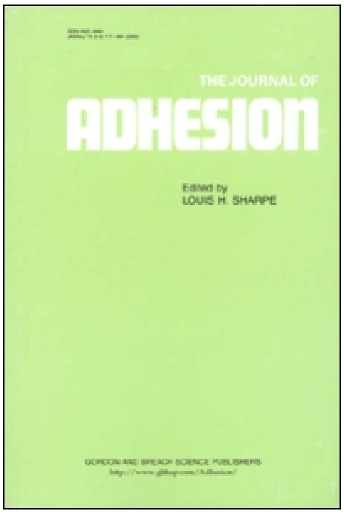

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The Structure of the Irreversibly Bound Adhesion Promoter-Substrate Interfacial Layer of γ-Aminopropylsilanetriol on Crystalline Si, as Measured by XPS and FTIR

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The irreversibly bound interfacial layer deposited by the γ-aminopropysilanetriol adhesion promoter onto a crystalline silicon substrate, which remains even after profuse washing, was found by XPS to have resulted from the fragmentation and rearrangement of the original γ-aminopropylsilanetriol molecule. A mechanism is proposed, involving the homolytic scission of the terminal N—C bond. One of the subsequent reactions is believed to involve hydrogen loss by abstraction and the formation of a terminal vinyl group, which bonds to the substrate. Support for this mechanism is found in IR spectroscopy of this layer.

KEY WORDS amine-terminated silane ester adhesion promoter; irreversibly bound surface layer; surface analysis; infrared spectroscopy; homolytic bond scission; fragmentation and rearrangement.

INTRODUCTION

Adhesion promotion by silane esters is simply the interposition of a thin layer of material capable of chemically bonding to both substrate and overlayer. Silane ester adhesion promoters are used to increase the adhesion of polymeric overlayers to inorganic surfaces, such as metal, semiconductor and glass. Qualitatively, the mechanism of adhesion to the substrate is thought to be understood:[1] when added to aqueous solution, these orthoesters [*i.e.*, Z—R—Si(OR′)$_3$, where Z is a specifically-chosen reactive group, and R and R′ are alkyl groups] quickly hydrolyze to form silanetriols, —Si(OH)$_3$. These silanetriols react, through their hydroxyl groups, not only with themselves but, supposedly, with hydroxyl groups present on the substrate. This results in the formation of a new crosslinked polysiloxane layer, 100–200 Å thick, on the original surface. The new layer is, then, bonded to the original surface by a mixture of hydrogen-bonded hydroxyls and Si—O—substrate linkages, whose equilibrium is determined, among other things, by the amount of water present. Among the groups protruding from the new polysiloxane surface are the Z groups, specifically chosen to react with the polymer to be deposited.

However, at the substrate interface, the polysiloxane structure differs from that in the bulk polysiloxane layer. This has been demonstrated[2–4] through the solvent extraction of deposited adhesion promoters and appears to depend on the structure of the adhesion promoter and, possibly, that of the substrate, as well. For example, boiling water extraction removed all but the interfacial layers of γ-aminopropyl,[2–4] γ-methacryloxypropyl[3] and γ-2′,3′-epoxypropoxypropyl[3] silanes but did not touch vinyl silane,[2] even after several days. While the effect of substrate is less clear, 181 glass,[2] E glass[3] and Pyrex[4] appear to be attacked at different rates.

Much work has been, and continues to be, carried out on the chemical, physical and use properties of deposited adhesion promoters. The interested reader is directed to a recent article[5] which contains a review of the literature on γ-aminopropylsilanetriol, the subject of the present paper. Therefore, except where we deem it necessary to make a connection between the as-deposited film and the irreversibly bound layer, we refrain from discussing the literature on the as-deposited film. Rather, we concentrate on the characterization of the irreversibly bound layer. A literature search has revealed little on the characterization of these layers.

Several suggestions have been made concerning the stability of the interfacial layer of adhesion promoters, which cannot be accounted for by the proposed reaction between hydroxyl groups: the Si—O—substrate linkages thus formed would be hydrolyzed and removed with the rest of the adhesion promoter. These suggestions include chemi/physisorption[4] and structural changes.[1,3,6] The present study was designed to resolve this issue through the use of X-ray photoelectron spectroscopy (XPS), a surface-sensitive technique capable of distinguishing valence states of atoms through the binding energy shifts of photoemitted core electrons. Infrared spectroscopy is then used to support the proposal.

EXPERIMENTAL

The substrates used for the XPS studies were undoped c-Si(100) wafers, 3 inches (7.6 cm) in diameter, and polished on one side. After removal of organic contaminants with acetone and isopropyl alcohol rinses, the oxide layer was removed by exposure to HF:40% NH_4F (1:7) for 5 minutes, followed by rinsing in freshly-prepared water of 18 MΩ resistivity. After rinsing in isopropyl alcohol and drying at 85°C, XPS revealed[7] a trace of oxygen as the only remaining contaminant. A kinetic study[7] showed the surface of this sample to be stable to oxidation for a period of several days, far longer than necessary to prepare the samples and enter them into the instruments. More recently, many laboratories from around the world[8–10] have used surface-sensitive IR, XPS and high resolution EELS to confirm the cleanliness of such surfaces and their oxidation resistance when exposed to air.

Samples thus cleaned were spin coated with a freshly-diluted solution of Union

Carbide A1100 (the orthoester of γ-aminopropyl-triethoxysilane), using a fresh sample stored under refrigeration and freshly-prepared deionized water of 18 MΩ resistivity. The pH of the solution was not modified, and remained at 10.4. The coating conditions used were 0.05% (w/w) A1100 in 95% (v/v) methanol-water at 5000 rpm for 30 seconds. This was followed by extensive washing with deionized water, in order to assure the removal of all but the interfacial layer.

Core level XPS spectra were obtained on a Vacuum Generators ESCALAB 3 Mark II electron spectrometer, using non-monochromatized Mg K_α radiation at 1253.6 eV. Under the conditions used, the measured resolution is 0.8 eV. The operating pressure in the analyzer chamber did not exceed 5×10^{-10} torr. A slight charge correction (~1 eV) was necessary.

After washing, spectral analysis was carried out at various take-off angles between 5 and 80°, measured with reference to 0° at the normal, so as to vary the depth probed, permitting analysis as a function of depth. At each angle, high resolution spectra were accumulated at the C 1s, O 1s, N 1s, Si 2s and Si 2p regions. Curve resolution was preceded by Shirley background subtraction,[11] and used Gaussian/Lorenzian ratios, peak widths and sensitivity factors determined on our instrument. To confirm that adhesion promoter was indeed deposited prior to washing, XPS spectra were taken on unwashed samples: they revealed the presence of the expected polysiloxane.

The substrates used for the IR studies were undoped samples of both c-Si(100) and c-Si(111), also polished on one side. They gave identical spectra. Because the c-Si(111) wafers were in more plentiful supply, they were used in preference to the c-Si(100), and are the substrates used for the spectra reported here.

IR spectra were obtained on a Mattson Research Series spectrometer having an MCT (*i.e.*, HgCdTe) detector cooled to liquid nitrogen temperature. The high S/N found for these spectra was obtained by coadding 15,000 spectra obtained at a resolution of 4 cm^{-1}. Spectra from the clean surface were recorded and used as the reference.

The sample preparation differed slightly from those used in the XPS study. Organic contaminants were removed with trichloroethane, acetone and propanol rinses. The oxide layer was removed by exposure to H_2SO_4:H_2O_2 (1:5) for 10 minutes, followed by HF:H_2O (1:10) for 15–20 minutes. After rinsing in freshly prepared deionized water of 15 MΩ resistivity, the samples were dried in a nitrogen stream. IR spectra revealed a trace of oxide near 1100 cm^{-1}, in addition to the phonon band near 615 cm^{-1}.

Substrates so prepared were dipped into a freshly diluted solution of Union Carbide A1100 (1% v/v) in fresh deionized water of 15 MΩ resistivity for 30 minutes, before washing several times with 15 MΩ water and redrying. Spectra so obtained were identical to those obtained on c-Si(100) substrates identically prepared, as well as on c-Si(100) substrates prepared as for the XPS studies.

RESULTS

Overlays of XPS spectra obtained at several angles are seen in Figure 1. Both the Si 2s spectra in Figure 1 and the Si 2p spectra (not shown) were decomposable into

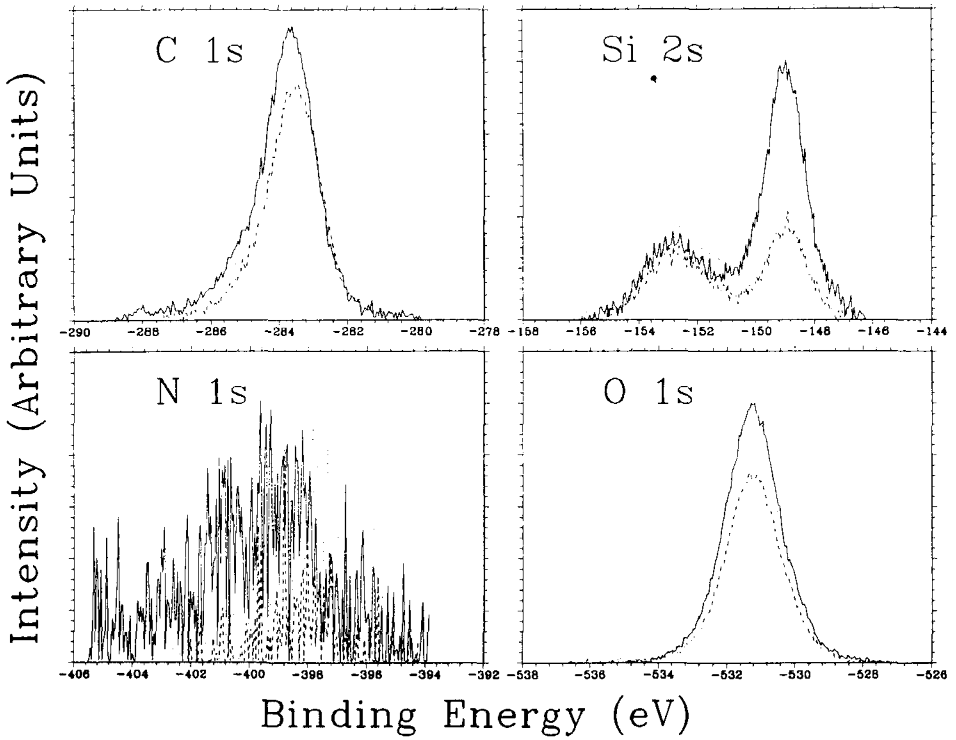

FIGURE 1 Overlays of XPS spectra obtained at various take-off angles with respect to the sample perpendicular: 5° (—), 60° (....) and 80° (---).

two components. The Si 2s peak at 150.4 eV in Figure 1 represents the c-Si substrate and the other, at 154.2 eV, represents the thin, irreversibly bound layer. The O 1s spectrum exhibits one symmetric peak at 532.7 eV, due to ether, alcohol and silanol moieties, all of which emit at the same binding energy. The C 1s spectrum contained two peaks, one at 285.0 eV due to paraffinic carbon and one at 286.5 eV, a binding energy representing both ether and alcohol moieties; their ratios were 0.85:0.15. The N 1s spectral intensity at 400.1 eV was extremely weak with a suggestion of asymmetry.

The γ-aminopropylsilanetriol has the chemical formula C_3O_3NSi (the H_{11} has been omitted since H has no core level XPS spectrum). Using sensitivity factors applicable to our instrument and data, the present XPS peaks for the irreversibly bound layer were converted into atomic percentages. These are found as a function of angle in Table I, along with the values expected for γ-aminopropylsilanetriol. It appears that no trends in atomic percentages exist for the layer as a function of angle (that for N is attributed to a decreasing S/N ratio of an already weak signal). The resultant composition corresponds to $C_{10}O_{5.7}N_{0.2}Si$, when normalized to Si (the reason for normalizing to Si is, as will shortly be discussed, because that end of the molecule does not participate in layer formation). This change in composition clearly indicates that fragmentation and rearrangement have occurred.

The thickness of this thin layer was determined in two ways. Firstly, from the slope of a plot of ln (Si 2s signal intensity) *vs* $(\cos \theta)^{-1}$; the linear slope gave a

TABLE I
Atomic percentages for polysiloxane films

Element	γ-Aminopropylsilanetriol	Interfacial layer		
		5°	60°	80°
C	28.5	49.0	48.5	49.9
O	38.2	37.9	39.6	38.7
N	11.1	2.9	1.3	0.8
Si[a]	22.3	10.2	10.1	10.6

[a]The c-Si contribution was not considered here.

thickness of ~0.1 λ. Secondly, a computer simulation was made of the Si 2s spectrum as a function of take-off angle, and the difference between simulation and experiment was minimized in terms of thickness; again, a value of ~0.1 λ was obtained. Using a value of 35 Å for λ,[7] one obtains a polysiloxane film thickness of ~3.5 Å, in good agreement with previous work on this adhesion promoter.[2-4]

IR spectra are found in Figures 2 and 3 for γ-aminopropylsilanetriol deposited

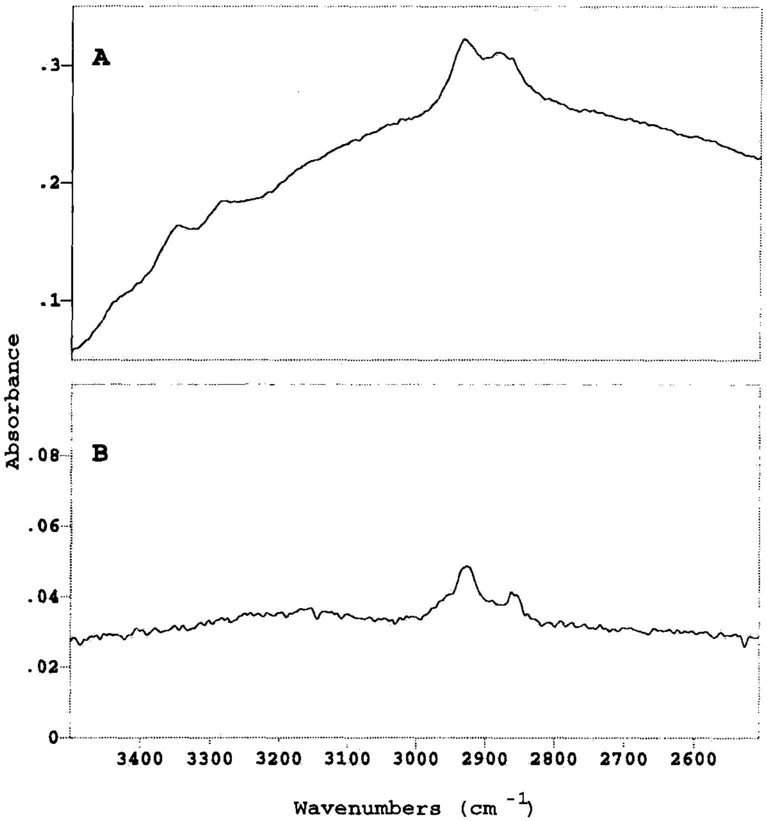

FIGURE 2 FTIR transmission spectra of the γ-aminopropylsilanetriol-treated substrate (A) before and (B) after washing, taken in the frequency range 2500–3500 cm^{-1}. Two samples were sandwiched to increase the signal intensity. Note the scale change in spectrum (B).

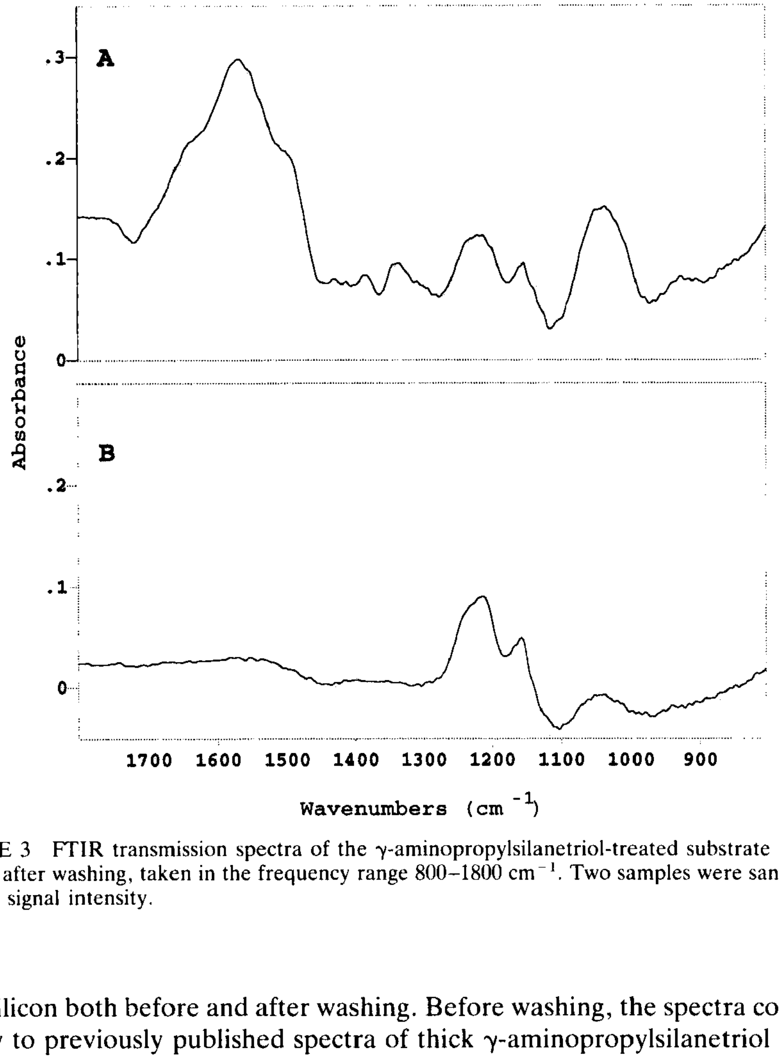

FIGURE 3 FTIR transmission spectra of the γ-aminopropylsilanetriol-treated substrate (A) before and (B) after washing, taken in the frequency range 800–1800 cm^{-1}. Two samples were sandwiched to increase signal intensity.

onto silicon both before and after washing. Before washing, the spectra correspond closely to previously published spectra of thick γ-aminopropylsilanetriol films.[12,13] The most important observation from our IR spectra is that the irreversibly bound layer which remains after washing is very different in nature from the initially deposited film. In particular, all features which are related to the presence of nitrogen before washing are absent in the washed layer, confirming the observation made by XPS.

In Figure 2, the peaks in the 3400–3200 cm^{-1} region, which are removed upon washing, are due to N—H$_n$ vibrations in alkylammonium carbamates,[14,15] previously identified as bicarbonates.[13,16–18] The C—H$_n$ vibrations between 3000 and 2800 cm^{-1} are reduced but not eliminated after washing. Close examination reveals that the washed and unwashed samples are qualitatively different in this region. This is to be expected for an alkyl chain which has lost N and has subsequently suffered fragmentation and rearrangement, as shown by the XPS results.

The 1700–1400 cm^{-1} region in Figure 3 contains three peaks. They are all removed upon washing. The strong bands at 1580 and 1500 cm^{-1} are due to N—H$_n$ deformations. The shoulder at 1660 cm^{-1} has previously been reported to be from imine, but it may in fact be the O—H bending motion of a contaminant hydroxyl in the overlayer.[19,20]

At least five bands are seen on the unwashed sample in the region below 1400 cm^{-1} in Figure 3. Four of these clearly correspond to bands previously observed on thick films of γ-aminopropylsilanetriol at 1330, 1124, 1032 and 926 cm^{-1}.[12,13] Upon washing, most of these bands are greatly decreased in intensity, as expected. The bands at 1250 and 1150 cm^{-1}, as well as a small band at 1040 cm^{-1}, which remain after washing are thought to be characteristic of the irreversibly bound layer. Based on the interpretation of the XPS results in the Discussion section, these are attributed to C—O—C and C—OH groups. Culler *et al.*[13] assigned bands at 1072 and 1111 cm^{-1} to an irreversibly bound layer of washed γ-aminopropylsilanetriol on oxidized silicon powder. They did not show any portion of the spectrum of a washed layer above 1200 cm^{-1}.

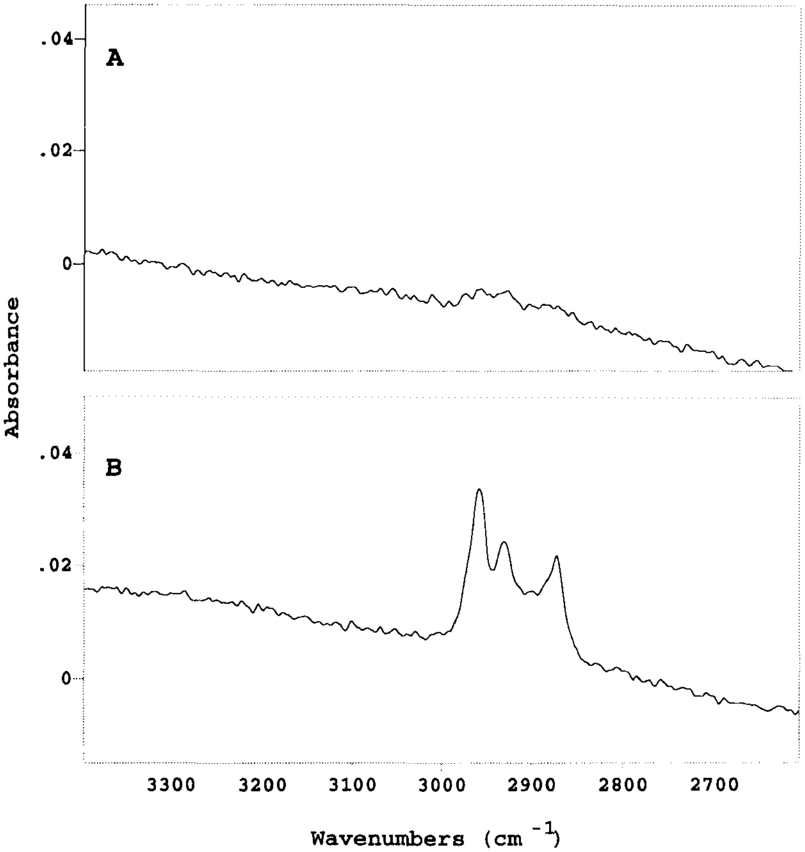

FIGURE 4 FTIR transmission spectra of the washed Si substrate after treatment with (A) n-propylsilanetriol and (B) n-propylsilanetriol and n-butylamine, taken in the frequency range 2600–3400 cm^{-1}.

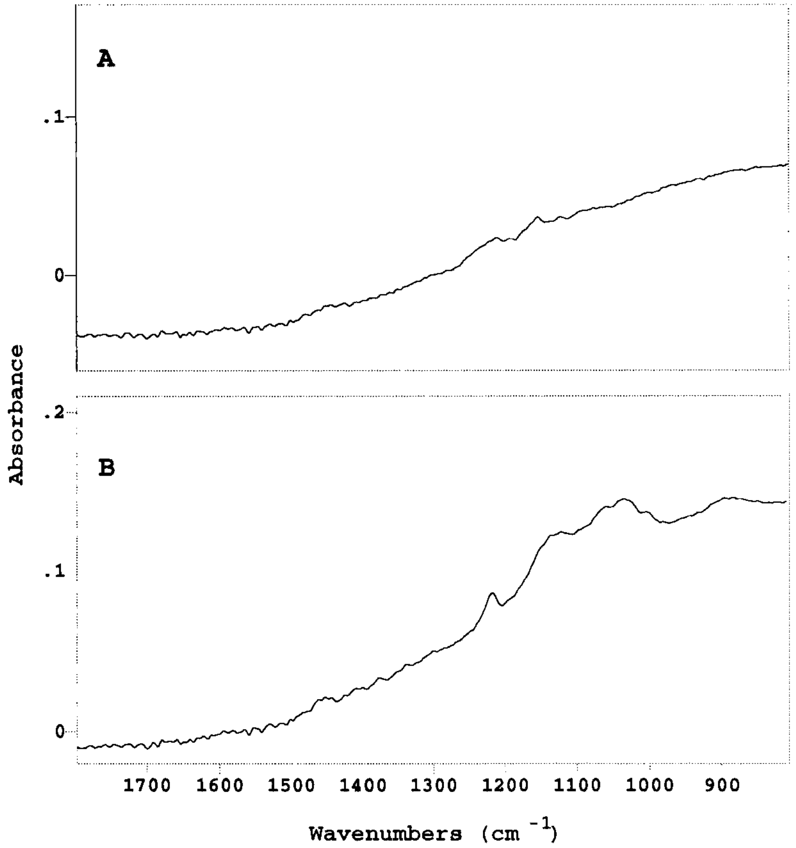

FIGURE 5 FTIR transmission spectra of the washed Si substrate after treatment with (A) n-propylsilanetriol and (B) n-propylsilanetriol and n-butylamine, taken in the frequency range 800–1800 cm^{-1}.

The key role of the amino group is illustrated in the following experiment. Silicon wafers were dipped into a solution of n-propylsilanetriol, either with or without a 1% n-butylamine catalyst. After the wafers were washed, IR spectra were obtained and are shown in Figures 4 and 5. When the n-butylamine is present, the resulting irreversibly bound layer is similar to that for γ-aminopropylsilanetriol. However, without the catalyst, no deposit was detected. It is interesting to note that the n-butylamine-catalyzed layer shows no N—H$_n$ vibrations, which confirms its role as a catalyst in layer formation, and that it is not incorporated directly into the deposited layer.

DISCUSSION

The identification of the Si 2s peak at 154.2 eV with the irreversibly-bound interfacial layer from γ-aminopropylsilanetriol is of the utmost importance since it requires an explanation of how and why the N was lost, as well as how this peak was distinguished from one arising from surface oxidation. We first consider the question of surface oxidation (and contamination, in general) in order to establish the existence of the irreversibly bound layer; next, we consider the question of the N loss.

Data from many laboratories[7–10] have confirmed that the cleaning procedure we used gives clean, oxygen-free surfaces. These surfaces are stable to atmospheric oxidation, depending on the laboratory, for periods of time from 5 hours[10] to 72 hours.[7] Even the shorter time period exceeds that required to prepare our samples and enter them into the instruments; in confirmation of this, similarly cleaned samples not treated with adhesion promoter manifested no Si 2s peak at 154.2 eV. Further, treated samples, which manifested this peak, evidenced no intensity changes over several days' exposure to atmosphere; surface oxidation causes an increase in the intensity of a Si 2s peak in the range 154.1–154.3 eV.[7,21] Thus, the facts that the peak at 154.2 eV is not present in cleaned, untreated samples and that its intensity is constant over a long period of exposure to air serve to distinguish it from surface oxidation. The similarity between the chemical shift of the irreversibly bound layer (154.2–150.4 = 3.8 eV) and that of SiO_2 from surface oxidation (3.7–3.9 eV) is due to similarities in structure: SiO_2 exists in a tetrahedral lattice, with each Si bonded to 4 O, and each O to 2 Si, while the Si in the irreversibly-bound layer is tetrahedrally bonded to 3 O and a C.

These results are fully supported by the FTIR results, which demonstrate the cleanliness of the untreated wafer, as well as the retention of the irreversibly-bound interfacial layer on washing. Also demonstrated is the catalytic effect of the amino group, whether present on the silanetriol or added separately; in neither case is it retained on washing.

The present results indicate that the interfacial layer formed on the deposition of γ-aminopropylsilanetriol onto c-Si is structurally different from the original adhesion promoter, having undergone fragmentation and rearrangement. This may also be true for other adhesion promoters and other substrates,[2–4] although the structures of those interfacial layers are, as yet, uninvestigated. In the present case, the elemental loss on formation of this interfacial layer increased in the direction N>Si>O>C, which is certainly consistent with bond strength tabulations[22] which indicate their order to be C—N<C—Si<C—C≈C—O. Such tabulations do not take account of bond energy changes due to electron density shifts.

Let us consider the N—C bond and the effect that a change in electron density has on its strength. Fliszar and coworkers have shown[23] that the intrinsic strength of a chemical bond, ϵ_{ij}, decreases in a predictable manner on the loss of electron density. For the case of the N—C bond, this decrease may be written as

$$\Delta\epsilon_{NC} = (-4.33 \text{ kJ mol}^{-1} \text{ me}^{-1})\,\Delta q. \qquad (1)$$

Note that a loss of only 10 millielectrons (me), $\Delta q = 10$ me ($= 0.01$ e), will reduce the intrinsic strength of this bond by over 43 kJ mol^{-1}, equivalent to >14% of the total bond strength.[22] It is clear that no great loss in electron density is necessary before the bond is broken.

That NH_3 is capable of giving up its lone pair to Si is clear; HREELS[24] and STM[25] studies on Si(111)-(7×7) have shown that enough electron density is transferred to break an N—H bond, which is stronger than an N—C bond; UPS studies[26] have shown this to occur on Si(100)-(2 × 1). Similar results have been found for butylamine, by XPS.[27] Thus, we propose the adsorption of the amino group of the γ-aminopropylsilanetriol on the substrate surface, leading to electron loss and homolytic scission of the N—C bond. The fact that the N lone pair is more easily donated than, say, that of a carbonyl oxygen, explains the catalytic effect of added amine on the deposition of adhesion promoters which do not contain amine moieties,[28] since the added amine can more readily react with the substrate surface to undergo homolytic scission to begin the deposition. This is clearly seen in Figures 4 and 5.

Based on our XPS results, an educated guess may be made in describing the chemistry leading to the interfacial layer; this will help in understanding its formation and function. Firstly, we posit that all the N is lost, the small amount still detected being trapped in the layer.

Secondly, the C 1s peak at 286.5 eV, comprising 15% of the total C, represents both ether and hydroxyl groups. The 15% of the total C means that one atom in six is bound to an oxygen, with the others being bound to carbon or silicon. For this to be so, chain extension must have occurred subsequent to N—C fragmentation. Otherwise, the terminal C would have reacted directly with water, in which case the C 1s peak at 286.5 eV would comprise 33% of the total C.

Further, if we make the reasonable assumption that all the Si—O bonds remaining on the interfacial layer are intact, the O 1s and the smaller C 1s peak are accounted for only by assuming the presence of both C—O—C and C—OH groups. Thus, we propose an initial scission of the N—C bond, leaving the —C· thus formed to react further. Chain extension, for example, is accounted for by reaction with another —C· while both ether and hydroxyl groups will form on reaction with water. Hydrogen loss by abstraction will form terminal vinyl groups, capable of bonding to the substrate.[29-32]

The reaction of the vinyl group with the substrate and its capacity to react further with other vinyl groups explain the fact that the vinyl silane deposit cannot be removed at all,[2] since the reaction of such groups is known to form an intractable polymer at the surface.[29] The formation of this intractable polymer layer has recently been the subject of a review.[30] It showed that, at room temperature, the initially-deposited hydrocarbon monolayers are extremely reactive and polymerize easily to a thick,[29] crosslinked hydrocarbon layer. Such layers cannot be removed by hydrolysis.

The Si—$(OH)_3$ groups still remaining in this interfacial layer may then react with similar groups on molecules still in solution, following the mechanism generally believed to occur.[1] That is, Si—OH groups form hydrogen bonds which split out water to form Si—O—Si linkages, ultimately giving the crosslinked polysiloxane layer mentioned in the Introduction. The Si—O—Si linkage is subject to hydrolysis, meaning that the polysiloxane layer may be washed away, leaving only the irreversibly bound interfacial layer, firmly bonded to the substrate, with its terminal Si—$(OH)_3$.

One feature of the IR spectra is of critical importance in support of the proposed mechanism: the loss of peaks due to N—H_n deformations on washing. This is seen in the losses of peaks in the 3200–3400 cm^{-1} region of Figure 2a and at 1590 cm^{-1} in Figure 3a. These losses are expected for the homolytic scission of the N—C bond and confirms the XPS results.

Comparison with previous studies is limited, aside from the single spectrum of Culler *et al.*[13] Several studies were made[33,34] on the ATR IR spectra of γ-aminopropylsilanetriol deposited onto sapphire prisms, with deposition thicknesses controlled by the solvent. Water gave a deposit 200Å thick and cyclohexane, 25Å thick. No effort was made to wash the deposited film. Using the absorption ratio A_{1590}/A_{2940} (N—H bending/CH_2 stretching) as a measure of crosslinking, it was concluded that the thinner film was more highly crosslinked.

An IETS study[35] of a monolayer of γ-mercaptopropylsilanetriol on Al_2O_3 concluded that bonding occurred through reaction of the silanetriol with surface hydroxyl groups. Unfortunately, this does not lead to irreversibly bound layers.

CONCLUSION

While there is a paucity of published data on the characterization of the irreversibly bound γ-aminopropylsilanetriol adhesion promoter layer left on silicon after extensive washing, two surface analytical techniques used in the present study, one electronic and the other optical, are in agreement. This irreversibly-bound layer has been found to have resulted from the severe fragmentation and rearrangement of the original molecule. Such fragmentation is proposed to be due to the homolytic scission of the N—C bond caused by the loss of electron density to the substrate, followed by reaction of the —C· thus generated.

The mechanism proposed considers only certain reactions; it is entirely possible that others also contribute. In addition, other adhesion promoters also deposit irreversibly bound interfacial layers, and do so on substrates as varied as metal, semiconductor and glass. Thus, it is impossible, at present, to confirm the generality of the presently proposed mechanism without further experimentation, which is presently planned.

Acknowledgments

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