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# A combined atomic force microscopy (AFM)/X-ray photoelectron spectroscopy (XPS) study of organosilane molecules adsorbed on the aluminium alloy L157-T6

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Organosilanes are extensively used to promote the adhesion of surface coatings and adhesives to different substrates, including metals. The surface concentration and spatial distribution of the organosilane on a particular material are important factors in determining its efficiency as an adhesion promoter. The powerful combination of atomic force microscopy (AFM) with X-ray photoelectron spectroscopy (XPS) was adopted to characterise the adsorption of aminopropyltriethoxysilane (APS) on the Al alloy L157-T6. Complementary information on the distribution of the adsorbed APS was obtained using the force–volume (FV) approach in AFM. The combined AFM/XPS study revealed that the coverage and stuctural integrity of the APS film were dependent on the concentration of the silane in solution. Greater coverage and better structural integrity were obtained by adsorbing the APS film from a 3% silane (in methanol) solution than from a 6% solution.

## Introduction

Organosilanes of the general structure R–Si(OR′)$_3$ (where R is an organo-functional group such as a vinyl, chloropropyl, epoxy, methacrylate, amino or mercapto group and R′ is a halide or alkoxide capable of hydrolysis) are used as coupling agents in composite materials[1] and as adhesion promoters between surface coatings and different materials including metals.[2] It is generally considered that the organosilane improves the hydrothermal stability of the surface coating on the metal by forming chemical bonds with both the metal and the surface coating. The organo-functional group is chosen to strongly bond with the surface coating. The mechanism by which the organosilanes bind to metal surfaces has been the subject of considerable research as the effectiveness of each silane coupling agent varies from metal to metal.[3] It is thought that the silane is hydrolysed to a silanol which then forms a primary oxane bond (Si–O–M) with the hydroxy groups on the metal oxide surface which are usually present on many metals under ambient conditions. The oxane bond is formed *via* a condensation reaction, eliminating water.

Some evidence for the existence of siloxane bonds at the interface between organosilanes and iron oxide surfaces[4] and aluminium oxide surfaces[5–8] has been reported. The techniques used to obtain this evidence include X-ray photoelectron spectroscopy (XPS),[4,5] time of flight secondary ion mass spectrometry (ToF SIMS),[4,5] inelastic electron tunnelling spectroscopy (IETS)[6] and IR spectroscopy, both transmission and reflection absorption (RAIRS).[7] Convincing evidence for the existence of siloxane bonds at the interface between an organosilane and a metal oxide surface comes from measurements of the Auger parameter measured by XPS for octadecylsilane adsorbed on an aluminium oxide surface.[8]

XPS and other surface analytical techniques cannot provide evidence for the topographic distribution of the adsorbed silane. Silane based adhesion promotors are known to agglomerate, especially when undergoing polymerisation by hydrolysis. Thus in this work, in addition to measuring the uptake of the silane by XPS, we have examined the surfaces by AFM to establish whether this technique can provide useful evidence regarding the uniformity of deposition.

AFM has been used in the past to investigate the growth of silanes on silicon substrates as self-assembled monolayers (SAMs)[9,10] and shows them to be well ordered. Within the context of adsorption on silicon, AFM has been able to show how the adhesion of the monolayer is affected by the structure of the silane head group[11] but there have been no related studies of adsoption on aluminium or its alloys.

The study centred on the adsorption of aminopropyltriethoxysilane (APS) on the aluminium alloy L157-T6. The stabilities of the APS films on the Al alloy were characterised by observing the action of sulfuric acid on these films and on the alloy itself.

## Experimental

### Materials

The aluminium alloy [Cu, 4.4; Mn, 0.8; Si, 0.8; Mg, 0.5 (average content); Fe, 0.5; Zn, 0.25; Ti + Zr, 0.2; Ti, 0.15; Ni, 0.1; Cr, 0.1; others, 0.15% (maximum content)] was supplied by DERA, Farnborough, UK. The alloy was supplied solution treated and artificially aged and designated (BSI) L157-T6. Aminopropyltriethoxysilane [$NH_2(CH_2)_3Si(OEt)_3$] (Silquest A1100) was obtained from OSi Specialities (UK) Ltd, Harefield, Middlesex, UK.

### XPS analysis

The XPS analysis was conducted using an ESCALAB Mk II electron spectrometer (VG Instruments, East Grinstead, UK) interfaced to a VGS 5000-S datasystem based on a DEC PDP 11/73 computer. For each specimen analysed, a survey spectrum was recorded at an analyser pass energy of 50 eV together with high resolution spectra of the elements of interest (C 1s, O 1s, Al 2p, Mg 2s, Cl 2p, N 1s, S 2p, Si 2p, Si KLL and Cu 2p) at an analyser energy of 20 eV. Mg-Kα radiation was employed at a power of 200 W; 20 mA at 10 kV. Quantitative



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**Table 1** Assignment of XPS binding energy and change in relative Si content on surface with treatment. Peak positions referenced to C peak at 284.8 eV

| Sample | Binding energy[a]/eV | | | Normalised atom% | | |
|---|---|---|---|---|---|---|
| | O 1s | Al 2p | Si 2p | Si 2p | Al 2p | Si 2p/Al 2p ratio |
| Al alloy L157-T6, as polished | 532.1 | 74.7 | 102.5[b] | 7.04 | 89.81 | 0.08 |
| Al alloy L157-T6, polished, $Ar^+$ ion etch, 6 kV, 15 min | 530 | 70.2[c] | — | — | 93.14 | 0.00 |
| Al alloy L157-T6, polished, $Ar^+$ ion etch, 6 kV, 15 min, $H_2O$–methanol–$H_2O$ | 531.7 | 74.1 | — | — | 100.00 | 0.00 |
| 3% APS film/Al alloy | 531.9 | 74.5 | 101.7 | 5.91 | 89.70 | 0.07 |
| 6% APS film/Al alloy | 531.6 | 74.2 | 102 | 10.12 | 78.57 | 0.13 |
| 3% APS film/Al alloy, $H_2SO_4$ 20% v/v 20 min | 531.7 | 74.3 | 101.7 | 5.65 | 87.44 | 0.07 |
| 6% APS film/Al alloy, $H_2SO_4$ 20% v/v 20 min | 532 | 74.4 | 102.2 | 5.67 | 86.11 | 0.07 |
| 3% APS film/Al alloy, vacuum, $H_2SO_4$ 20% v/v 20 min | 531.8 | 74.6 | 102 | 5.97 | 90.44 | 0.07 |
| 6% APS film/Al alloy, vacuum, $H_2SO_4$ 20% v/v 20 min | 531.5 | 74.5 | 101.9 | 7.87 | 86.69 | 0.09 |
| Assignment[12] | $Al_2O_3$ | $Al_2O_3$ | APS | | | |

[a] $\pm 0.2$ eV. [b] Assignment: poly(dimethylsiloxane) removed by $Ar^+$ ion etch. [c] Assignment: Al.

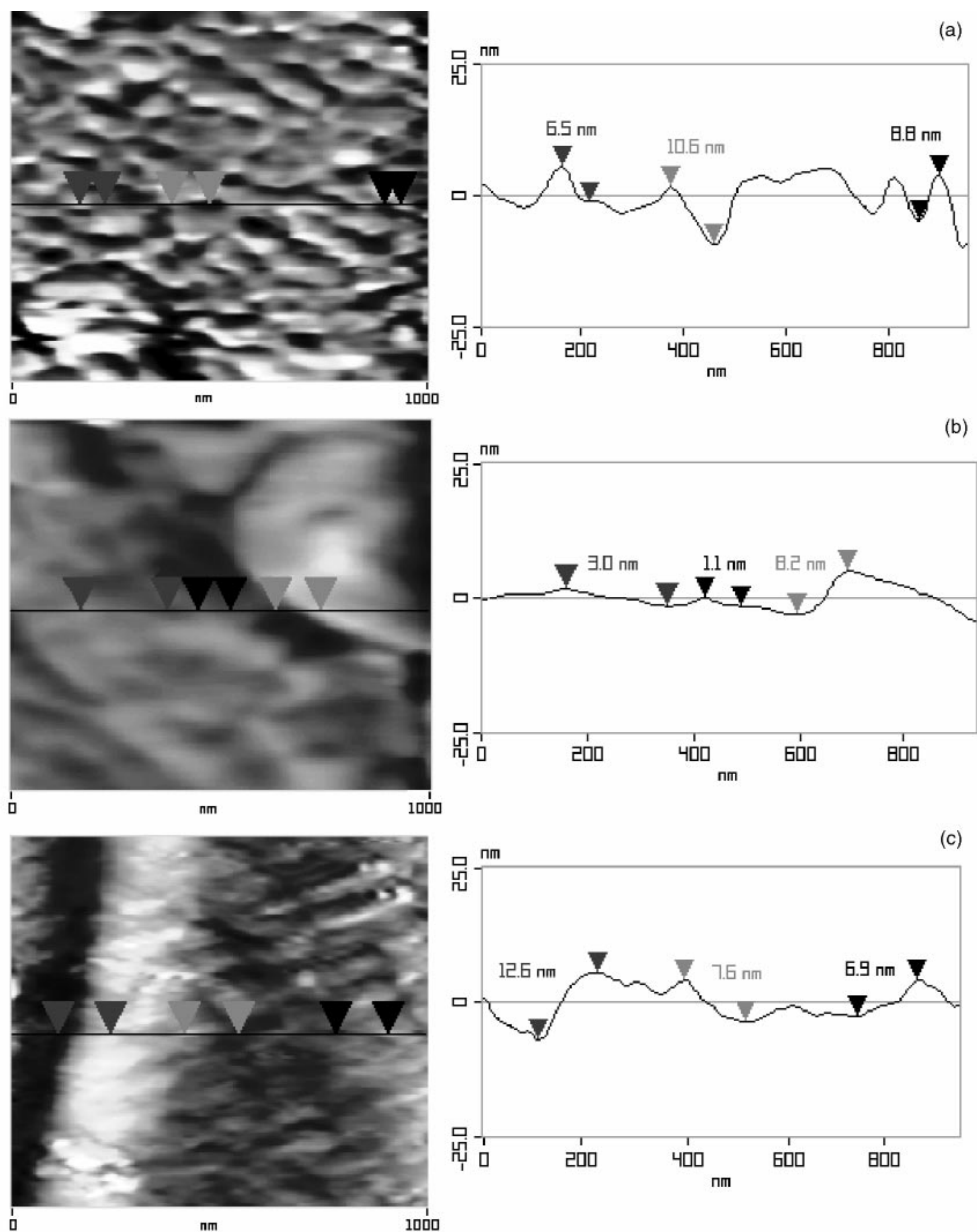


**Fig. 1** AFM images and section analyses of Al alloy samples; (a) Al alloy reference: the surface pattern, produced by an $Ar^+$ ion etch, acts as a surface structural indicator, (b) after deposition of a 3% APS film and (c) after deposition of a 6% APS film. Scale: all AFM images are $1 \times 1$ µm, $z$ range = 50 nm.

analysis was achieved using the peak areas of the high resolution spectra following the removal of a linear background. The instrument software was employed to correct for the analyser transmission function and electron inelastic mean free path. Wagner's sensitivity factors were used to calculate the normalised peak areas. Both qualitative and quantitative data was obtained for each sample.

### AFM imaging

The adsorption of APS films were studied *ex situ* using a Nanoscope III atomic force microscope (Digital Instruments, Santa Barbara, CA, USA) with a Si cantilever and tip. Images were obtained in the height mode where the tip–sample distance was maintained by a feedback system allowing the topography of the sample to be mapped. Section and roughness analyses were performed on the data contained in the images.

### Substrate preparation

The silanes were adsorbed onto elliptically shaped samples of the aluminium alloy (major axis 14 mm, minor axis 13 mm) which enabled each sample to be positioned with some degree of freedom on the AFM scanner head (diameter 15 mm). These samples were polished to reduce the effects of large-scale topography, which could obscure small features. Both sides of each sample were hand-polished using a coarse polishing paper (800 grit) to ensure that both sides were flat. One side was then polished mechanically (Pedemax 2, Struers UK, Glasgow) using the protocol described below.

The samples were polished at 300 rpm through papers of grit size; 800 (3 min), 1200 (3 min), 2400 (4 min) and 4000 (5 min) at a load of 80 N using water as a lubricant. Following this, the samples were polished at 150 rpm using DP-Mol 3 μm (load, 160 N) and 1 μm (load, 80 N) cloths for 5 min. The lubricant was DP-Red. The final, 0.25 μm, finish was achieved by polishing the samples for 0.5 min using an OP-Chem 0.25 μm cloth at 150 rpm. The load was 80 N and the lubricant was OPS.

All washing and hydration of surfaces was undertaken using a high purity (MilliQ) grade of water.

### Deposition of organosilane films

Polished samples of the Al alloy, which had been etched by an $Ar^{+}$ ion beam, were immersed in water for 10 s to hydrate the surface. The samples were subsequently immersed in 3 and 6% solutions of the APS in methanol for 2 min (each solution having been freshly prepared and allowed to stand for 60 min prior to use). The samples were then immersed in fresh water for 30 s to remove any residual silane solution. Excess water was removed from the surface by touching the edge of the sample to a lens tissue. The samples were allowed to dry in air. Al alloy references were created by the same procedure, except that the references were immersed in fresh methanol rather than a silane solution.

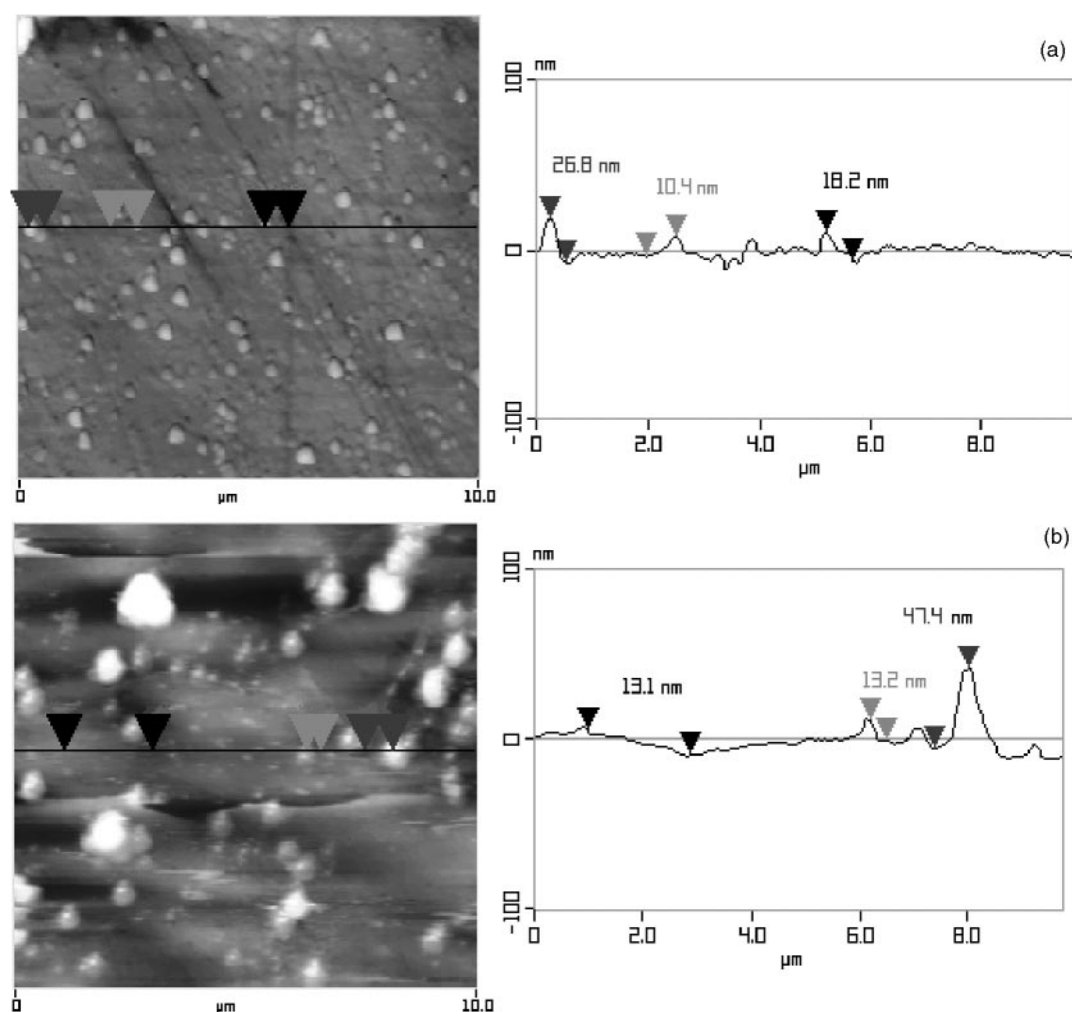


**Fig. 2** AFM images and section analyses of a 3% APS film on an Al alloy substrate; (a) before and (b) after etching with 20% $H_2SO_4$ for 20 min. Scale: all AFM images are $10 \times 10$ μm, $z$ range = 200 nm.

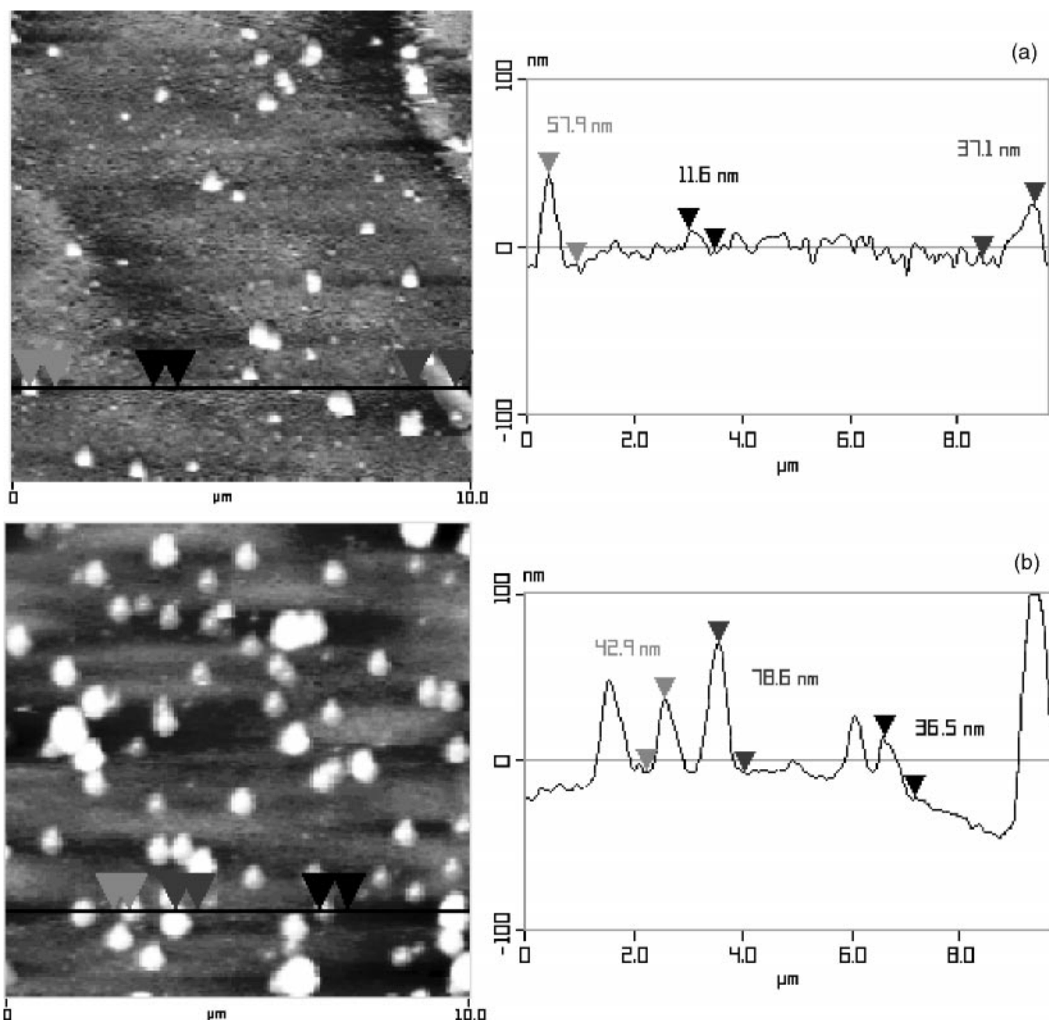


**Fig. 3** AFM images and section analyses of a 6% APS film on an Al alloy substrate; (a) before and (b) after etching with 20% $H_2SO_4$ for 20 min. Scale: all AFM images are $10 \times 10$ μm, $z$ range = 200 nm.

## Results and discussion

### AFM and XPS analysis of the samples prior to silane treatment

The oxide thickness on the Al alloy reference, determined from the oxide/metal peak ratio, was 3.4 nm (Table 1). Little sign of surface structure was observed in the polished Al alloy surface after this preparation. In this study, all the samples used were etched using an $Ar^+$ ion beam (6 kV, 15 min) prior to adsorption of the silane films. The $Ar^+$ ion etch formed a pattern of small depressions across the whole surface [Fig. 1(a)] and thus served as a marker for the Al alloy surface.

### AFM and XPS analysis of the adsorption of the APS

APS films were adsorbed onto the Al alloy surface for 2 min from 3 and 6% solutions of the silane in methanol [Fig. 1(b) and (c)]. In both cases, the $Ar^+$ ion etch pattern on the surface was altered. For the surface obtained using the 3% silane solution, the etch pattern completely disappeared and was replaced by a smooth surface, as demonstrated by the section analyses [Fig. 1(a) and (b)]. This suggested that a silane film had formed on the Al alloy surface. For the surface obtained using the 6% silane solution, the etch pattern was suppressed but not completely removed suggesting that the deposited silane film was less uniform than the film obtained from the 3% silane solution. It was also observed that the coverage of the 6% silane film on the surface was fragmented compared to the 3% film coverage; areas were observed where the $Ar^+$ ion etch pattern was clearly visible [Fig. 1(c)].

XPS survey spectra showed the presence of Si peaks after the adsorption of the 3 and 6% APS films. The binding energies of the individual peaks and their probable chemical states for the different samples are summarised in Table 1. The Al alloy surfaces used for the adsorption of the APS film were $Ar^+$ ion

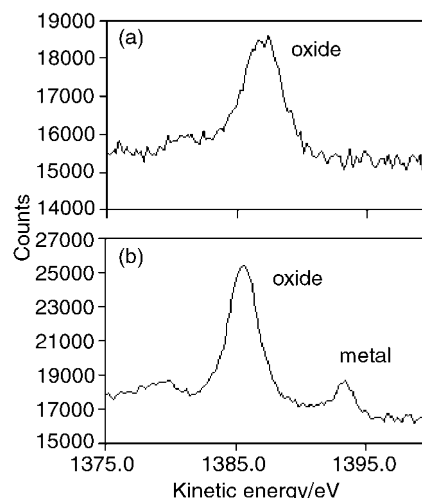


**Fig. 4** Auger electron spectra of a particle present on the surface of the 6% silane film (a) and of the film/substrate itself (b), both after etching with 20% $H_2SO_4$ for 20 min. The presence of only the Al oxide peak in spectrum (a) suggests that the particle is aluminium oxide created by the etching process.

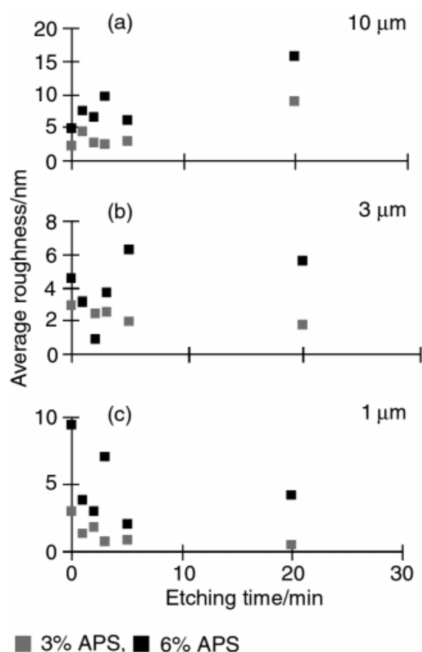


**Fig. 5** Graphs of average surface microroughness (nm) *versus* etching time (min) using 20% $H_2SO_4$; (a) 10 μm scan, (b) 3 μm scan and (c) 1 μm scan.

etched for the same period as the reference sample. Thus, it was assumed that the Si present on these samples was due to the APS $[H_2N(CH_2)_3\mathit{Si}(OEt)_3]$ film. Table 1 shows that the deposition of the 6% silane film resulted in a greater percentage of Si on the surface of the Al alloy as compared to the 3% film, as expected even though it seemed from AFM to have a patchy distribution.

XPS analysis showed that the 3% APS film was relatively stable towards a 20 min etch using $H_2SO_4$ (20% v/v) as the Si to Al ratio (0.07) remained constant (see Table 1). This result suggested that the acid etch could be used to determine the distribution of the APS on the surface of the Al alloy, as the etch would highlight areas of the surface not covered by the silane film. The 6% APS film was less stable towards $H_2SO_4$, as the Si to Al ratio was reduced from 0.13 to 0.07 after immersion in the acid bath. It has been reported that silane solutions above 4% lead to excessively thick and weakly polymerised silane films which can exhibit cohesive failure.[13] This finding is consistent with the AFM result indicating that the surface coverage of the 6% APS film was poor compared to the 3% silane film. This suggests that cohesive failure within the silane film occurs for the 6% silane film during the etch. A check was made (Table 1) to establish whether prior analysis, which involved exposure of the silane film to spectrometer vacuum, had an influence on the subsequent exposure to the acid bath: it did not.

Chemical etching by $H_2SO_4$ was used to characterise the surface coverage of the silane films using AFM. Both films

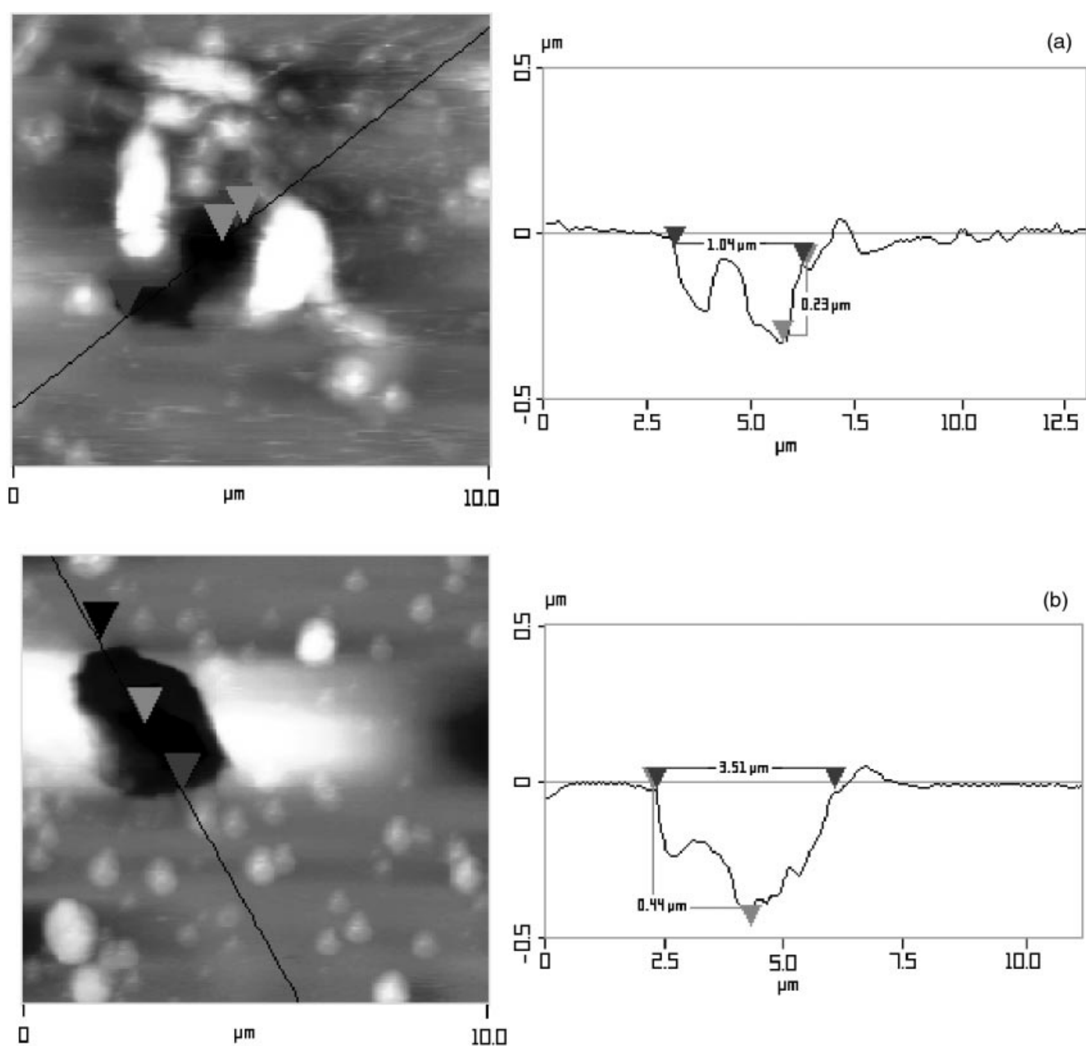


**Fig. 6** AFM images and section analyses of pits obtained after etching with 20% $H_2SO_4$ for 20 min; (a) in the Al alloy substrate covered by a 3% APS film and (b) in the Al alloy substrate covered by a 6% APS film. Scale: all AFM images are 10 × 10 μm, *z* range = 1 μm.

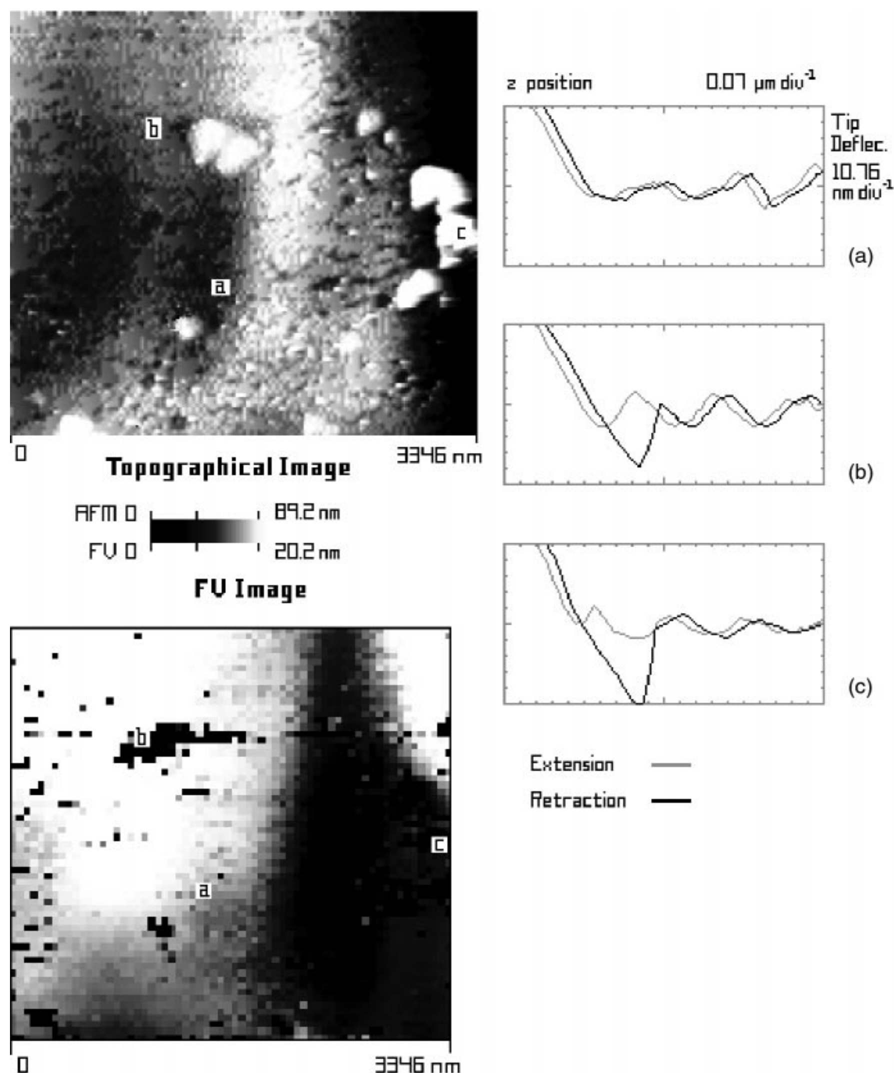


**Fig. 7** Topographical AFM image and force–volume (FV) image of a 6% APS film on an Al alloy substrate; the forces obtained on extension and retraction of the AFM tip are shown for the points indicated. Scale: all AFM images are 3346 × 3346 nm, *z* range (topographical image) = 89.2 nm, *z* range (force–volume image) = 20.2 nm.

contained small protrusions before etching [Fig. 2(a) and 3(a)]. For the 3% film, the maximum size observed for a protrusion was *ca.* 300 nm in diameter and 25 nm in height. Larger protrusions were observed in the 6% film with the maximum observed size being *ca.* 500 nm in diameter and 50 nm in height. Following etching, these features could still be observed in the background. However, both films now contained larger protrusions in greater numbers, with the maximum size observed being *ca.* 1 μm in diameter and up to 100 nm in height [Fig. 2(b) and 3(b)]. Examination by Auger electron spectroscopy (AES) showed that the surface features present after etching were in fact aluminium oxide (Fig. 4). A greater number of these aluminium oxide areas were present in the 6% film than in the 3% silane film. This behaviour was reflected in the roughness analysis (Fig. 5). Three fields of view were used (10 × 10 μm, 3 × 3 μm or 1 × 1 μm) and these showed that the mean roughness of the 3% film was less than that measured for the 6% film in all but one of the exposures. This behaviour enables the two films to be distinguished.

These roughness data suggest that the silane films provide corrosion protection for the surface of the Al alloy from the acid and that the degree of corrosion protection varies with the film coverage of the surface. Indeed, pitting of the substrate was observed after etching. Larger pits were obtained when the 6% silane film was covering the aluminium alloy substrate than when the substrate was covered by the 3% silane film, as shown in Fig. 6. It is possible that the coverage of the silane films is affected by inclusions present in the alloy surface.

### Force–volume AFM imaging of APS films

The force curve, obtained as the tip is lowered onto the surface, provides information on the interaction forces operating between the tip and sample and can be measured at every point on the surface of the sample simultaneously with the topography. The image obtained in this mode of use, known as the force–volume (FV) image, is displayed in tandem with the topographical image. The FV image would provide further information on the non-uniform distribution of the silane film resulting from the 6% solution. The outcome is shown in Fig. 7 with the conventional topographical image at the top left. The letters **a**–**c** indicate the points from which the complete force curves shown on the right were obtained. Such force curves from every point on the topographical image are combined to obtain the FV image shown at the bottom left. The colour scale in this FV image shows the deflection range of the tip due to the forces perpendicular to the surface, acting on the tip at each point across the surface, at a set *z* distance between the cantilever and sample surface. The force curves are shown to allow a more quantitative assessment of the scale of interaction to be obtained. We note that the black area in the FV image related to a region of the surface in the topographical image, which still carried the characteristic ripple resulting from ion

etching. The white areas in the FV image correspond to particularly smooth regions in the topographical image, which are presumably those areas where the film has been well deposited. The force curve at point **a** indicates that there is a low degree of interaction between the tip and the APS film. At point **b**, a stronger interaction between the tip and the surface is obtained. The nearby presence of an aluminium oxide particle suggests that the APS film may be disrupted at this point. The strongest interaction is obtained at point **c**, on the surface of an aluminium oxide particle where there is no APS film. This preliminary FV data obtained from the 6% silane film suggests that the technique can be used to probe the structure and properties of the silane films directly, such as mapping the defect sites present in the organosilane films and elucidating their performance as adhesion promoters.

## Conclusions

The results reported here have shown that AFM in combination with XPS has enabled study of the deposition of silane films onto the surface of the aluminium alloy (L157-T6) and their resulting behaviour in an aggressive environment. The presence of APS films adsorbed on the Al alloy has been revealed by an *ex situ* AFM/XPS study. This was achieved by using an $Ar^+$ ion beam etch as a surface structural indicator. The study showed that the silane film obtained from a 3% solution of the silane in methanol exhibited greater coverage of the alloy Al substrate and was structurally more stable towards a sulfuric acid etch than the film obtained from a 6% silane solution.

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