peel strengths achieved with the three coupling agents. When they were applied in the standard manner from aqueous solution, AAPS gave the highest value, APS the next, and MPS the lowest. The three adhesion promoters presumably bond similarly to the silica surface and form

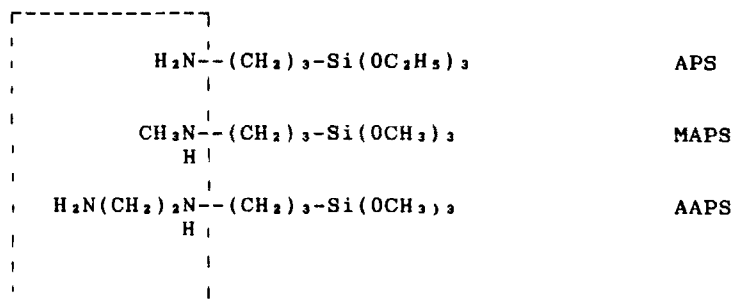
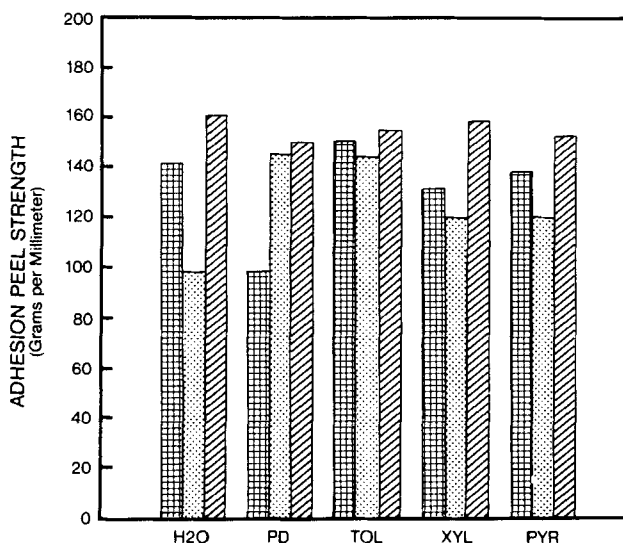
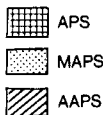


FIGURE 2 Variation in chemical structure of adhesion promoters.



Values reported are for 0.1% solutions of adhesion promoter in solvent

ADHESION PROMOTER



SOLVENTS

H2O	(natural pH)
PD	2, 4 -pentanedione
TOL	toluene
XYL	xylene
PYR	pyridine

FIGURE 3 Solvent effects on adhesion.

layers of comparable strength since all three are trihydroxysilanes at the time the surface is treated.<sup>15</sup> To explain the observed differences in adhesion values it is reasonable to consider primarily the difference in the amino-containing "tail groups" and their ability to interact with the polyamic acid to form amide and imide links.

When the uncured PMDA-ODA is applied to the treated surface, the adhesion promoter reacts with the amic acid to form a salt. During the subsequent curing the amino and carboxyl groups are first regenerated and then amide formation occurs. If the original amino group was primary, further conversion to an imide can take place, accompanied by simultaneous cleavage of an amido group of the polyamic acid chain.<sup>5</sup> Figure 4 illustrates this sequence for the reaction of APS with the polyamic acid.



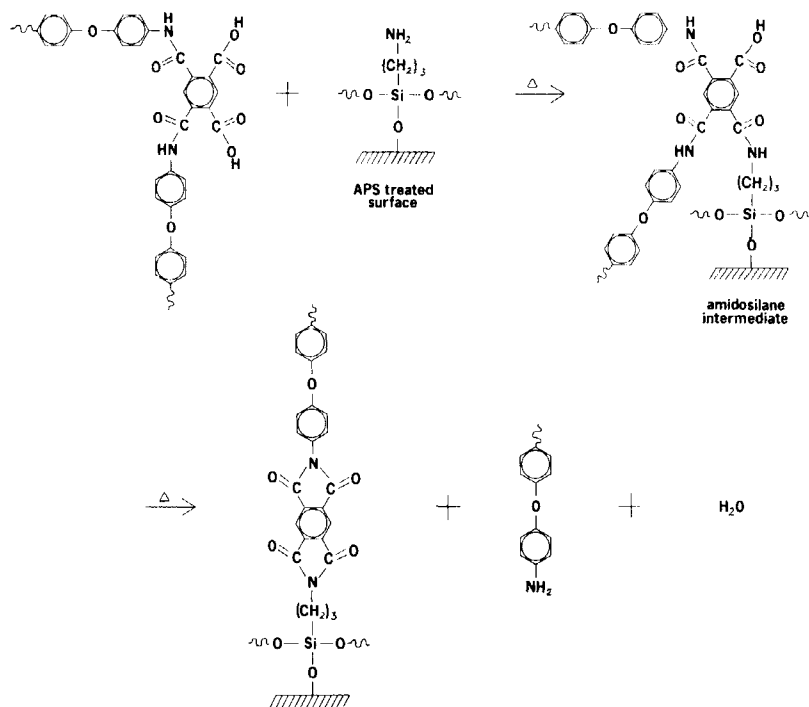


FIGURE 4 Sequence of reactions in the coupling of polyimide to a silicon dioxide surface treated with APS adhesion promoter.

Both APS and AAPS have primary amino groups, so both can give strong imide linkages to the polyimide. AAPS, in addition, has a secondary amino group which could form an amide link to a second chain. The better adhesion obtained with AAPS can be rationalized on the basis of its greater functionality.

MAPS, on the other hand, has only a secondary amino group, so it could not form imido linkages without the elimination of a methyl cation. Such an unsymmetrical cleavage of the carbon–nitrogen bond would be unlikely to occur even at high temperature. Furthermore, even the formation of amido linkages is slower for secondary than for primary amines because of steric hindrance by the additional substituent. It is not necessarily true that imide formation results in better adhesion than can be brought about with

amide formation, even though, with imides, there are two bonds between each silane unit and the polyimide. When applied from aqueous solution MAPS was less effective than either APS or AAPS but still gave peel strengths that were about four times as great as those obtained when no adhesion promoter was used.

Three additional and possibly relevant points should be mentioned here. First, the molecular packing of a polyimide has a profound effect on adhesion. In the experiments of this study entrained dust should not have affected the results because of the care taken in sample preparation; however, it is possible that molecular fragments such as ODA or oligomers liberated during imide formation may have had an effect on the molecular packing.

Second, it is assumed for the present study that all three adhesion promoters form layers of comparable mechanical strength. This is reasonable as the adhesion promoters have similar "head groups"; therefore it is not thought that differences in adhesion were due to differences in the strength of the interfaces between the promoters and the silica surfaces.

Third, interdiffusion of the adhesion promoter into the polymer film can provide enhanced adhesion.<sup>4</sup> Variations in chemical structure can have a substantial effect on polarity and thereby on solvent-polymer interactions, leading to differences in swelling and interdiffusion. Such swelling is also controlled by a three-dimensional network formed by the "head groups" which lead to interpenetrating polymer networks and thereby fosters good adhesion through molecular entanglement of the adhesion promoters with the cured polyimide.

The optimum pH range for the reaction of alkoxy silanes with silica surfaces is 7 to 10.<sup>5</sup> Since the organosilanes in the present study give aqueous solutions in this range, it can be considered that their amino groups are in effect catalyzing the reaction and might also have such an effect when the organosilane is applied from an organic solvent rather than water.

### **Effects of organic solvents on adhesion**

Water is generally considered a key to the proper performance of alkoxy silane adhesion promoters in view of the necessary initial hydrolysis. It was of interest, however, to see how adhesion

promoters applied from essentially anhydrous organic solvents could affect the  $\text{SiO}_2$ /PMDA-ODA system. The results should shed light on the fundamental role of water, and, furthermore, examination of solvent variations could uncover additional factors of importance in promoting adhesion.

Four organic solvents, including a weakly acidic one and a weakly basic one, were studied:

<i>Solvent</i>	<i>Maximum water content</i>
2,4-Pentanedione— $\text{p}K_a = 9.0^{16}$	0.1% by weight
Toluene	0.03
Xylene	0.05
Pyridine— $\text{p}K_b = 8.8$	0.1

Tests with deionized water as the solvent were also conducted as standards for comparison.

The results are summarized in Figure 3 and Table I. AAPS was in all cases the superior adhesion promoter. With all three promoters the organic solvents gave comparable adhesion values, though APS, when applied from pentanedione solution, gave lower-than-expected values. This can be explained on the basis of blockage of the primary amino group by reaction with the ketone solvent to form a Schiff's base. AAPS also has a primary amino group, but its blockage would still leave the secondary amino group available for amide formation.

The adhesion values generated using the organic solvents were all quite good in spite of the very low water content of these solvents. Since these materials are less apt than water to interact with the  $\text{SiO}_2$  surface, they do not compete with the adhesion promoter, as water does, for interaction with the silicon dioxide surface, and they therefore are good media for the application of the promoter.

In addition to the very small amounts of water present in the organic solvents, some was presumably present as water adsorbed on the silica surface or introduced *via* atmospheric humidity after the spin application. Nevertheless, it is clear that good adhesion can be achieved with only a very small amount of water present. For example, in the application of APS from a 0.1% solution in toluene of 0.03% water content, there were, assuming for the moment no additional gain from ambient water, only about four molecules of water per molecule of APS—little more than is equivalent to the

TABLE I  
Solvent effects on adhesion (see text and refer to Figures 2 and 3)

Solvent	Adhesion promoter	pH	Conc. (%)	Baking temp., °C	Peel strength (g/mm)
Water	AAPS	NAT	0.1	85	160.5*
Water	APS	NAT	0.1	85	141.2*
Water	MAPS	NAT	0.1	85	97.9
Water	AAPS	2	0.1	85	1.6
Water	APS	2	0.1	85	0.8
Water	MAPS	2	0.1	85	0.8
Water	AAPS	12	0.1	85	138.0*
Water	APS	12	0.1	85	101.1
Water	MAPS	12	0.1	85	93.1
PD	AAPS	NAT	0.1	85	149.2*
PD	APS	NAT	0.1	85	97.9
PD	MAPS	NAT	0.1	85	144.4*
Toluene	AAPS	NAT	0.1	85	154.1*
Toluene	APS	NAT	0.1	85	149.2*
Toluene	MAPS	NAT	0.1	85	142.8
Xylene	AAPS	NAT	0.1	85	157.3*
Xylene	APS	NAT	0.1	85	130.0
Xylene	MAPS	NAT	0.1	85	118.7
Pyridine	AAPS	NAT	0.1	85	150.8*
Pyridine	APS	NAT	0.1	85	136.4
Pyridine	MAPS	NAT	0.1	85	118.7

Note: PD = 2,4-pentanedione, Conc. = concentration.

\* = tear values (see text).

Natural pH of AAPS in water (0.1%) = 9.8.

Natural pH of APS in water (0.1%) = 10.

Natural pH of MAPS in water (0.1%) = 9.9.

three ethoxy groups—yet adhesion values of around 150 grams per millimeter were obtained. Since water is also formed when the hydroxysilanes react with the hydroxyl groups on the silica surface, all that is theoretically required is a small amount of water to get the condensation started. Direct reaction of the alkoxy silanes with the hydrated silica surface, with liberation of alkanol, may also occur.

When applied from organic solvents, MAPS was much more effective as an adhesion promoter than it was when applied from aqueous solution. The reason for this is not obvious though it may be the result of better accessibility of the hydrophobic aminoalkyl

groups when the adhesion agent has been applied from an organic solvent.

## CONCLUSIONS

For improving the adhesion of a polyimide film to a silicon wafer, organo trialkoxysilane coupling agents with primary amino groups are more effective than ones containing only a secondary amino group when the agents are applied from aqueous solution to the clean, native silicon dioxide surface of the silicon wafer. The formation of imide links between the coupling agents and the polyimide—possible with the primary amine derivatives but not with the secondary—may contribute to the superior performance, though steric interference to amide formation in the case of the secondary amine undoubtedly also plays a part.

The presence of more than one amino group in the silane molecule increases the opportunity for chemical bonding of the coupling agent to the polyimide and results in improved bonding.

Highly satisfactory adhesion can be obtained, even with a silane having only a secondary amino group, when the agents are applied from essentially anhydrous organic solvents.

It should be possible to develop an "ideal" application medium by adjustment of the water content of an appropriate water-miscible organic solvent.

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