An Adhesion Study of Poly(Phenylquinoxaline) on Silicon Wafers

C. McGARVEY, P. BECCAT, and N. ZANIER-SZYDLOWSKI*

Institut Français du Pétrole, 1, 4 avenue de Bois-Préau, 92 500 Rueil-Malmaison, France

SYNOPSIS

This study is an investigation of the adhesion between poly(phenylquinoxaline) (PPQ) and γ-aminopropyltriethoxysilane (γ-APS)-treated silicon wafers. In order to determine the locus of failure of the PPQ film-coated wafers, when the coating was mechanically removed from the surface, the surface-sensitive techniques of X-ray photoelectron spectroscopy and contact angle measurements were employed. This permitted an analysis of the surface that was exposed when the film was removed from the substrate. In addition, FTIR spectroscopy was used to study the effect of the thermal treatment of the film-coated wafers on the silane layer. Treatment of the coated wafers up to temperatures in excess of 250°C caused a deterioration of the γ-APS layer, leading to a loss in adhesion of the coating, which was likely a result of the decrease in the density of the PPQ chains, which become anchored in the silane layer as the silanol groups condense during curing. When treatment temperatures are allowed to reach 400°C, the silane layer becomes severely degraded. It was found that the locus of failure remained the same, regardless of whether or not the coated wafer was subjected to aging in boiling water. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Poly(phenylquinoxaline) polymers constitute a group of polymers that are derived from the same group as are the polyimides[1-5] and, as thermostable polymers, they are used as dielectric coating materials for multichip modules using high-density multilayer interconnect technology (HDMI). Poly(phenylquinoxalines) (PPQs) offer distinct advantages over polyimides for this purpose. Polymer solutions of PPQ are stable at ambient temperature, which means that the coating thickness and film quality are reproducible. The curing of the polyamic acid precursors, used in polyimide coatings, involves an imidization reaction with the loss of water and solvent, whereas with PPQ, the polymer solution used in the coatings is composed of a fully cyclized polymer in a solvent mixture and, therefore, only solvent removal is necessary. The thermal stability of PPQ in air (stable to 500°C) is attractive for the processing of components that require repeated deposition of metals at high temperatures.

It is important to note that the adhesion between the film and the substrate surface remains strong, which is often a difficult end to achieve, especially when the system is subjected to a humid environment for a prolonged period of time. Generally, good adhesion between an organic polymer and an inorganic substrate, especially one that must be forcibly smoothed and polished, is difficult to obtain. It has been our experience that, when the PPQ-coated silicon wafers are heated to the temperatures required for the eventual application of the coatings, the adhesive strength of the film often deteriorates, especially when the polymer-coated wafer is subjected to aging in boiling water to simulate exposure to prolonged humid conditions. This deterioration occurs even when a silane coupling agent, such as γ-aminopropyltriethoxysilane, is used to enhance adhesion.

The aim of this study was to determine the effect of the curing process on the adhesion of PPQ coatings to γ-aminopropyltriethoxysilane-treated silicon wafers, in terms of the locus of failure when the polymer detaches from the wafer, whether it be

* To whom correspondence should be addressed.

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within the silane layer, the polymer, or the interphase region. The study centered on an examination of the silicon wafer surface, following the mechanical removal of the polymer films from the substrate. In order to determine the locus of failure, an investigation of wafer surfaces was carried out using the surface-sensitive techniques of XPS and contact angle measurements, coupled with FTIR spectroscopy, used to determine the effect of the heat treatment programs on the silane coupling agent.

EXPERIMENTAL

Materials

Poly(phenylquinoxaline) (trade name SYNTORG IP 200) was supplied by Cemota (Solaize, France), as an 11% by weight solution of the polymer in a solvent system of 65/35 v/v *meta*-cresol/xylene. The structure of the polymer is shown in Figure 1. The silicon wafers were supplied from Centre National d'Etudes en Telecommunications (CNET), Grenoble, France. γ-aminopropyltriethoxysilane (γ-APS) was obtained from Fluka and was used as received.

Procedures

FTIR Spectroscopy of γ-APS Films

ZnSe disks (12 mm in diameter and 1 mm in thickness) were treated with concentrated H_2SO_4 for several hours and were then rinsed with high-purity water to ensure their cleanliness. Reference spectra were obtained for the clean disks prior to the deposition of the silanes. The discs were then immersed in a solution of 1% v/v γ-aminopropyltriethoxysilane in a mixture of 95% methanol/5% water (v/v). The solution had been aged for 48 h to ensure a high degree of hydrolysis of the silane. The discs were immersed in the solution for 40 sec and were then allowed to air-dry before being submitted to one of the following heat treatment sequences:

1. 100°C: 30 min in an oven in air.
2. 250°C: 30 min at 100°C in air, followed by a ramp in temperature of 15°C/min to 250°C, heating for 2 h under flowing nitrogen.
3. 320°C: 30 min at 100°C in air, followed by a ramp in temperature of 15°C/min to 250°C, heating for 30 min in flowing nitrogen, followed by a ramp in temperature of the same rate to 320°C, heating for 2 h, in flowing nitrogen, then cooling to 200°C slowly, before removal of disks from the furnace.
4. 400°C: 30 min at 100°C in air, followed by a ramp in temperature of 15°C/min to 250°C, heating for 30 min in flowing nitrogen, followed by a ramp in temperature of the same rate to 320°C, heating for 30 min under flowing nitrogen, followed by a ramp in temperature of the same rate to 400°C, heating for 30 min, under flowing nitrogen, then cooling to room temperature.

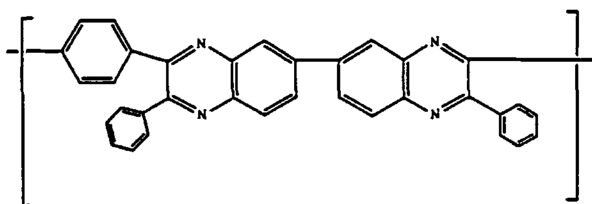

Figure 1 Structure of the poly(phenylquinoxaline).

The heat treatment sequences described above were selected to conform to the heat treatment processes used industrially (at CNET) for the conditioning of poly(phenylquinoxaline) on silicon wafers, which have first been primed with γ-APS.

For the attenuated total reflectance spectra, the silicon crystals (10 mm × 5 mm × 0.5 mm (parallelograms, with end faces cut at 45°), prepared from the silicon wafers (supplied by CNET), were first treated with a cleaning solution of $\frac{2}{3}$ concentrated H_2SO_4 and $\frac{1}{3}$ H_2O_2 (v/v) for 20 min. The crystals were treated with the same γ-APS solution as above, by immersion in the solution for a period of 40 sec, followed by air-drying of the crystals. The crystals were then dipped into the polymer solution. The plaques were then put through the same sequences as above, except for the plaque at 100°C, which is a temperature that is insufficient to remove all the solvent from the film. Some of the samples were boiled in water for 2 h to simulate long-term aging in a humid environment.

Following the heat treatments, the spectra of the coated crystals were obtained using a clean silicon ATR crystal for recording the reference spectrum. After the spectra were obtained, the polymer film was peeled from the surface of the crystals in an attempt to analyze the residue left on the surface of the silicon after removal of the film. It was found that complete removal of the film was only possible in the case of the samples treated at 400°C, so that analysis of the other samples, after peeling, proved to be impossible.

The infrared spectra were obtained for the samples immediately after the silane deposition and after

the heat treatment. The reference spectra were digitally subtracted from the sample spectra in each case, in order to produce the resulting spectrum of the silane films without interference from the crystal or surrounding background. Infrared spectra were obtained on a Bio-Rad Digilab FTS-40 spectrometer, equipped with a TGS detector, at a resolution of 4 cm^{-1}. The spectrophotometer was purged with dry nitrogen to reduce the concentration of water vapor and carbon dioxide. For the ATR studies, a Harrick, continuously variable ATR accessory, set at 45°, was used. Generally, 256 scans were gathered for the transmission spectra. For experiments using the ATR accessory, 1024 scans were recorded.

X-ray Photoelectron Spectroscopy

Standard samples were prepared by spin-coating silicon wafers with one of two different solutions of γ-APS: either 0.05% or 1% γ-APS (by volume) in a solution of 5% water and 95% methanol (v/v). Prior to the deposition of the silanes, the wafers were cleaned by immersion in a solution composed of $\frac{2}{3}$ concentrated H_2SO_4 and $\frac{1}{3}$ H_2O_2 (v/v) for 20 min. The wafers were then rinsed well with purified water and were dried in air at 100°C before coating with the silane. The films were spin-coated onto the wafers at a velocity of 5000 rpm and the treatment time for each plaque was 40 sec. A constant volume of solution was applied to the silicon wafer and, following the 40 sec treatment time, the wafer was removed and was allowed to air-dry without rinsing. Subsequently, the coatings on the wafers were conditioned, following one of the heat treatment sequences described above for the experimental procedure for the infrared samples. Several wafers were cleaned, but not coated with silane, and served as reference samples.

Following the treatment of the wafers with either 0.05% or 1% γ-APS, the wafers were coated with poly(phenylquinoxaline) (PPQ). Coating was also done using a spin-coater. The PPQ solution [11% PPQ in a solution of 65% meta-cresol and 35% xylene (v/v)] was deposited on the wafer turning at 4500 rpm (round per min), in varying amounts, depending on the desired thickness of the final dry film. The wafer was then accelerated at 20,000 rpm per sec from 1500 rpm to a fixed rotation velocity of 6000 rpm and then spun at this rate for 45 sec. The majority of the solvent evaporated to leave a film of polymer containing approximately 15% by weight residual solvent. The wafers were then conditioned, following one of the three schedules as described above, with the maximum temperatures attained either 250, 320, or 400°C. Films could not be prepared by treatment at only 100°C as it is not possible to remove adequately the solvents at that temperature.

Following the deposition of the silanes and PPQ, and the curing procedures, the samples were prepared for XPS analysis. The standards were cut into small squares of approximately 1 cm in size. Those with polymer films were cut to a similar size after the PPQ film had been manually peeled from the surface of the wafer. It was found that only in the case of the samples that were treated to 400°C was it possible to peel manually the film from the surface to a sufficient extent so that a specimen of adequate size for XPS, bearing no visible traces of adhering PPQ film, could be obtained. Only for the wafers treated with 0.05% γ-APS and treated to 400°C was it possible to obtain a sample of PPQ film, of adequate size for analysis, whose surface had been in contact with the wafer. Several samples of PPQ film on cleaned silicon wafers, which had not been treated with the coupling agent, were prepared.

The XPS analysis was performed on any one of three surfaces, denoted *A*, *B*, and *C*, as shown in Figure 2. Surface *A* is the surface of the polymer film on the silicon wafer before the film is peeled from the surface. Surface *B* consists of the surface of the film of PPQ, which had been in contact with the wafer, but is exposed following the removal of the film from the plaque. Surface *C* is the surface of the wafer uncovered after the polymer has been peeled.

The analyses were performed on a Kratos XSAM-800 dual chamber spectrometer, using AlKα radiation (energy 1486.6 eV), at a typical pressure of 10^{-8} Torr in the sample chamber. Binding energies were referenced to C_{1s} at 284.6 eV.

Contact Angle Measurements

The analyzed samples were cut from the same wafers that were studied by means of XPS spectroscopy.

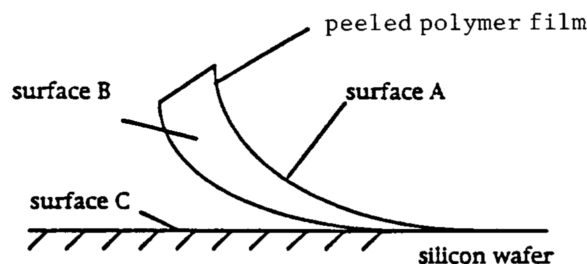

Figure 2 Schematic of the three surfaces of the assemblage, analyzed by XPS.

The contact angles were obtained on any one of three surfaces, denoted *A*, *B*, or *C*, as shown in Figure 2.

The contact angles were obtained with fresh water, which had been purified by means of an Elgastat UHQ II water purifier, to a resistivity of 18 $M\Omega$/cm. The measurements were made with a Kruss 88104 goniometer under hexadecane (Aldrich, 99%, used as received). The values reported are an average of at least 5 different equilibrium static drop measurements, obtained on different areas of the wafer surface. The contact angles, obtained on the plaques after removal of the polymer film, were measured just after the manual peeling of the PPQ, while the wafer was already immersed in hexadecane to ensure that the wafer surface was not contaminated by exposure to the ambient atmosphere.

RESULTS AND DISCUSSION

FTIR-Spectroscopy

A spectrum of γ-APS, deposited on ZnSe disks from the solution of 1% silane in the mixture of water and methanol, is shown in Figure 3. The C—H stretching region is superimposed on a large broad absorption of the OH groups from silanols, formed during the hydrolysis of the silane. There is no evidence of CH_3 absorptions, which indicates that after 48 h of aging of the treating solution, hydrolysis is essentially complete, although condensation of the silanols to form a siloxane network is not extensive, as indicated by the existence of the broad OH envelope. The two bands, at 1575 and 1479 cm^{-1}, are believed to arise from amino bicarbonate, formed by complexation of the amino groups with dissolved carbon dioxide in the treatment solution.[6]

The spectra of the silane film on ZnSe after treatment, as detailed above at 100°C, is shown in Figure 4(a). The spectrum shows three absorption bands in the aliphatic stretching region. All are believed to arise from the CH_2 groups of the silane, which are more or less incorporated into the siloxane network. The absence of a methyl stretch from any residual ethoxy groups (expected at around 2974 cm^{-1}) seems to preclude these groups as a source of the band at 2884 cm^{-1}. The amino deformation band is now shifted from 1575 to 1586 cm^{-1} and the Si—O—Si antisymmetric stretching modes of highly cured polysiloxane are visible at 1122 and 1034 cm^{-1}.

The spectra in Figure 4(b) is that of a film of γ-APS, deposited onto ZnSe from solution, and treated following the heating sequence to 250°C. The use of this treatment program is shown, from the spectrum, to lead to the degradation of some of the amino groups of the siloxane to imine functionalities. A shoulder on the 1584 cm^{-1} band is visible at 1663 cm^{-1},[7] which arises from the conversion of the

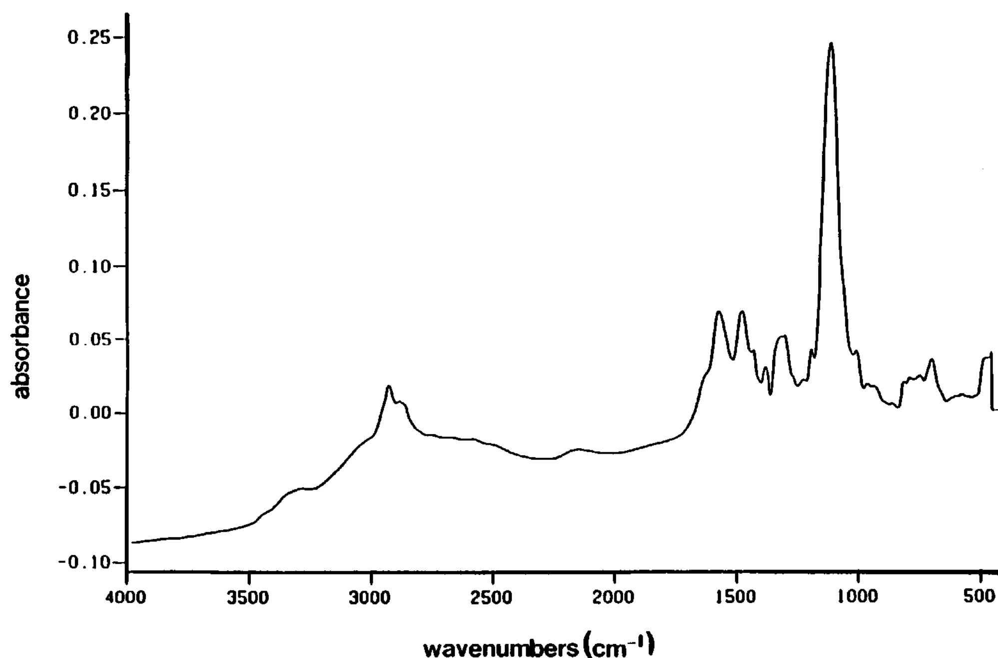

Figure 3 Transmission spectrum of a film of γ-APS, deposited from a 1% solution, on ZnSe.

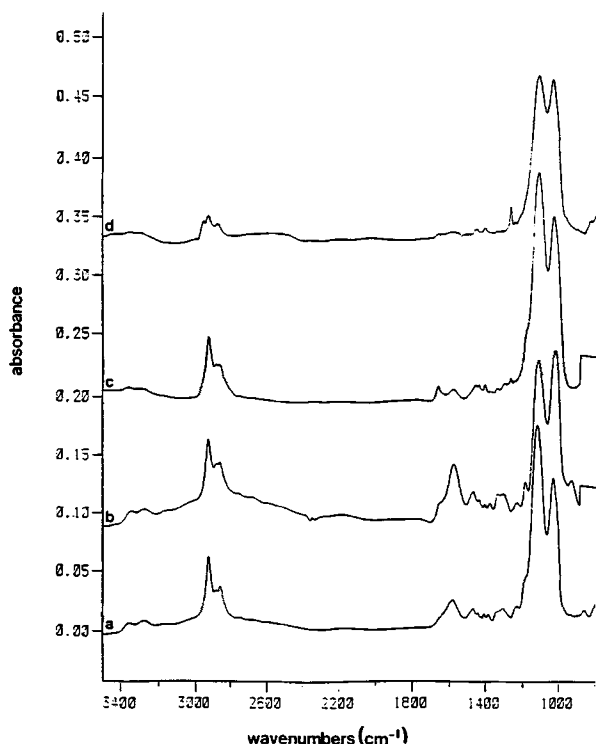

Figure 4 Transmission spectrum of a film of γ-APS, deposited from a 1% solution, on ZnSe, treated to: (a) 100°C, (b) 250°C, (c) 320°C, and (d) 400°C.

amino group to the imine by thermal degradation, even at temperatures as low as 250°C.

The spectrum, obtained for a silane film deposited on ZnSe, and subjected to the curing sequence to 320°C, is shown in Figure 4(c). The bands, due to the N—H stretches, have broadened and shifted from their original values, probably as a result of an overlap between the bands of the amino and imine groups. As a result of the curing, the imine N—H deformation band at 1668 cm^{-1} has increased in intensity, such that it has become more intense than the amino band at 1589 cm^{-1}, which indicates that treatment up to 320°C seriously degrades the —NH_2 moiety of the siloxane film.

Figure 4(d) shows the spectrum of a film of γ-APS, deposited on ZnSe from solution, and treated according to the program where the maximum temperature reached 400°C. A new band, centered at 2957 cm^{-1}, arises, which has not been assigned to any one product, but is likely to be a result of the substantial degradation of the siloxane film at this temperature. The absorption is not present, as a result of residual methyl groups from unreacted silane, since this band would be expected to be around 2973 cm^{-1}. There is also a broad, featureless absorption in the region extending from 1700–1550 cm^{-1}, which is also indicative of the degradation of the organic portion of the siloxane film. The band at 1270 cm^{-1}, which also has not been assigned, is assumed to be a result of the degradation products.

Figure 5(a) shows the ATR spectrum, obtained from an ATR silicon wafer-derived crystal, coated with γ-APS and a PPQ film and treated up to 400°C. The bands from both the aromatic stretching region of the polymer, and the aliphatic stretches of the siloxane film, are visible in the spectrum.

The spectrum, obtained from the crystal following peeling of the polymer from the crystal surface, is shown in Figure 5(b). In this case, only the bands arising from the siloxane film are observable. It is interesting to note that the band locations are consistent with those obtained on the ZnSe discs for the transmission experiments. No bands are seen in the aromatic stretching region between 3000–3200 cm^{-1}. This result suggests that if there is a polymer film remaining on the wafer, it is so thin that it cannot be detected by this technique, meaning the thickness of the residue must be less than 100 Å.

Figure 5(c) shows the spectrum of the silicon crystal, which had been treated with γ-APS and PPQ, treated to 400°C, aged for 2 h in boiling water, and then stripped of the polymer film. As in the previous case, no bands are observed in the aromatic stretching region. The CH_2 stretching bands of the siloxane are visible and, although it is difficult to make quantitative assessments using the ATR technique, it appears that the siloxane film has been partially degraded by the water treatment, as the band intensities have decreased in comparison to those observed for the non-aged sample.

Degradation is believed to occur in the organofunctional linkage of the siloxane film. This is in keeping with the results of Nishio et al.,[8] who studied the pyrolysis of various organosilanes, including γ-APS, using GC–FTIR detection methods. The authors found that scission of the siloxane did not occur through the Si—O or Si—C bonds, but rather in the organofunctional group.

X-Ray Photoelectron Spectroscopy

Table I lists the results for the XPS analysis of reference samples treated with γ-APS and treated according to the heating schedules described above. The values obtained for the binding energies are in agreement with those published previously in the literature.[9,10] The peak, detected at 97.7 eV, is the $Si^{(0)}$ signal of the silicon wafer. The signal detected at 101.1 eV is for the silicon of the native silicon oxide layer and the siloxane, which, unfortunately,

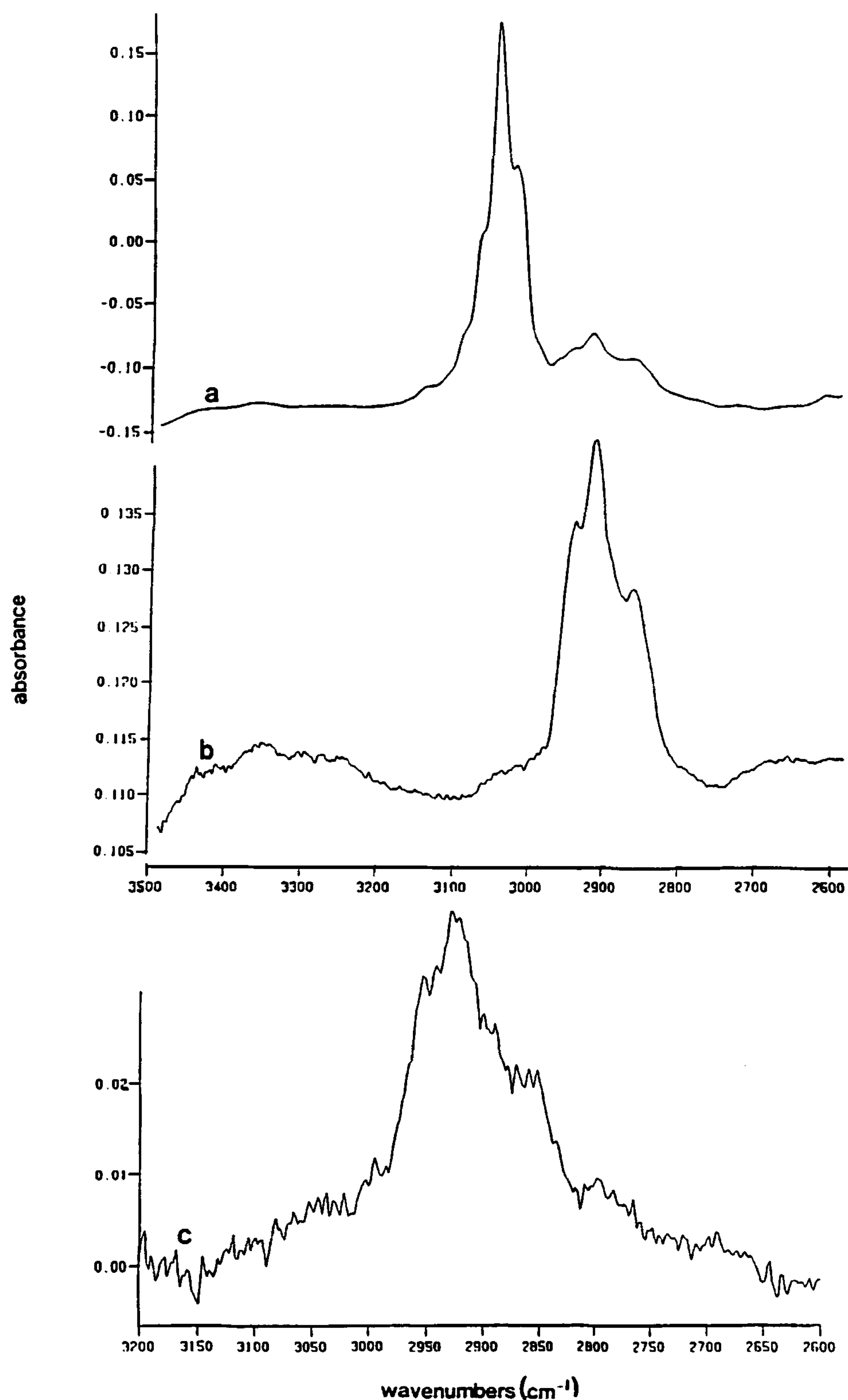

Figure 5 (a) ATR spectrum of a film of γ-APS and PPQ coating on a silicon wafer ATR crystal. (b) ATR spectrum, after peeling of PPQ film from the crystal. (c) ATR spectrum, after aging in boiling water and after peeling of the PPQ film from the crystal.

Table I XPS Analysis Results for γ-APS Treated Reference Silicon Wafers

Sample	Element	Binding Energy (eV)	Atomic Concentration (%)
1. Si	Si_{2p}	97.7	37
	Si_{2p}	101.1	11
	C_{1s}	284.6	11
	N_{1s}	398.3	0.8
	O_{1s}	532.3	41
2. Si/0.05% APS/400°C	Si_{2p}	97.7	14
	Si_{2p}	101.2	9
	C_{1s}	284.6	41
	N_{1s}	398.4	5
	O_{1s}	532.7	32
3. Si/1% APS/ 400°C	Si_{2p}	97.7	2.8
	Si_{2p}	101.2	12
	C_{1s}	284.6	42
	N_{1s}	397.6	6
	O_{1s}	532.2	36
4. Si/1% APS/ 320°C	Si_{2p}	97.7	0.6
	Si_{2p}	101.2	11
	C_{1s}	284.6	47
	N_{1s}	397.6	10
	O_{1s}	532.2	32
5. Si/1% APS/ 100°C	Si_{2p}	97.7	0.2
	Si_{2p}	101.2	11
	C_{1s}	284.6	46
	N_{1s}	397.6	10
	O_{1s}	532.2	32

cannot be separated. The results for the analysis of the silicon wafers, treated with γ-APS and cured at 400°C, both for the wafer treated with the 0.05% solution and the plaque treated with 1% solution, are in keeping with the values that would be expected for an idealized film of polymerized silane on the surface, as shown in Figure 6. In reality, the film is expected to be multilayer, but the surface analyzed would be expected to be similar to that shown in Figure 6. In the case of the film obtained from the 0.05% solution, the percentage of silicon detected on the surface (14%) is greater than that for the film obtained from the more concentrated solution. This shows that the use of the less concentrated solution results in a siloxane film, which either contains voids, or is so thin that the silicon (0) is also observed. In the case of the siloxane film obtained from the 1% γ-APS solution, only 2.8% silicon is detected, which indicates that the siloxane coating in this case is thicker and more complete on the surface.

The coating thickness may play a role in the adhesion of the polymer film to the silicon wafer. Studies have shown that the siloxane film thickness, as controlled by solution concentration, can significantly affect the adhesion between the primed surface and the adhering film. Kaul et al.[11] found that when α-Al_2O_3 is primed with γ-APS, and then is coated with polyethylene (which, like PPQ, is not expected to react with the coupling agent), the peel strength depended on the thickness of the siloxane layer, with an optimum thickness of around 1000 Å.

With respect to the samples treated with 1% promoter, it is interesting to note that, for the case of the promoter cured to 400°C, the quantity of nitrogen detected is lower than for those samples treated at lower temperatures, and the quantity of $Si^{(0)}$ (from the wafer) is higher. This would indicate that degradation of the silane (as was also observed using infrared spectroscopy), is indeed occurring, leading to a deterioration of the siloxane film, which is detrimental to the adhesion of the polymer on the wafer surface, especially in the case of the thinner films prepared with 0.05% promoter.

Table II contains the XPS results for reference samples that were aged by treatment in boiling water for 2 h. From a comparison of the XPS results in Table I and Table II, it is evident that a 2-h treatment in boiling water leads to the partial destruction of the siloxane coating on the wafer. For each of the three samples with different heat-treatment histories, the quantity of $Si^{(0)}$ is much higher than prior to the water aging. The quantities of carbon and nitrogen are significantly decreased. It is also important to note that the degradation of the siloxane by boiling water appears to be inversely proportional to the extent of heat treatment. The sample, treated to only 100°C, shows a much larger quantity of $Si^{(0)}$ on the surface (41%), as compared to the sample treated at 320°C (27%) or to 400°C (13%). These

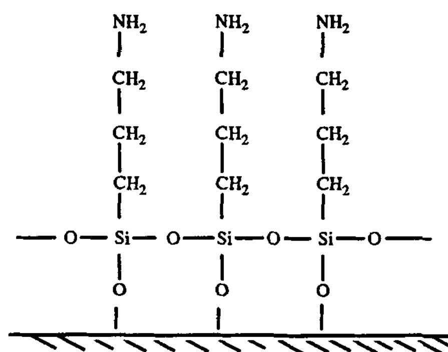

Figure 6 Idealized structure of a film of γ-APS film on a silicon wafer surface.

Table II XPS Analysis Results for γ-APS Treated Silicon Wafers after Aging 2 H in Boiling Water

Sample	Element	Binding Energy (eV)	Atomic Concentration (%)
6. Si/1% APS/ 400°C	Si_{2p}	97.7	13
	Si_{2p}	101.2	10
	C_{1s}	284.6	35
	N_{1s}	397.6	2.5
	O_{1s}	532.2	40
7. Si/1% APS/ 320°C	Si_{2p}	97.7	27
	Si_{2p}	101.2	10
	C_{1s}	284.6	24
	N_{1s}	397.6	2.0
	O_{1s}	532.2	37
8. Si/1% APS/ 100°C	Si_{2p}	97.7	41
	Si_{2p}	101.2	10
	C_{1s}	284.6	14
	N_{1s}	397.6	1.1
	O_{1s}	532.2	34

results suggest that the crosslinking of the silanols, deposited on the wafer surface, that were encouraged by heating to form a dense, highly-crosslinked film, is necessary to impart good water stability to the siloxane film. Consequently, although the film treated to 400°C may degrade somewhat during the heating sequence, the remaining film appears to have better water stability than those treated to lower temperatures, which may ultimately have an effect on the adhesion of the polymer to the wafers.

Analysis of the substrate surface, following removal of the PPQ film for assemblages composed simply of silicon wafers covered with PPQ (samples 9 and 10, Table III), shows that there is probably a small amount of polymer remaining on the surface after peeling has been completed. This is evident from the fact that more nitrogen is detected on the surface of these plaques than on the reference (sample 1). These results support the view of some authors, who believe that it is impossible for true, complete, interfacial failure to occur.[12] More likely, a small amount of low molecular weight polymer is left on the surface following the peeling. Contact angle results will support this view. In addition, comparisons of the results for samples 9 and 10 indicate that the locus of failure, both before and after treatment with boiling water, is the same.

A comparison of sample 2 with sample 11 yields some interesting observations. First, the quantity of nitrogen is lower in the latter case, which may indicate a covering of the siloxane film by a layer of PPQ, which contains a lower percentage of nitrogen than does the siloxane film. This point is reinforced by the fact that the N1s signal could not come from the siloxane layer, considering that the signal Si (101.2 eV) is certainly due to the SiO_2 that is associated with the 15% of $Si^{(0)}$, and is not due to siloxane. The appearance of an XPS band for silicon may be a result of the thinness of the residue on the wafer and may not be indicative of exposure of the silicon surface, as the depth of penetration during XPS analysis can be as high as 50 Å. There are not significant differences in the values obtained for samples 11 and 12, which fact indicates that the locus of failure before and after the treatment in boiling water is consistent.

Table III XPS Results of Analysis of Silicon Wafers Following Film Peeling (Surface C)

Sample	Element	Binding Energy (eV)	Atomic Concentration (%)
9. Si/PPQ/ 400°C	Si_{2p}	97.8	35
	Si_{2p}	101.2	9
	C_{1s}	284.6	19
	N_{1s}	397.7	2.0
	O_{1s}	532.6	35
10. Si/PPQ/ 400°C/H_2O	Si_{2p}	97.8	35
	Si_{2p}	101.2	10
	C_{1s}	284.6	15
	N_{1s}	397.7	1.4
	O_{1s}	532.6	39
11. Si/0.05% APS/PPQ/ 400°C	Si_{2p}	97.8	15
	Si_{2p}	101.2	6
	C_{1s}	284.6	45
	N_{1s}	397.7	3.0
	O_{1s}	532.6	30
12. Si/0.05% APS/PPQ/ 400°C/H_2O	Si_{2p}	97.8	21
	Si_{2p}	101.2	7
	C_{1s}	284.6	35
	N_{1s}	397.7	2.9
	O_{2s}	532.6	33
13. Si/1% APS/PPQ/ 400°C	Si_{2p}	97.7	15
	Si_{2p}	101.2	5.1
	C_{1s}	284.6	53
	N_{1s}	397.6	4.7
	O_{1s}	532.2	22
14. Si/1% APS/PPQ/ 400°C/H_2O	Si_{2p}	97.7	19
	Si_{2p}	101.2	6.4
	C_{1s}	284.6	46
	N_{1s}	397.6	4.9
	O_{1s}	532.2	24

Samples 13 and 14 show a lower concentration of oxygen and a larger concentration of carbon in comparison to the reference (samples 3 and 6), which were also treated at 400°C. Since the polymer contains no oxygen, and 90% carbon, this would indicate a masking of the siloxane coating by a partial or complete film of polymer left on the surface after peeling. The quantity of nitrogen on the surface of the samples is also lower than on the reference.

Table IV contains results from the analysis of three PPQ films. The results of the analysis of the top surface of a PPQ film on a wafer, after treatment up to 400°C, are reported for sample 15. The agreement between the carbon and nitrogen values is close to the theoretically predicted values. For the films peeled from the silicon wafers, and analysis of the surface that had been in contact with the plaque (and forcibly with the siloxane), there was no evidence whatsoever for silicon or siloxane on the films (samples 16 and 17). This indicates that the failure of the assemblages during peeling does not occur through the siloxane layer, neither before nor after treatment with boiling water. This reinforces the view that the locus of failure probably exists close to the interface between the siloxane and the polymer film, but within the polymer film, exposing a thin coating of polymer.

It is unfortunate that the signal from the native oxide of silicon cannot be differentiated from the siloxane film covering the wafer. In addition, since both the silane and the polymer contain nitrogen, it was not possible to use this element to differentiate between residue consisting of siloxane and that composed of polymer. In any case, the thickness of the residue was apparently so thin that silicon was always observed in the analyses. It is evident that the use of a dilute treatment solution leads to a siloxane film, which may not completely cover the surface of the wafer, or is insufficiently thick to serve as an effective coupling agent between the polymer and the silicon wafer. The results also indicate that, as the temperature to which heat treatment is allowed to progress is increased, the resulting siloxane film becomes increasingly resistant to degradation by boiling water. This would suggest that treatment at higher temperatures leads to greater crosslinking of the siloxane film, meaning that hydrolysis of more siloxane linkages is necessary before film desorption. Desorption, in this sense, means a gradual hydrolysis of the siloxane bonds, leading to the release of portions of the siloxane film when sufficient siloxane bonds have been broken to allow this release to occur. This means that, as the temperature is increased, desorption will occur more slowly. Although degradation of the siloxane film is significant at 400°C, the siloxane skeleton of the layer is expected to remain intact during heat treatment, but becomes highly crosslinked as a result of the increased temperature employed, since the degradation occurs in the aliphatic linkages and scission is not through the Si—O or Si—C linkages. The resulting layer proves to be significantly more resistant to hydrolysis than the siloxane film, which results from heating at 100°C.

Table IV XPS Analysis of PPQ Films

Sample	Element	Binding Energy (eV)	Atomic Concentration (%)
15. Si/PPQ/ 400°C[a]	Si_{2p}	99.9	0.2
	C_{1s}	284.6	86
	N_{1s}	398.0	9.5
	O_{1s}	533.4	4.3
16. Si/0.05% APS/ 400°C[b]	C_{1s}	284.5	85
	N_{1s}	397.9	10
	O_{1s}	533.3	5
17. Si/0.05% APS/ 400°C/ H_2O[b]	C_{1s}	284.6	87
	N_{1s}	397.9	10
	O_{1s}	533.3	3

[a] Surface A, PPQ film on the plaque before peeling.
[b] Surface B, PPQ film surface, after peeling, which had been in contact with the plaque.

The locus of failure for assemblages of silicon wafers covered with PPQ, but not treated with coupling agent, appears to be between the wafer and the polymer, as expected, perhaps with a small quantity of polymer left on the wafer. In the case of samples treated with γ-APS, the failure appears to occur close to the siloxane–polymer interface, probably through a layer of polymer that may be weaker than the bulk. This concept will be discussed later.

Contact Angle Measurements

The contact angles obtained on the standard samples are shown in Table V. All wafers were treated with a 1% γ-APS solution, as described in in the experimental section.

From Table V, it is clear that the contact angles on the wafers covered with siloxane films do not vary widely following the different heat treatment sequences employed. It is also interesting to note that the surfaces that are generated by the heating of the silane films are not highly hydrophobic. This is in keeping with the results of Herder et al.,[13] who

Table V Contact Angle Values (Water–Hexadecane) for Silicon Wafer Standards Treated to Various Temperatures

Wafer Treatment	Maximum Treatment Temperature (°C)	Aging in Boiling (H_2O)	Contact Angle
1. H_2SO_4–H_2O_2		No	11
2. γ-APS	100	No	120
3. γ-APS	100	Yes	32
4. γ-APS	250	No	95
5. γ-APS	250	Yes	56
6. γ-APS	320	No	116
7. γ-APS	320	Yes	45
8. γ-APS	400	No	115
9. γ-APS	400	Yes	59

found low advancing and receding contact angles for γ-APS on mica surfaces. When the silane film is cured, the silanol groups condense to form a network crosslinked to the surface and to one another. This reaction is known to be driven by heating.[14] In the case of γ-APS, the observed contact angle on the surface of the wafers will clearly be a function of the degree of crosslinking, but also of the degree to which the silane film becomes degraded. Even at temperatures as low as 250°C the extent of conversion of the amino groups to imine functionalities is significant. These two factors explain the difference in the contact angles of the silane-treated wafers, cured at different temperatures.

The results for the treated wafers, after aging in boiling water, are instructive. The contact angle on the wafer treated to 100°C is more than 20° lower than that treated to 400°C. This is further evidence to support the idea that, first, the higher temperatures lead to greater crosslinking of the siloxane film (and consequently fewer Si—OH groups, meaning a more hydrophobic surface) and that, because the crosslinking is more extensive, the desorption of the film from the surface during aging will be less pronounced (also likely to lead to a more hydrophobic surface). These results support the XPS findings.

Table VI contains the results obtained from the contact angle measurements of the PPQ films on silicon wafers, before the peeling of the polymer film (surface A, Fig. 2), and on wafers following removal of the film (consequently, the contact angle measurement of the residual film, if any, is left on the wafer after peeling).

The above results indicate that, in the case of the assemblages consisting of silicon wafers and PPQ without coupling agents, the angle of contact on the plaques after peeling is high, but following treatment of the assemblage in boiling water for 2 h, the contact angle has dropped to 88°. This may be due to a migration of low molecular weight polymer material from the surface, leading to a more hydrophilic surface, composed mainly of the silicon wafer and/or the adsorption of some water on the surface of the plaque, which leads to a correspondingly low contact angle.

In contrast, for sample 5, which was heated to the same temperature, and had been treated with γ-APS prior to deposition of the polymer, the angle of contact is 180°. The surface of the plaque is completely hydrophobic, in fact a drop of water placed on this surface rolls off. It should be noted that as the temperature of heat treatment decreases, so does the contact angle on the peeled surface. If one considers that the coupling agent serves to "anchor" the polymer film to the surface by crosslinking the silanols around the polymer chains during curing, and upon peeling, a film of polymer is forcibly left

Table VI Contact Angle Values for Silicon Wafers Following Peeling of PPQ

Sample	Treatment	PPQ Film Thickness (μm)	Contact Angle on PPQ	Contact Angle on Si Wafer
1. Si/PPQ	400°C	8.0	128	123
2. Si/PPQ	400°C/H_2O	8.0	125	88
3. Si/0.05% γ-APS/PPQ	400°C	8.4	125	153
4. Si/0.05% γ-APS/PPQ	400°C/H_2O	8.4	133	157
5. Si/1% γ-APS/PPQ	400°C	8.2	131	180
6. Si/1% γ-APS/PPQ	400°C/H_2O	8.2	127	173
7. Si/1% γ-APS/PPQ	320°C	8.0	130	163
8. Si/1% γ-APS/PPQ	320°C/H_2O	8.0	132	161
9. Si/1% γ-APS/PPQ	250°C	8.0	147	142
10. Si/1% γ-APS/PPQ	250°C/H_2O	8.0	145	143

on the wafer, because of this interpenetration of polymer and siloxane, then it would follow that, as the final heat treatment temperature and crosslink density rise, more polymer would be incorporated into the siloxane network at higher temperatures, leading to a denser polymer film being left on the wafer after peeling, and consequently a higher contact angle, indicative of a more hydrophobic surface.

It should be recognized that the contact angle on the peeled wafers may be higher than that measured on the PPQ surface of the film deposited on the wafers, because the top surface may be somewhat contaminated and the surface will not have the same properties as the bulk film, where the locus of failure may occur.

The contact angles, obtained for the peeled surfaces after treatment in boiling water, do not vary significantly, as compared to those on plaques that were not aged. This is an interesting result in that it seems to suggest again that the failure occurs within the PPQ film, albeit close to the interfacial region. Otherwise, the residue on the surface would consist of a mixture of siloxane and polymer. Knowing that hydrolysis of the siloxane occurs during aging, one would expect the degradation of the siloxane, and the resulting silanols that would be formed on the surface, to lead to a significant decrease in the contact angle measured on the peeled surface. This was not the case.

In order to determine whether the measured contact angles were affected by surface contamination of the peeled wafers, resulting from interfacial contamination by residual *meta*-cresol or other impurities, solvent rinses were performed. Samples of the wafers were peeled and were then rinsed with reagent-grade acetone to remove any contaminants not composed of polymer or siloxane, both of which are insoluble in acetone. Following this, some samples were peeled, were then rinsed once with acetone, and then with chloroform. Chloroform is a good solvent for PPQ and therefore should remove any polymer not firmly adhering to the wafer by interaction with the silane and it should also rinse away any other chloroform-soluble contaminant. The results of the contact angle measurements on these samples are shown in Table VII.

The results indicate that, for the plaques that had not been treated with γ-APS, rinsing with the two solvents leads to a significant decrease in the contact angle on the surface. The contact angle on sample 1 (123°) drops to 87° after rinsing with acetone followed by chloroform. This would indicate that the residue on the silicon wafers following peeling of the film is likely to be composed of polymer, which is easily removed by rinsing. In all likelihood, this is low-molecular-weight PPQ that is left behind after detachment of the film.

In the case of the assemblage treated to 400°C, then aged in water (samples 2 and 10), the contact angle also drops dramatically following the rinse with chloroform, and is lower than before treatment with boiling water. This may be due to desorption of the polymer from the silicon wafer surface during aging, leaving less residual PPQ on the polymer after peeling. By contrast, there is little difference in contact angles between samples 3 and 11, following an acetone rinse of the latter. This demonstrates that the residue left on the surface of the silicon wafers after peeling is not composed of residual solvent, which would be eliminated by the rinse. Rather, these results seem to indicate that the residue is indeed composed of a polymer film. A rinse of sample 11 with chloroform results in a small drop in the value of the contact angle on the wafer, perhaps due to the removal of a small amount of polymer that was not firmly entangled in the crosslinked siloxane.

For the case of the wafers treated with 1% γ-APS, similar results were found. An acetone rinse

Table VII Contact Angles on Silicon Wafers Following Peeling of PPQ, and after Rinsing with Acetone or Acetone and Chloroform

Sample	Contact Angle after Acetone Rinse	Contact Angle after Acetone and $CHCl_3$ Rinse
9. Si/PPQ/400°C	112	87
10. Si/PPQ/400°C H_2O	90	68
11. Si/0.05% γ-APS/PPQ/400°C	149	129
12. Si/0.05% γ-APS/PPQ/400°C/H_2O	130	128
13. Si/1% γ-APS/400°C	153	141
14. Si/1% γ-APS/PPQ/400°C/H_2O	149	140
15. Si/1% γ-APS/PPQ/320°C	147	135
16. Si/1% γ-APS/PPQ/250°C	148	138

of samples 13 and 14 resulted in a decrease in the contact angle, presumably due to the elimination of interfacial contamination. The rinse with chloroform results in contact angles of approximately 140°, far above the values of 115° and 59° that were observed for the wafer reference samples coated with siloxanes (Table V). Following the chloroform rinse, a small decrease in contact angle was observed, again suggesting the removal of the nonentangled polymer chains on the surface, leading to a slightly less dense packing of PPQ chains in the residual film and, consequently, a less hydrophobic surface. Again, it is interesting to note that one would expect the aging treatment to result in a substantial lowering in the observed contact angle, if the locus of failure were in a region composed of coupling agent and polymer combined. Samples 15 and 16 support these results.

The contact angles measured on the reference samples showed, as was expected, that the water treatment results in a deterioration of the siloxane films, as indicated by the decrease in the contact angles on the wafer surfaces, as a result of hydrolysis first to silanol species, followed by a gradual desorption of the films, as made evident by XPS data. This decrease in contact angle with water treatment was not observed for the samples that were coated with PPQ, after aging, and following the peeling of the films. The contact angles on the silicon wafers remained high, which indicates that the silane coupling agent is not exposed on the wafer surface following failure of the assemblage. This suggests that the locus of failure occurs within the polymer film itself. This is supported by the fact that the rinsing of the plaques with chloroform leads to a small drop in the contact angle, which would be consistent with the loss of some polymer, presumably not well-entangled in the crosslinked siloxane film, through dissolution in the solvent.

CONCLUSIONS

On the basis of the results obtained from infrared spectroscopy, several conclusions can be drawn. First, modification of the siloxane films begins at temperatures as low as 250°C, primarily as a result of the thermal instability of the amino groups. As the curing temperature is increased, degradation becomes more pronounced, especially at 400°C, where degradation of the organic portion of the siloxane film appears to occur extensively, as indicated by IR spectroscopy. The degradation is especially detrimental to the adhesion of the PPQ films to the silicon wafers when a dilute silane solution (0.05%) is used. Apparently, the amount of siloxane organic moieties remaining on the wafers following curing is insufficient to promote adequate adhesion between the two phases. On the other hand, it is evident that heating leads to extensive crosslinking of the siloxane, leading to a more tenacious film on the surface, which is necessary for good resistance to hydrolysis under humid conditions, and leads to good entanglement and anchoring of the polymer chains to the siloxane layer, needed for favorable adhesion.

The adhesion of PPQ on silicon wafers is improved when 1% silane solutions are used, as opposed to dilute 0.05% solutions. These results are in keeping with those of Kaul et al.,[11] who found that the thickness of γ-APS films affects the adhesion of certain polymers on aluminum, when a reaction between the coupling agent and polymer is not possible, as evidenced by peel test measurements. Peel strength for the systems studied in that case increased with increasing siloxane layer thickness, up to a value of 1000 Å.

The results obtained from X-ray photoelectron spectroscopy clearly show that the use of a dilute silane solution results in a thinner or less homogeneous film on the wafer surface, as indicated by the fact that the silicon signal from the plaque is much more evident. Degradation of the siloxane layer occurs as a result of the aging of the wafers in boiling water. However, heating the film to 400°C before aging seems to produce a better adherence of the siloxane film on the wafer, despite the evident degradation of the organic groups of the coating during curing at this temperature. XPS data indicate that the locus of failure is definitely not within the siloxane layer, since the surface analysis of peeled samples yielded results that were different from the reference samples, and no siloxane was found on any of the three polymer films, which had been in contact with the siloxane-covered wafer.

Based on the results of this project, a mode of failure for the system studied, silicon/γ-APS/poly(phenylquinoxaline), can be proposed, which is in keeping with these findings. On the basis of the experimental data, it appears that the locus of failure is within the polymer film, but is close to the interfacial region, probably within approximately 20 Å of the interface between the siloxane layer and the polymer film. The polymer chains in the interfacial region may be partially held in the siloxane layer and may penetrate only superficially into the bulk polymer phase. The rigidity of the entirely aromatic polymer chains means that, when stress is imposed, for example during mechanical peeling of the film from the wafer, chains anchored in the siloxane film

are likely to remain embedded in the matrix, leaving a thin polymer film exposed on the surface, rather than being removed with the bulk of the PPQ coating.

Figure 7(a) shows a schematic diagram of the interface of the system before peeling, and Figure 7(b) shows the system following the peeling of the PPQ film. The variation in adhesion, as a function of the thickness of the siloxane film, is proposed to occur as a result of the number of points of contact that exist between the siloxane film and the polymer chains. The adhesion between the two phases is believed to occur as a result of "bridging" polymer chains, which are entangled in the siloxane layer and in the bulk polymer phase. If the siloxane film becomes thermally degraded, such that the entanglements between siloxane and polymer decrease, the points of contact between the siloxane and PPQ are lowered and a zone of weakness will be produced, in which polymer chains in the bulk PPQ phase will no longer be anchored in the siloxane film. In this case, the polymer will be removed more easily from the substrate, leaving a thin film of polymer on the wafer. Figure 8(a) shows a schematic diagram of the interfacial region, following the degradation of the silane, and Figure 8(b) shows the same region following the peeling of the film. In addition, the destruction of organic portions of the siloxane film, leaving mostly an inorganic system, may contribute to a decrease in the adhesion of the polymer on the substrate, simply for reasons of incompatibility of the two phases.

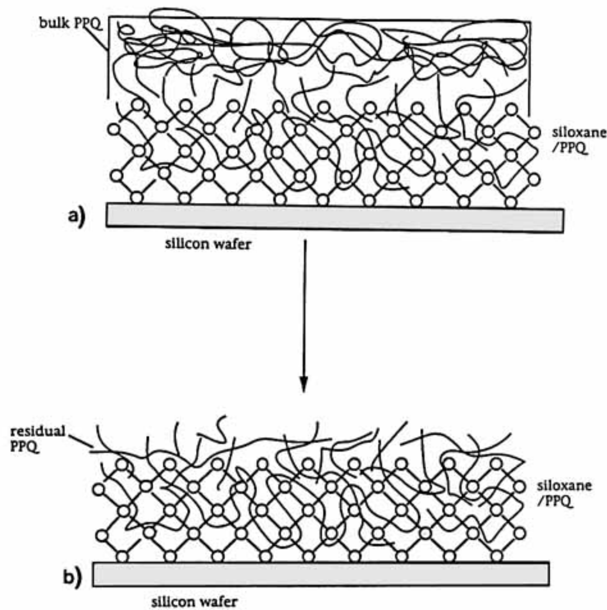

Figure 7 (a) Schematic of the silicon/γ-APS/PPQ interphase. (b) Schematic of the silicon/γ-APS/PPQ interphase, following peeling of the PPQ film.

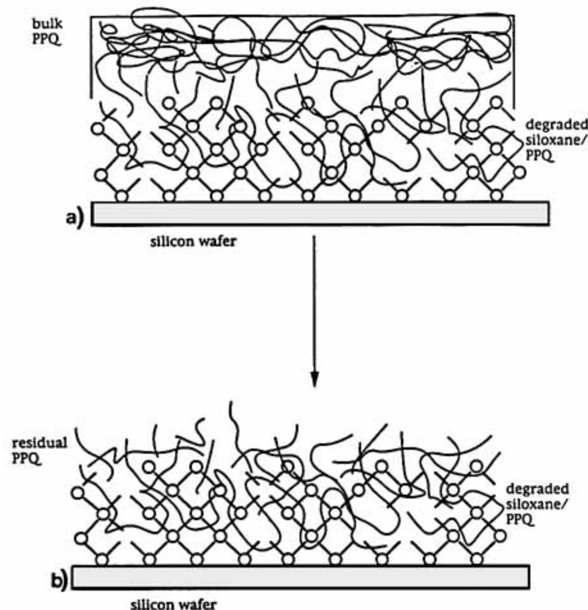

Figure 8 (a) Schematic of the silicon/γ-APS/PPQ interphase, following aging in water. (b) Schematic of the silicon/γ-APS/PPQ interphase, following aging and the peeling of the PPQ film.

The same situation results from the exposure of the silicon wafers to water. Deterioration of the siloxane coating will occur, to some extent, decreasing the number of polymer chains that are bridging between the two phases. In addition, the transformation of siloxane linkages into silanol groups leads to a greater hydrophilicity of the siloxane coating and a decreased tendency for wetting of the substrate surface by the polymer, leading to decreased adhesion. If a film of water succeeded in penetrating between the polymer and the substrate at the interface, the adhesion would then be further deteriorated, simply due to the incompatability of the polymer with the water.

Regardless of the factors that are involved in the deterioration of the adhesion, the locus of failure after peeling would remain the same. The fact that the siloxane film is not completely destroyed during the aging process, means that there will always be a certain amount of polymer anchored in the siloxane film, which will remain as a thin film on the surface, following peeling of the coating. The model suggests a thin layer of polymer remains on the surface following the peeling of the polymer film, regardless of whether or not exposure of the assemblage to moisture has occurred. Clearly, the loss in adhesion of the PPQ films on the wafers is as a result

of the degradation of the siloxane layer, leading to a decrease in the siloxane network and, consequently, a decrease in the number of PPQ chains that are anchored to the wafer through the siloxane system. Consequently, the bulk PPQ film is more prone to lose adhesion to the surface.

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