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Surface analytical study of the interaction between γ-amino propyl triethoxysilane and E-glass surface

Part II *X-ray photoelectron spectroscopy*

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Angle-resolved X-ray photoelectron spectroscopy (XPS) has been used to study the interaction of hydrolysed γ-aminopropyltriethoxysilane (HAPS) with a flat E-glass slide surface. Formation of a HAPS coating with a thickness of about 6 nm, which consists of three components of differing molecular structure on the glass surface, was confirmed. The results provided further evidence for the incorporation of aluminium ions from the glass substrate into the HAPS coating. At the outer surface, a warm-water-soluble oligomer exists in which the amino group of the HAPS molecule is in the form of a free $-NH_2$. Beneath, there is a three-dimensional graded network whose ends, after extraction with warm water, are involved in an internally hydrogen-bonded structure between the amino and silanol groups, probably in a cyclised conformation. Adjacent to the glass surface, a molecular layer of HAPS remained after extraction with hot water, which was chemically bound to the glass surface through siloxane and/or aluminoxane bonds. The results tend to favour the former with $Al(OH)_3$ copolymerized into the siloxanol deposit.

1. Introduction

Hydrolysed γ-aminopropyltriethoxysilane (HAPS) interaction with the glass or metal oxide surfaces has been widely examined by X-ray photoelectron spectroscopy (XPS) [1–7]. A general conclusion is that a thick, dense poly(aminosiloxane) coating is formed on the surface. Cain and Sacher [5] using Auger electron spectroscopy (AES) proposed that the amino group of the HAPS on silicon wafers was oriented towards the outer surface. Koenig and co-workers [8–10] and Vågberg *et al.* [11] suggested that at pH = 11, the amino group was present as $-NH_2$, but at pH = 2 in the presence of hydrochloric acid it was present as $-NH_3^+Cl^-$.

However, understanding of the full chemical nature of the HAPS deposit is still limited. Thus, in our previous papers [12, 13] the interaction of HAPS with a flat E-glass slide surface was studied by the extremely sensitive surface technique of time-of-flight secondary ion mass spectrometry (TOF SIMS). This technique primarily gives molecular structural information and differences in the maximum degree of polymerization of the secondary ions emanating from these three distinct components were observed. This was attributed to a gradation in the cross-link density of the deposit towards the glass surface. This XPS study is complementary to the TOF SIMS study, because it provides chemical-state information which can be quantified using appropriate calibration and sensitivity factors. Another advantage is that XPS enables the sampling depth to be estimated by angle-resolved measurement.

2. Experimental procedure

The preparation of the E-glass slides has been described previously [12, 13].

The slides were treated in a fresh 1.5 wt % HAPS (A-1100, Union Carbide) solution in deionized water at pH values of 1, 3, 5, 7, 9, natural (10.6) and 13 for 45 min at room temperature, then washed several times with deionized water and dried *in vacuo* at 50 °C. The adjustment of pH of the solution from the natural value of 10.6 to 1, 3, 5, 7 and 9 was accomplished with glacial acetic acid and for pH = 13 using aqueous sodium hydroxide. Some as-coated slides, pretreated at natural pH, were extracted in deionized water at 50 °C for 24 h, and some further at 100 °C for 4 h.

All spectra were recorded on a VG MICROTECH CLAM100 XPS spectrometer. An AlK_α X-ray source (1486.6 eV) was used operating at a power 10 keV, 10 mA with a pass energy of 50 eV. The analysing vacuum was $<10^{-8}$ torr (1 torr = 133.322 Pa). The narrow scan spectra for individual elements were obtained at 15°, 30° and 45° relative to the slide surface with a view to varying the analysis depth. C1s (285 eV) was employed as a reference for the calculation of the binding energies.

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3. Results

3.1. Heat-cleaned E-glass slide surface

In Tables I and II we have calculated the relative surface concentration of all elements detected. The carbon emanates from commonly recognized hydrocarbon contamination. That it arises from surface contamination is confirmed by its reduction with take-off angle. For comparison with bulk glass, the results are represented in Table II ignoring the carbon. Tables I and II show that the heat-cleaned E-glass slide surface has a silica-rich surface as indicated by the higher silicon and oxygen surface concentrations than in the bulk. This is consistent with the results obtained by TOF SIMS [12, 13]. Typical positive and negative ions for glass, Si^+ (28/29 a.m.u.), SiO_2^- (60 a.m.u.), SiO_2H^- (61 a.m.u.), SiO_3^- (76 a.m.u.) and SiO_3H^-(77 a.m.u.), were all observed. However, this was accompanied by a lower surface calcium concentration. The aluminium concentration is less affected as would be expected of a glass network modifier.

3.2. E-glass slides coated with silane from differing media

From Table III it can be seen from the nitrogen signal in XPS that deposition of HAPS from a 1.5 wt % aqueous solution at natural pH on to the E-glass slide surface has occurred. It is also observed from the differing nitrogen concentration that a thicker HAPS coating was formed on the surface from an aqueous solution rather than from the methanol one. However, Pawson and Jones [1] found that approximately twice as much adhesion promoter was deposited on to an AR-glass surface from the methanol solution than from the aqueous one.

Furthermore, another noticeable point from a comparison of Tables I and III is that after aqueous HAPS treatment the surface aluminium concentrations show an increase not a decrease, as expected for the glass surface covered with the HAPS deposit.

3.3. E-glass slides coated with silane solutions of differing pH

Fig. 1 shows that deposition of HAPS from an aqueous solution on to the glass surface is highly pH-dependent in confirmation of the observation of Naviroj *et al.* [14] using Fourier transform infrared spectroscopy (FTIR). Maximum adsorption of the HAPS occurs at natural pH and the minimum at $pH = 1$.

As controls, a series of the heat-cleaned E-glass slides were treated with deionized water at differing pH values. The results are presented in Fig. 2. It can be seen that both the aluminium and calcium surface concentrations are strongly dependent upon the pH of the solution. Clearly, the surface aluminium and calcium concentrations were reduced, by extraction, in the acidic solutions, to effectively zero at $pH = 1$, but remained relatively stable in alkaline solutions at a pH greater than 7.

From Fig. 3, it can be seen that the aluminium and calcium concentrations present on the HAPS-coated surface are also a function of pH. The aluminium concentration increases simultaneously with nitrogen concentration reaching a maximum at $pH = 9$. Even at $pH = 1$ a significant aluminium surface concentration still existed in comparison with the results of the controls shown in Fig. 2. Thus, the HAPS coating thickness is maximized under conditions which would cause the surface aluminium concentration to decrease to a minimum, if a uniform coating were deposited. Because extraction with hot water (see Section 3.4), which removes much of the silane, leads to a higher aluminium concentration than is originally present on the surface, we conclude that the aluminium ion has diffused away from the glass into the HAPS deposit. Similarly, some indication of a lesser calcium incorporation at $pH = 9$ was also observed.

TABLE I The variation in relative atomic surface composition (%) of a heat-cleaned E-glass slide obtained by angle-resolved XPS

Element	Atomic surface composition (%) 15°	30°	45°
Si	26.1	25.3	23.9
Al	5.3	6.1	6.8
Ca	5.6	6.9	7.5
O	52.3	51.9	53.3
C	10.8	9.8	8.5
Mg	–	–	–
B	–	–	–
Fe	–	–	–

TABLE II A comparison of the relative atomic bulk and XPS angle-resolved surface compositions (%) for a heat-cleaned E-glass slide

Element	Atomic surface composition (%) 15°	30°	45°	Bulk analysis[a] (%)
Si	27.3	26.1	25.1	22.3
Al	7.5	7.9	8.4	7.4
Ca	6.3	8.5	9.6	16.4
O	58.9	57.5	56.9	49.6
Mg	–	–	–	0.4
B	–	–	–	2.1
Fe	–	–	–	0.6

[a] Using ICP.

TABLE III The variation in relative atomic surface composition (%) of hydrolysed HAPS-coated E-glass slides obtained by angle-resolved XPS

	Atomic surface composition (%)					
	Aqueous solution			Methanol		
Element	15°	30°	45°	15°	30°	45°
Si	22.2	22.1	22.3	23.1	22.9	23.0
Al	6.5	6.0	5.5	6.1	5.8	5.6
Ca	3.8	3.0	2.8	4.1	3.6	3.1
O	41.5	44.4	45.2	42.5	44.6	45.8
C	17.1	16.4	16.5	17.5	16.8	16.6
N	8.9	8.1	7.7	6.7	6.3	5.9

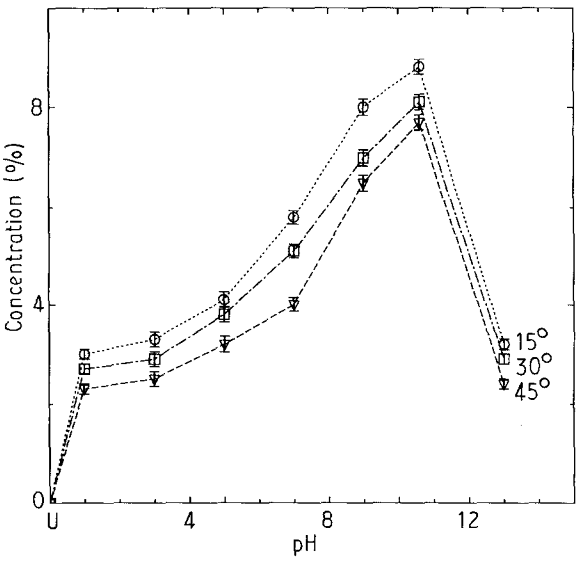

Figure 1 The variation in surface concentration of HAPS deposited on to an E-glass (as N1s) from an aqueous silane solution at 1.5 wt % at differing media pH. The analysis angle is denoted on the curves. U, uncoated E-glass slide surfaces after heat cleaning.

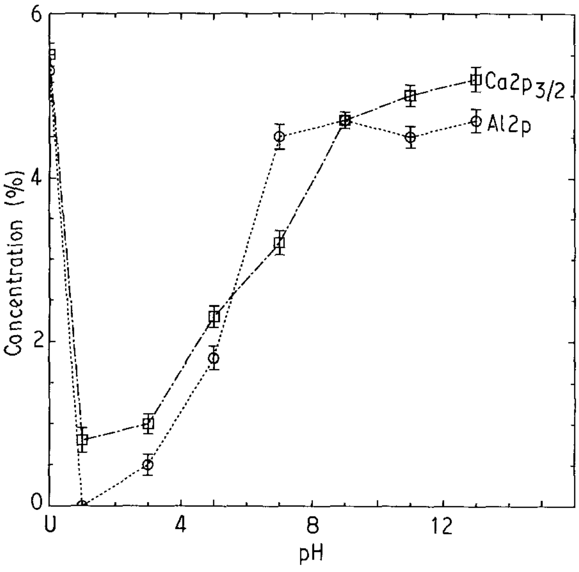

Figure 2 The variation in surface concentration of aluminium (as Al2p) and calcium (as $Ca2p_{3/2}$) on the heat-cleaned E-glass slide surface after treatment with deionized water at differing media pH. The analysis angle is 15°.

With differing pH the chemical environment of the amino group of the HAPS molecule is also affected. As shown in Fig. 4 the surface, coated at the natural pH of 10.6, gave an N1s peak at 400.3 eV, whereas at pH = 1 and 7 it occurs at 402.6 and 401.6 eV, respectively. With the structural assignments in the literature [8–11, 14] we conclude that at a natural pH the amino group is present in its free form, $-NH_2$, but at low pH it is protonated, $-NH_3^+$. At neutral pH it is more likely that the HAPS molecule is involved in an internally hydrogen-bonded cyclic structure [9, 10] (see Fig. 5) which can only arise from oligomeric or partially polymerized silane. Thus, the hydrogen bond gives rise to an amino group with a partial positive charge which accounts for the chemical shift to higher binding energies of 1.3 eV, compared to the free NH_2 group.

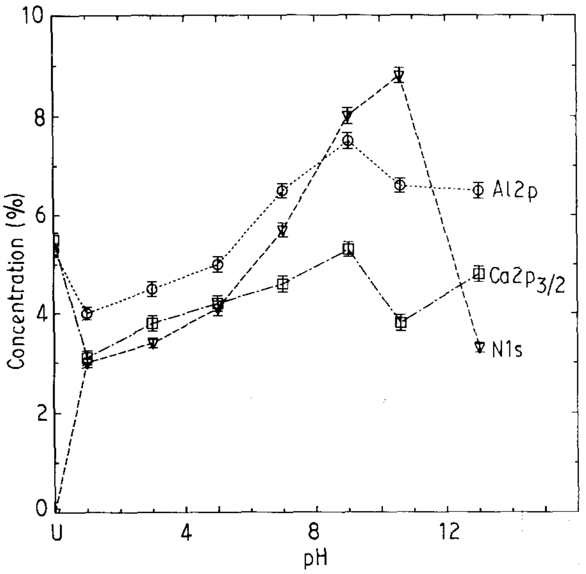

Figure 3 The variation in surface concentration of aluminium (as Al2p), calcium (as $Ca2p_{3/2}$) and HAPS (as N1s) of an E-glass slide after treatment with an aqueous (1.5 wt %) silane solution at differing media pH. The analysis angle is 15° (see tables for details). U, uncoated E-glass surface after heat treatment.

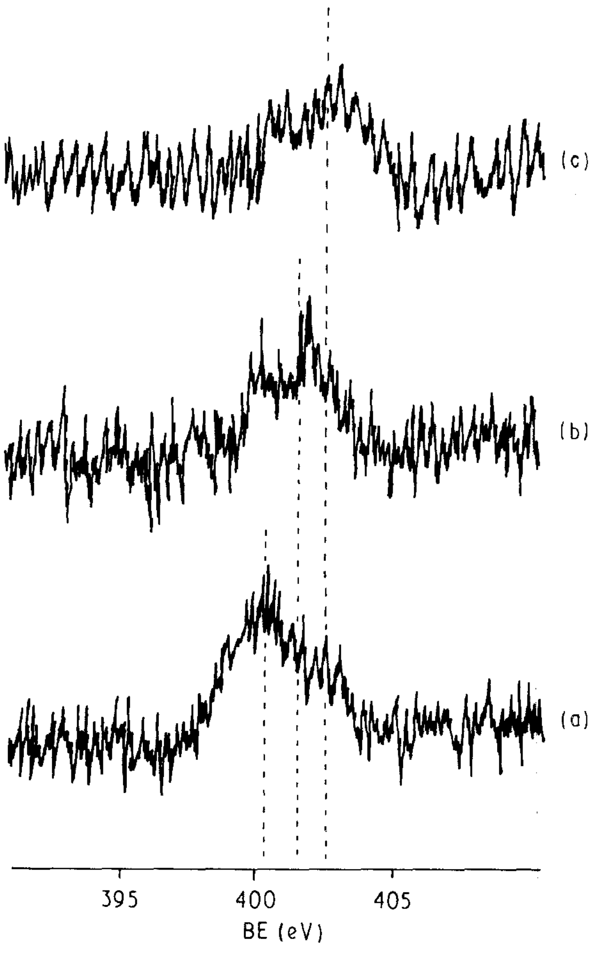

Figure 4 Narrow band N1s XPS spectra taken at a resolved angle of 15° for the as-coated E-glass slide surfaces after immersion in a 1.5% HAPS solution of varying pH: (a) 10.6, (b) 7, (c) 1.

3.4. As-coated slides after extraction with warm and hot water

It is reported elsewhere [15] that a thermodynamic equilibrium exists between the oligomers and polymers of HAPS. Furthermore, it is generally considered

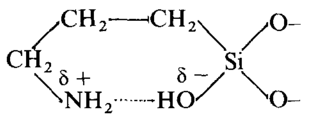

Figure 5 The structure of a HAPS molecule involved in an internally hydrogen-bonded cyclic form.

TABLE IV The variation in relative atomic surface composition (%) for extracted HAPS-coated E-glass slides obtained by angle-resolved XPS

	Atomic surface composition (%)					
	Warm water			Hot water		
Element	15°	30°	45°	15°	30°	45°
Si	18.5	18.3	18.5	17.5	18.2	19.1
Al	6.2	5.7	5.5	10.1	8.1	7.5
Ca	–	3.8	4.1	3.5	3.9	4.5
O	50.1	48.8	48.5	47.1	50.0	51.2
C	19.1	17.7	18.0	17.3	16.7	15.7
N	6.1	5.7	5.4	4.5	3.1	2.0

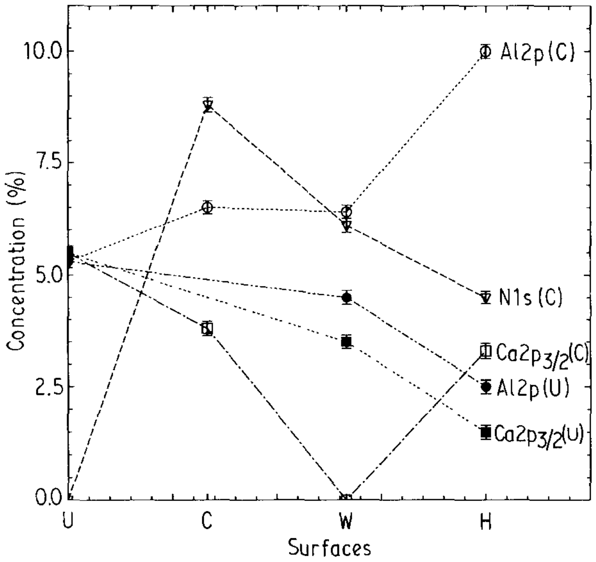

Figure 6 The HAPS (as N1s), aluminium (as Al2p) and calcium (as Ca2p$_{3/2}$) concentrations for differing modified surfaces. The analysis angle is 15°. U, uncoated; C, the HAPS as-coated surfaces; W, the HAPS as-coated surfaces after warm-water extraction; H, the HAPS as-coated surfaces after hot-water extraction; N1s(C) is the nitrogen signal from the as-coated surface; Al2p(C) is the aluminium signal from the as-coated surface; Al2p(U) is the aluminium signal from the uncoated surface; Ca2p$_{3/2}$(C) is the calcium signal from the as-coated surface; Ca2p$_{3/2}$(U) is the calcium signal from the uncoated surface.

that an oligomeric-rich surface exists. In our TOF SIMS studies [12, 13], warm- and hot-water extraction was used to demonstrate the presence of an oligomeric component and a graded polymeric network. To examine this phenomenon further and to confirm the role of substrate ions in the deposition process, we have examined fully the changes which occur as a result of water extraction. Therefore, the as-coated samples were extracted with water at 50 and 100 °C for 24 and 4 h, respectively. Table IV shows that extraction has led to a noticeable decrease in the surface nitrogen concentration. These results are in agreement with the observation that the largest molecular fragment in TOF SIMS increased after warm-water extraction as would be expected from the removal of soluble HAPS oligomers [16–19]. Similar conclusions have been inferred from FTIR and nuclear magnetic resonance (NMR) studies [8, 9, 20, 21].

As seen on the curve for Ca2p$_{3/2}$(C) in Fig. 6 and Table IV, warm-water extraction also resulted in the absence of calcium in the outer surface layers. This indicates that the calcium is present in the as-coated film in an extractable form. As a consequence, at the higher analysis angles the calcium signal can be assumed to have arisen from the substrate. Furthermore, it is possible to infer that the calcium signal, observed for the as-coated surface most likely arises from some weakly bound and soluble form such as $Ca(OH)_2$. This consideration has been confirmed by our TOF SIMS spectra [12, 13] where there is a secondary positive ion at 57 a.m.u. for $CaOH^+$ which is typical of $Ca(OH)_2$.

Subsequently, this sample was extracted with hot water at 100 °C for 4 h. Fig. 6 (curves for N1s(C), Al2p(C) and Ca2p$_{3/2}$(C)) and Table IV show that the intensity of the nitrogen signal further decreased while that for aluminium and calcium increased as the contribution from the substrate also increased with decreasing thickness of HAPS. Similarly, extraction of ^{14}C-labelled HAPS on the glass surface has been studied by Schrader *et al.* [18, 19] who reported that after hot-water extraction only a monolayer remained on the surface. Thus, it is possible to suggest that after hot-water extraction of these coated samples a monomolecular silane layer is present on the immediate glass surface.

Moreover, the binding energy for the N1s indicates that at the immediate glass surface the structure of the HAPS appears to be different. As shown in Fig. 7, the physisorbed HAPS component gave an N1s peak at 400.3 eV. After warm-water extraction this peak shifted to 401.4 eV, but with hot-water extraction it returned to 400.3 eV.

The curve for the Al2p(C) intensity in Fig. 6 also shows that the aluminium concentration on the as-coated glass surface increases as the thickness of the HAPS deposit decreases, particularly after hot-water extraction. However, for the heat-cleaned glass surface it is reduced significantly after extraction with warm water and further with hot water (see curve for Al2p(U) in Fig. 6). Thus in comparison these results demonstrate that the aluminium ion on the coated glass is not removed proportionally together with the soluble HAPS deposit and appears to be chemically bonded to the HAPS deposit left on the surface after hot-water extraction.

4. Discussion

4.1. Estimation of the coating thickness

The presence of a monolayer of the HAPS deposit on the immediate glass surface after extraction with

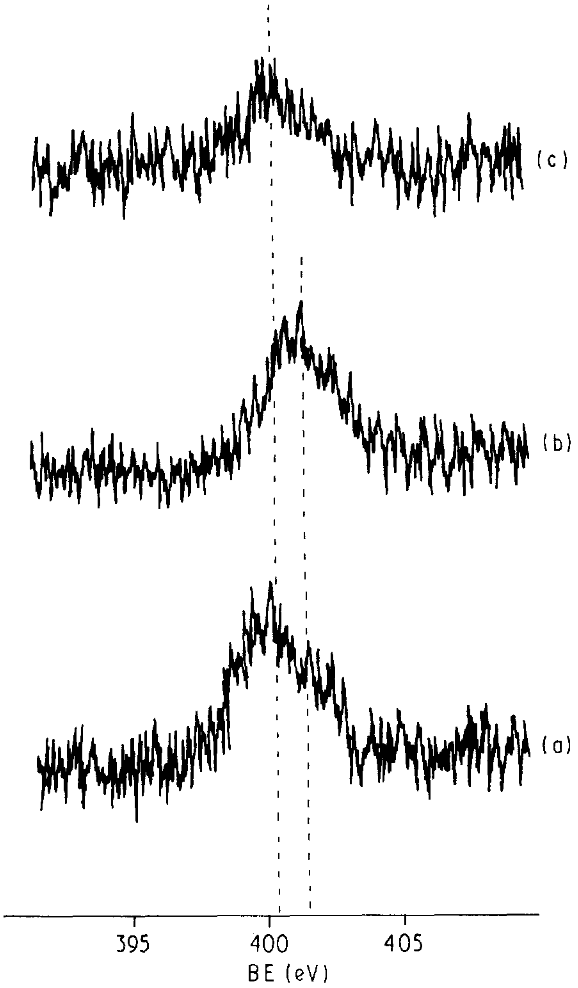

Figure 7 Narrow band N1s spectra taken at a resolved angle of 15° for the E-glass slide surfaces after immersion in a 1.5% of aqueous HAPS solution (a) at natural pH at room temperature, (b) after extraction in warm water for 24 h, (c) after extraction in hot water for 4 h.

hot water is indicated. Therefore, on the basis of the method used to calculate the photoelectron mean free path, λ, for the monomolecular layer of butylamine on an iron surface by Bailey and Castle [3], we have used Equation 1 to estimate λ_{N1s} of the N1s photoelectron from a monomolecular HAPS layer on the E-glass slide surface

$$\lambda_{N1s} = -l_{HAPS}/\sin\theta \ln(1 - I_H/I_C) \qquad (1)$$

where l_{HAPS} is the length of the extended HAPS molecule reacted at a surface; θ is the angle between the sample surface and the analyser; I_H is the N1s intensity from HAPS monolayer on the coated glass surface after extraction with hot water; and I_C is the N1s intensity from the as-coated glass surface.

From the following bond lengths reported by Bailey and Castle [3] and Ishida *et al.* [22]: C–C 0.15 nm, N–C 0.09 nm, Si–C 0.12 nm and Si–O 0.16 nm; the value for l_{HAPS} is calculated to be 0.64 nm. Thus, λ_{N1s} can be estimated to be 3.0 ($\pm$ 0.25) nm. This agrees with the relationship between the square-root dependence on kinetic energy of the N1s electron. In this case the sampling depth, d, of the N1s photoelectron from the HAPS coating on the as-coated glass surface can be estimated from λ_{N1s} through Equation 2 [23]

TABLE V The sampling depth of N1s photoelectron from the HAPS-coated glass surface as a function of the resolved angles

	θ (deg)		
	15	30	45
Sampling depth, *d* (nm)	2.3 ($\pm$ 0.2)	4.5 ($\pm$ 0.4)	6.4 ($\pm$ 0.5)

$$d = 3\lambda \sin\theta \qquad (2)$$

Using Equation 2, approximate values of the sampling depth of N1s photoelectron as a function of the resolved angles are obtained and are presented in Table V. It should be recognized that the monolayer of silane which remains after hot-water extraction contains some copolymerized aluminium. Therefore, this analysis may underestimate λ_{N1s} and hence *d*.

Moreover, another complementary fact shown in Fig. 6 for estimation of thickness of the HAPS coating on the as-coated glass surface is that the absence of calcium from a layer of depth of 2.3 nm on the glass surface after extraction with warm water is obtained at 15° (see Tables IV and V and Fig. 6). This indicates that all elements observed on the as-coated surface before extraction at 15° (see in Table III) must emanate from the HAPS deposit not from the substrate. Thus, the observation of aluminium and calcium signals in the as-coated surface confirms their incorporation in the deposit. Because the latter is water soluble it must have diffused from the substrate into the coating and physically re-adsorbed in the form of $Ca(OH)_2$ from the solution. For the non-extractable aluminium it must be co-reacted with the HAPS. Therefore, with these arguments and the fact of the observation of the N1s signal at 45° (see Table III) the thickness of the HAPS coating on the as-coated glass surface before extraction with warm water could be estimated to be at least 6 nm in terms of the values given in Table V. For comparison, this represents at least ten monolayers which is consistent with previous estimates [24].

After warm-water extraction, the reappearance of the calcium signal from the substrate on increasing the analysis angle from 15° to 30° indicates that the remaining silane deposit has a thickness which approximates to the analysis depth at 15°, i.e. >2.3 to <4.5 nm.

4.2. Aluminium incorporation into the silane coating

Aluminosilicate glasses, such as E-glass, in contact with aqueous environments are sensitive to the pH of the solutions [25, 26]. Firstly, we consider the effect of pH of the solution on dissolution of alumina. The reaction between alumina and water can be written as follows,

$$Al_2O_{3(s)} + H_2O_{(l)} \rightleftharpoons 2H^+_{(aq)} + 2AlO^-_{2(aq)} \qquad (3)$$

ΔG° for this reaction is + 32.06 kcal and $\log K$ is −23.5 [25], thus

$$K = \frac{a^2_{\mathrm{H^+}} a^2_{\mathrm{AlO_2^-}}}{a_{\mathrm{Al_2O_3}} a_{\mathrm{H_2O}}} \qquad (4)$$

Taking $a_{\mathrm{Al_2O_3}}$ and $a_{\mathrm{H_2O}}$ as unity and in such dilute solution, $a_{\mathrm{H^+}} = c_{\mathrm{H^+}}$ and $a_{\mathrm{AlO_2^-}} = c_{\mathrm{AlO_2^-}}$, then

$$\log c_{\mathrm{AlO_2^-}} = 1/2 \log K + \mathrm{pH} \qquad (5)$$

Accordingly, the effect of pH on the concentration of $\mathrm{AlO_2^-}$ in solution can be estimated and is given in Fig. 8.

Secondly, another reaction of alumina with water should also be considered

$$\mathrm{Al_2O_{3(s)}} + \mathrm{3H_2O_{(l)}} \rightleftharpoons \mathrm{2Al(OH)_{3(s)}} \qquad (6)$$

The dissolution of $\mathrm{Al^{3+}}$ ions from solid aluminium hydroxide is also pH dependent

$$\mathrm{Al(OH)_{3(s)}} \rightleftharpoons \mathrm{Al^{3+}_{(aq)}} + \mathrm{3OH^-_{(aq)}} \qquad (7)$$

For this reaction ΔG° is +44.12 kcal and $\log K$ is −32.3 [25], thus

$$K = \frac{a_{\mathrm{Al^{3+}}} a^3_{\mathrm{OH^-}}}{a_{\mathrm{Al(OH)_3}}} \qquad (8)$$

For a solid, $a_{\mathrm{Al(OH)_3}}$ can be taken as unity and at these concentrations $a_{\mathrm{Al^{3+}}}$ and $a_{\mathrm{OH^-}}$ can be equated with concentrations, then

$$\log c_{\mathrm{Al^{3+}}} = \log K + 3\mathrm{pOH} \qquad (9)$$

Therefore, the concentrations of $\mathrm{Al^{3+}}$ in solutions of differing pH can be estimated as shown in Fig. 8. The analysis presented in Fig. 8 is entirely consistent with the results given in Fig. 2 for the surface element concentrations of the glass slides after treatment with varying pH. Thus, under acidic conditions, $\mathrm{Al^{3+}}$ is extracted from the surface, whereas above a pH of 7, the aluminium is not extracted. The slight reduction in concentration probably results from the expected increase in surface hydroxyl concentration and/or adsorption of surface water.

Because with increasing pH of the silane solution, the surface aluminium concentration of the coated glass increases simultaneously with the HAPS coating thickness (see Fig. 3) it is possible to postulate that the aluminium is extracted from the glass and trapped in the coating. Comparison of Figs 2 and 3 shows that the entrapment of the aluminium ion into the HAPS coating is related to the variation of its solubility with pH. Over the pH range 1–9 the surface aluminium concentration increased, reaching a maximum at a pH = 9. However, from an examination of Fig. 8 in this range of pH, it is likely that neither $\mathrm{AlO_2^-}$ nor $\mathrm{Al^{3+}}$ are at a sufficient concentration for them to be codeposited with the silane. Analysis of another alumino-silicate system by Bailey and Hampson [27] indicates that in solution the aluminate ion has the formula $\mathrm{Al(OH)_4^-}$ and at high concentration polymerization occurs and at pH > 13 the $\mathrm{AlO_2^-}$ ion forms. In addition, a neutral species may arise by dissociation

$$\mathrm{Al(OH)^-_{4(aq)}} \rightleftharpoons \mathrm{Al(OH)_{3(aq)}} + \mathrm{OH^-_{(aq)}} \qquad (10)$$

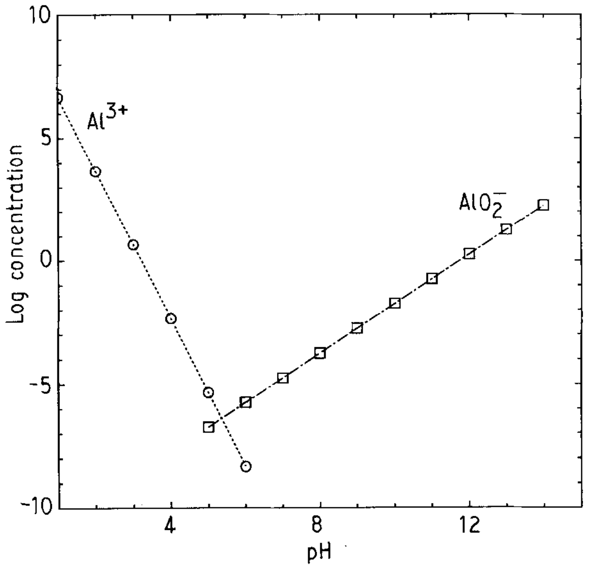

Figure 8 Estimated concentrations of $\mathrm{Al^{3+}}$ and $\mathrm{AlO_2^-}$ in aqueous solutions of varying pH in contact with $\mathrm{Al_2O_3}$ surface. Similar results are expected for an E-glass surface in contact with an aqueous solution of differing pH at 25 °C.

They also proposed that the concentration of $\mathrm{Al(OH)_3}$ in solution only becomes significant below pH = 9. Thus, it appears that $\mathrm{Al(OH)_3}$ could co-react with the aminosilane in aqueous solution as follows

$$\begin{aligned} &\mathrm{Al(OH)_{3(aq)}} + \mathrm{NH_2(CH_2)_3Si(OH)_{3(aq)}} \\ &\rightleftharpoons \mathrm{NH_2(CH_2)_2Si(OH)_2OAl(OH)_{2(aq)}} + \mathrm{H_2O_{(l)}} \\ &\rightleftharpoons \mathrm{NH_2(CH_2)_2Si(OH)O_2Al(OH)_{(aq)}} + \mathrm{2H_2O_{(l)}} \\ &\rightleftharpoons \mathrm{NH_2(CH_2)_2SiO_3Al_{(aq)}} + \mathrm{3H_2O_{(l)}} \qquad (11) \end{aligned}$$

This would appear to be contrary to the data given by Paul [25] where the concentration of $\mathrm{Al(OH)_3}$ in solution is shown to remain constant over this range of pH. As shown in Fig. 3, probability of interaction of $\mathrm{Al(OH)_3}$ with organosilanol molecules in solution increases with its concentration reaching a maximum at pH of 9 and then they were co-deposited on to the glass surface finally giving rise to a copoly-(aluminoxane-aminosilane) coating. This is in a good agreement with the TOF SIMS results [12]. There were three negative secondary ions which could be assigned to an aluminoxane structure observed at 75 a.m.u. for $\mathrm{AlO_3^-}$, at 77 a.m.u. for $\mathrm{AlO_3H_2^-}$ and at 120 a.m.u. for $\mathrm{H_2Al_2O_4}$.

4.3. Molecular structure of the differing silane components

Structure of the HAPS deposit on the glass surface has been shown to affect directly the adhesion between the glass and matrix resin [15]. In Table III the highest intensity of the N1s signal from the as-coated surface was observed at 15°. Therefore, the HAPS molecules in the outermost layers are probably orientated perpendicular to the glass surface [3]. Further, the binding energies of N1s electron was observed to be 400.3 eV which demonstrates that the amino groups are in a free form ($\mathrm{NH_2}$) [5].

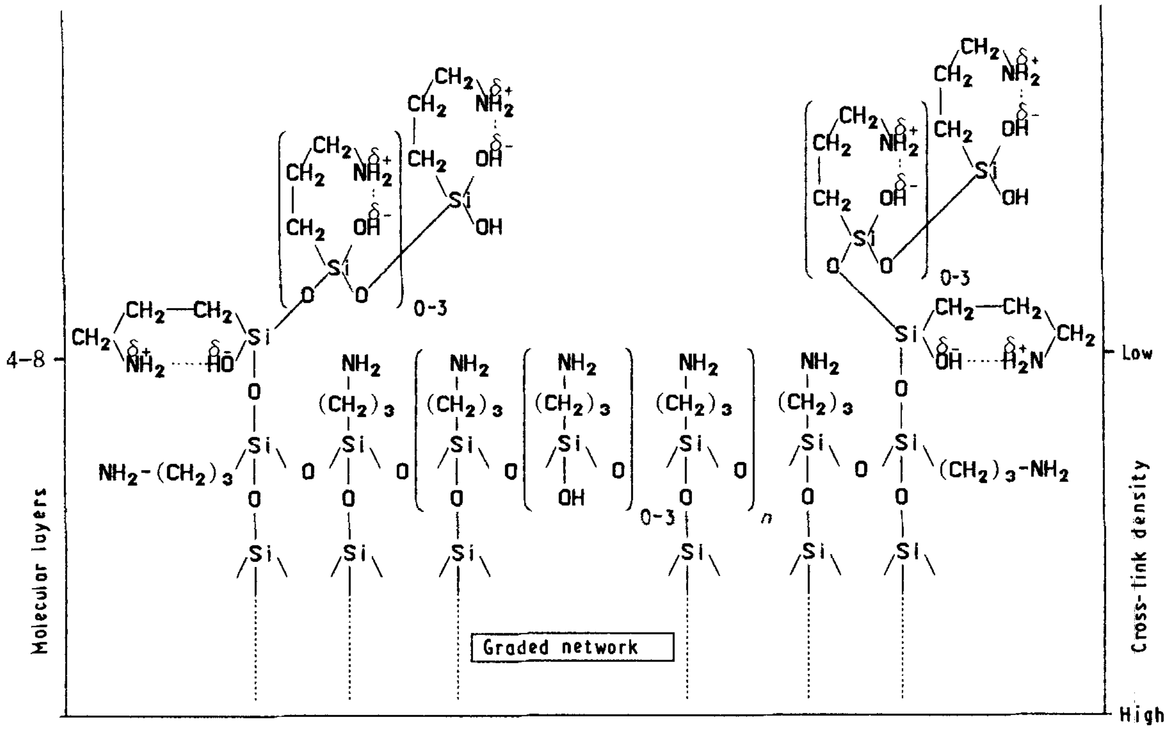

Figure 9 Model of the three-dimensional poly(aminosilane) network exposed by warm-water extraction. *n* is the structural repeat unit.

However, a chemical shift of the N1s peak from 400.3 eV to 401.4 eV was observed after warm-water extraction (see Fig. 7). From the structural assignment for the N1s peak at 401.6 eV (see Fig. 5) it is possible to propose that for the warm-water-extracted samples, N1s peak at 401.4 eV also arises from an hydrogen-bonded amino group. However, if the hydrogen bonding was random, then in the presence of the oligomeric component the N1s binding energy would be similar. Thus, it is likely that after warm-water extraction the amino group is involved in an internally hydrogen-bonded cyclic arrangement. However, because we consider that a three-dimensional network is present after warm-water extraction, these cyclic HAPS structures are more likely to arise from the ends of the polymeric network, which are now free to conform into the most stable hydrogen-bonded arrangement as shown in Fig. 9.

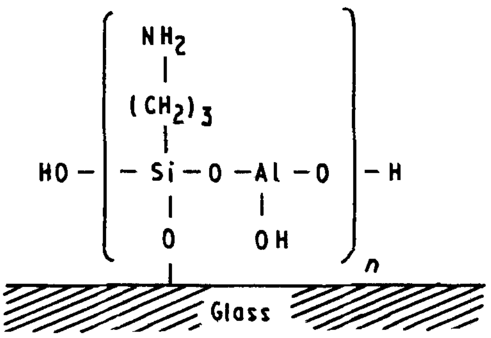

Figure 10 Model of the interfacial layer of the "silane" and "aluminoxane" exposed by hot-water extraction.

Fig. 7 shows that after hot-water extraction, the N1s peak shifted back to a binding energy of 400.3 eV, indicating that the amino group of the remaining HAPS molecules were in a non-hydrogen bonded form. Because hot-water extraction is known to involve hydrolysis leading to a monomolecular remnant of relatively high cross-link density [12, 13], this result indicated that the network-ends are of insufficient length for internal hydrogen bonding to occur. Taken together with the previous TOF SIMS results, this confirms (a) the argument that the network-ends probably provide much of the peak intensity of TOF SIMS, and (b) that the cross-link density of the deposit near to the glass surface is higher. This is entirely consistent with the argument presented elsewhere [12, 13, 28]. Furthermore, confirmation of the incorporation of aluminium chemically into the HAPS coating is obtained because the aluminium concentration increases after hot-water extraction (see Fig. 6). Therefore, a model of the interfacial "silane" and "aluminoxane" after extensive extraction must include these bond types as shown in Fig. 10.

5. Conclusion

Estimation of the thickness of the silane coating and identification of the structures of the HAPS molecules have been achieved using angle-resolved XPS. Confirmation of the incorporation of the aluminium ions from the glass into the HAPS coating has been obtained. The deposition of HAPS on to the glass surface as a function of pH was observed. The HAPS molecules at the outer layers were adsorbed perpendicular to the surface. In the three-dimensional network the involvement of the ends into an internally hydrogen-bonded cyclic form between the amino group and one of the silanol groups in the HAPS molecular structure were identified. At the silane/glass interface a covalent chemical bond between the HAPS monomolecular layer and the immediate glass surface exists.

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