

Examination of the Interphase Chemistry between Metallic Substrates and Organosilanes:

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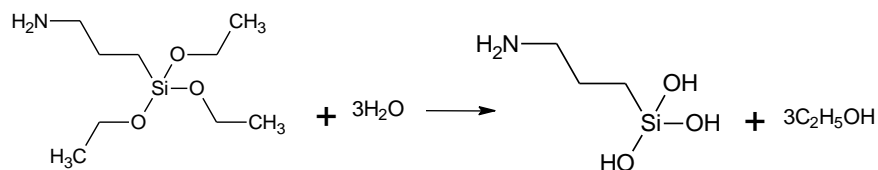
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Background

- Silanes are used in many applications and not only as adhesion promoters, other examples include:
 - Control of thixotropy
 - Functionalisation
 - Temperature resistance
- As adhesion promoters they are included in formulations as well as used as primers
- Parameters that may influence their effects include:
 - Temperature
 - Concentration
 - Type of solvent
 - Their own chemistry:
 - Type of alkyl
 - Organic functionality
 - Presence of catalysis (self or otherwise)
 - Etc.....
- What tools are necessary to study such phenomena:
 - ToF-SIMS
 - XPS
 - FTIR
 - NMR
 - AFM

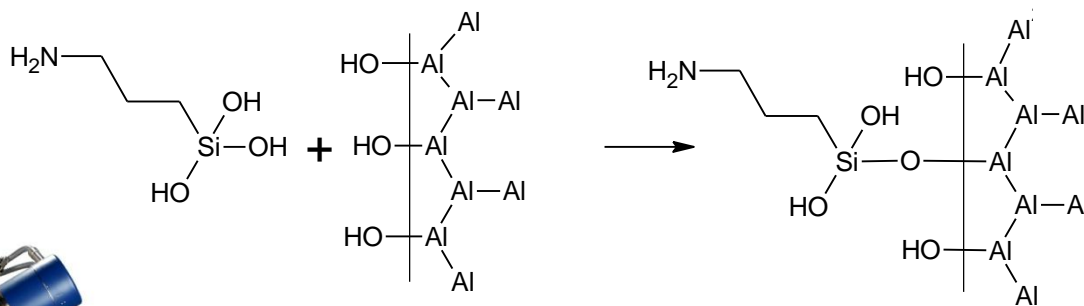
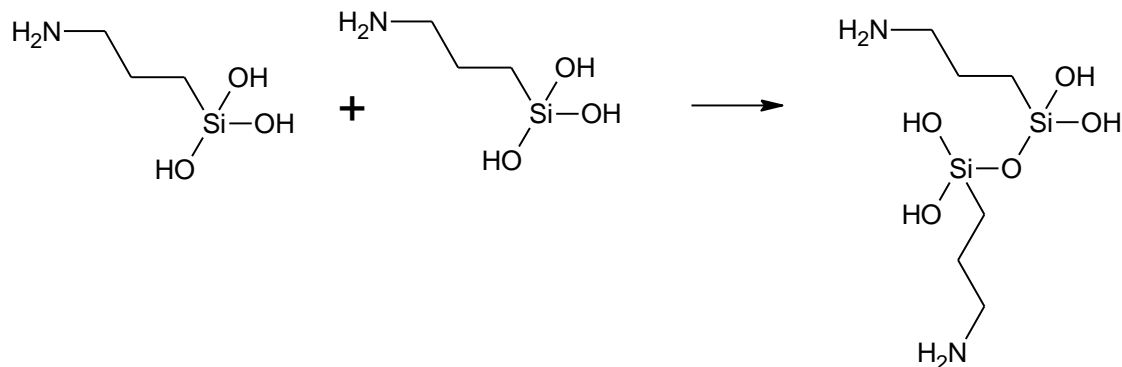


Silanes Major Reactions (APS)



Hydrolysis

Self-condensation
“crosslinking”



Reaction with substrate (eg.
aluminium)

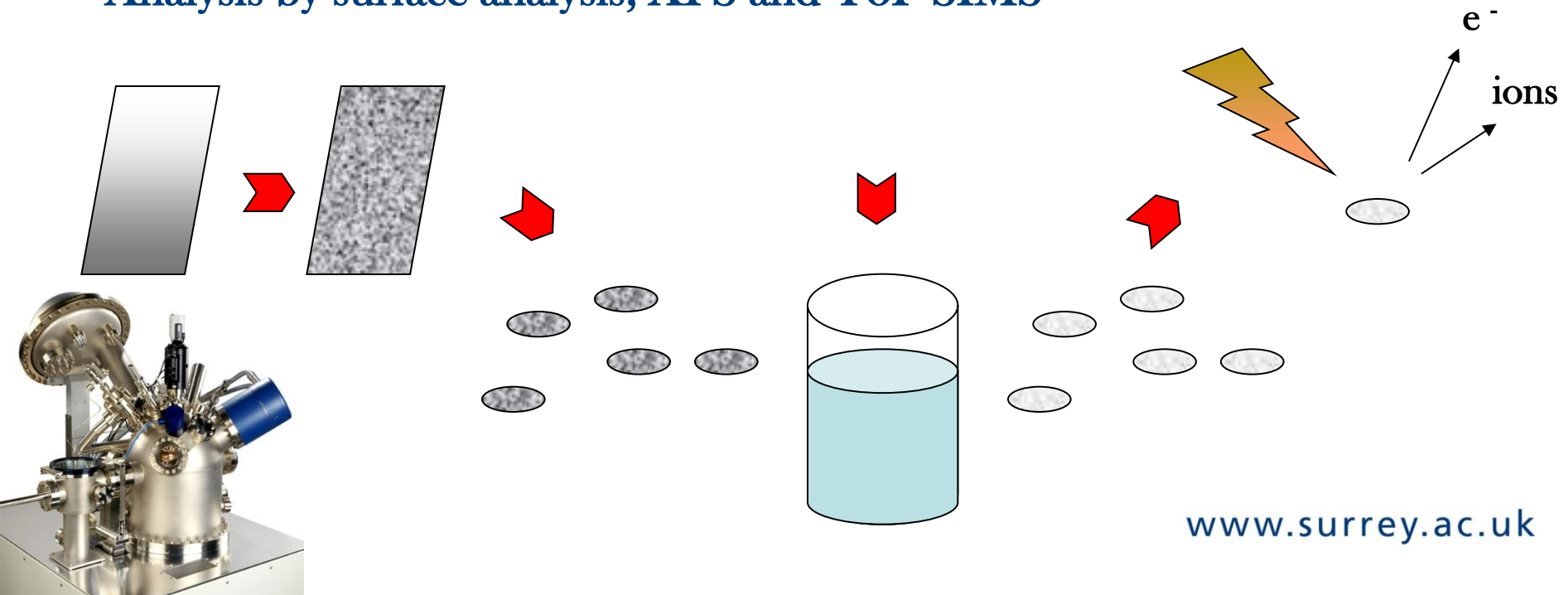


Reaction of Silanes in Thin Films



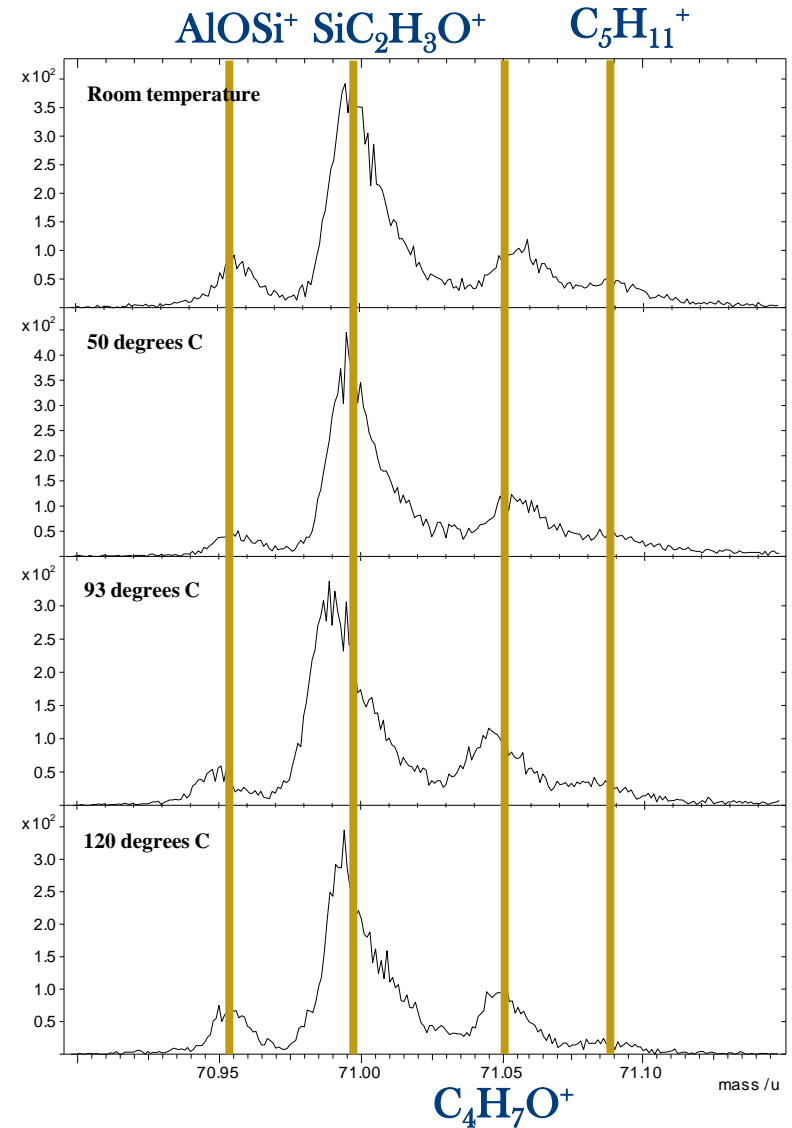
Sample Preparation: Coated Discs

- Commercially pure aluminium grit blasted with 60 μ m alumina
- Discs one cm diameter cut then dipped in a solution of silane (0.5%) in aqueous or ethanolic solution for 10 minutes. Drying of discs tipped on their side on absorbing tissue
- Drying temperature ranging from RT to 120 $^{\circ}$ C (RT, 50, 93, 120 $^{\circ}$ C)
- Analysis by surface analysis, XPS and ToF-SIMS



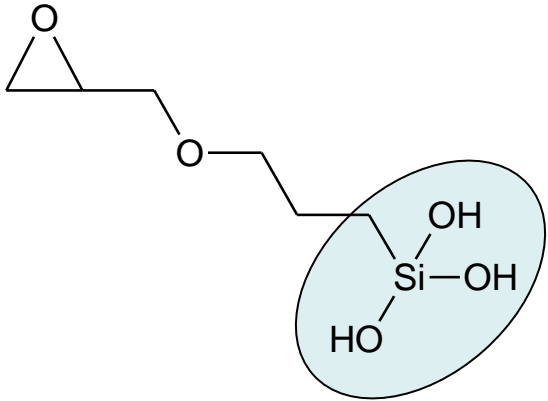
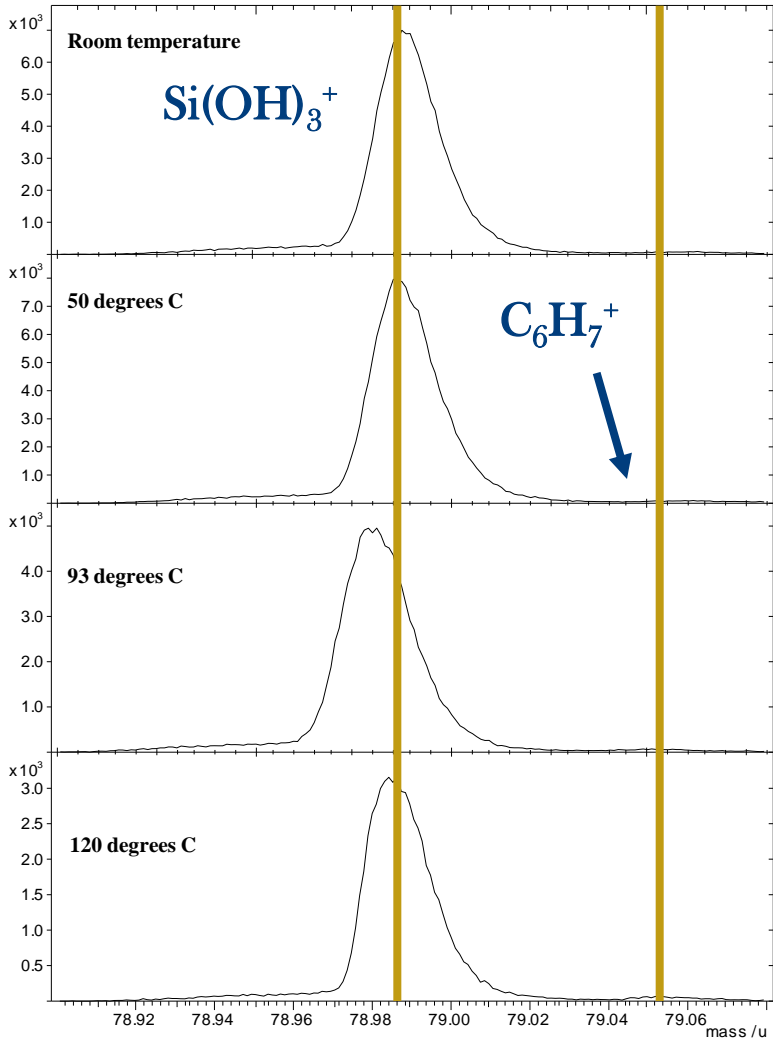
ToF-SIMS of GPS Thin Films

- Examination of the thin films signal in the region of the AlOSi indicates presence of a covalent bond between aluminium and GPS
 - This bond is formed at all temperatures. No temperature threshold for bond formation



ToF-SIMS of GPS Thin Films

- All films indicate a high amount of hydrolysed silane
- Another peak present at nominal mass 79 ($C_6H_7^+$) indicates the amount does not vary versus temperature

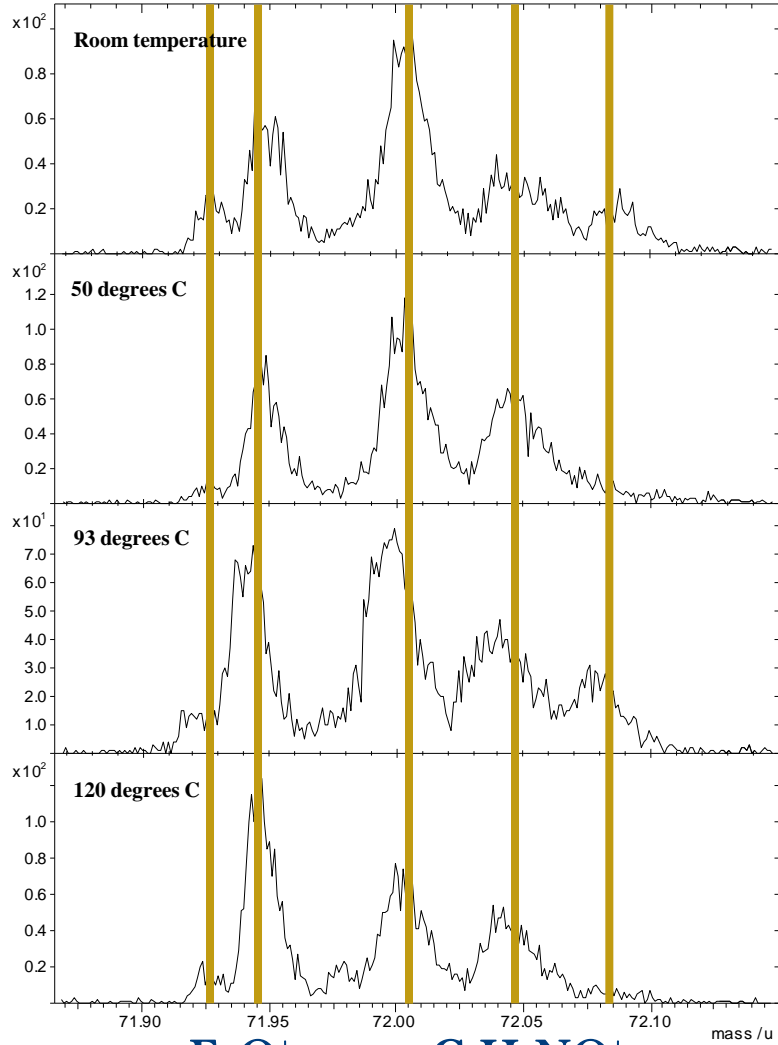
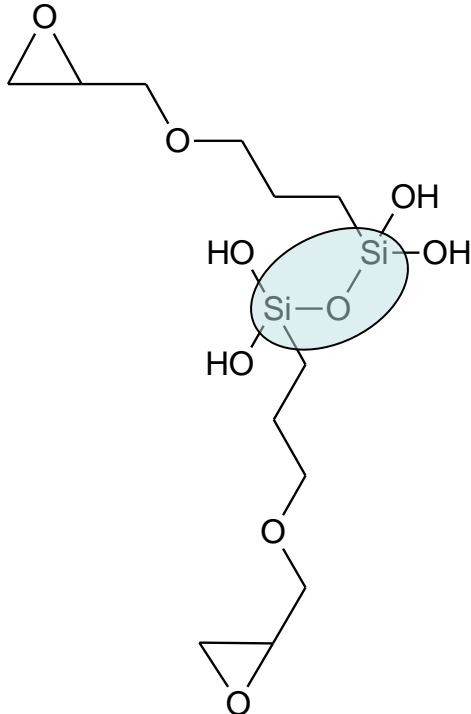


ToF-SIMS of GPS Thin Films



Si_2O^+ $\text{SiC}_2\text{H}_4\text{O}^+$ $\text{C}_4\text{H}_{10}\text{NO}^+$

- Presence of Si_2O^+ (mass 72) indicates crosslinking within the thin films
- This peak seems to increase as a function of temperature



FeO^+

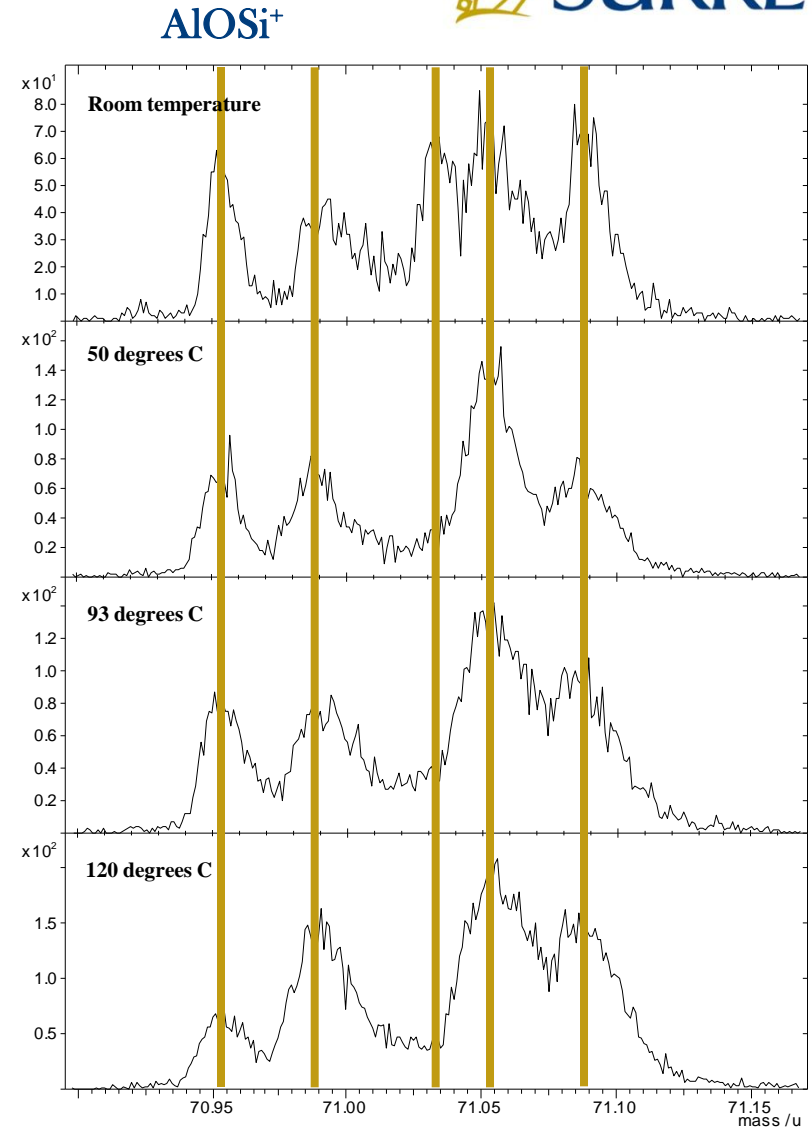
$\text{C}_3\text{H}_6\text{NO}^+$

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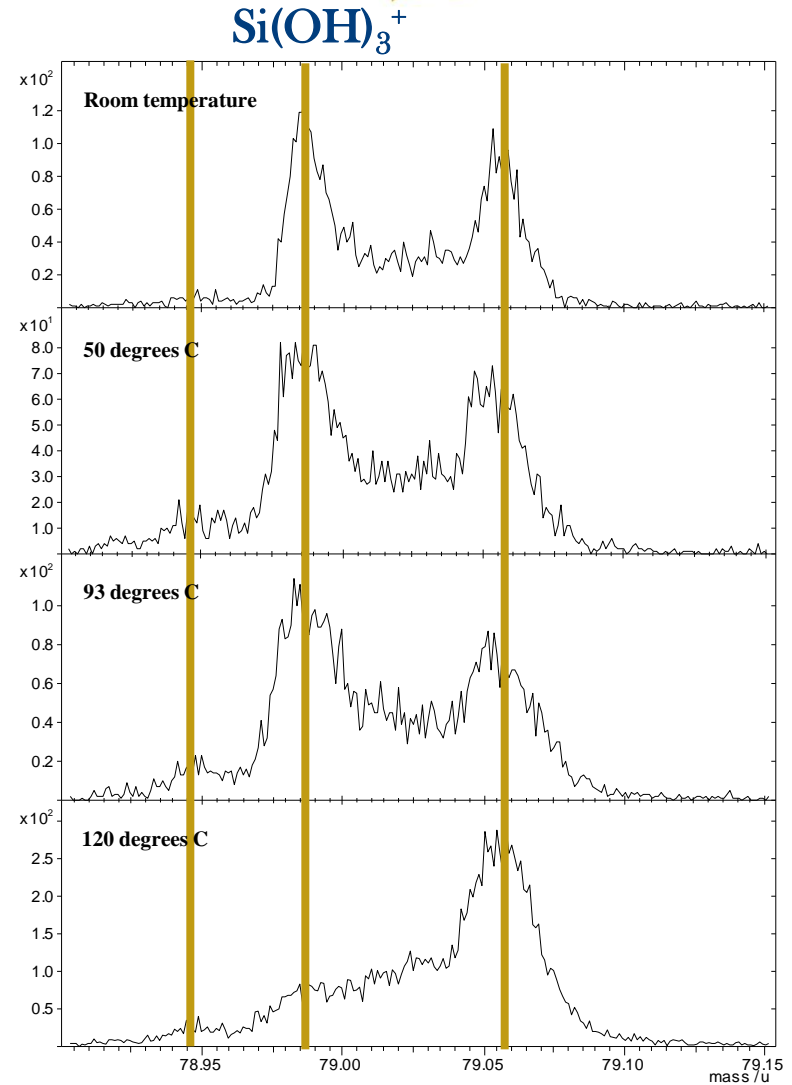
APS Thin Films examined with ToF-SIMS

- Similarly to GPS the region of AlOSi^+ indicates presence of a covalent bond between aluminium and APS
- Once again this bond is formed at all temperatures. There does not seem to be any threshold but seems more intense than for GPS



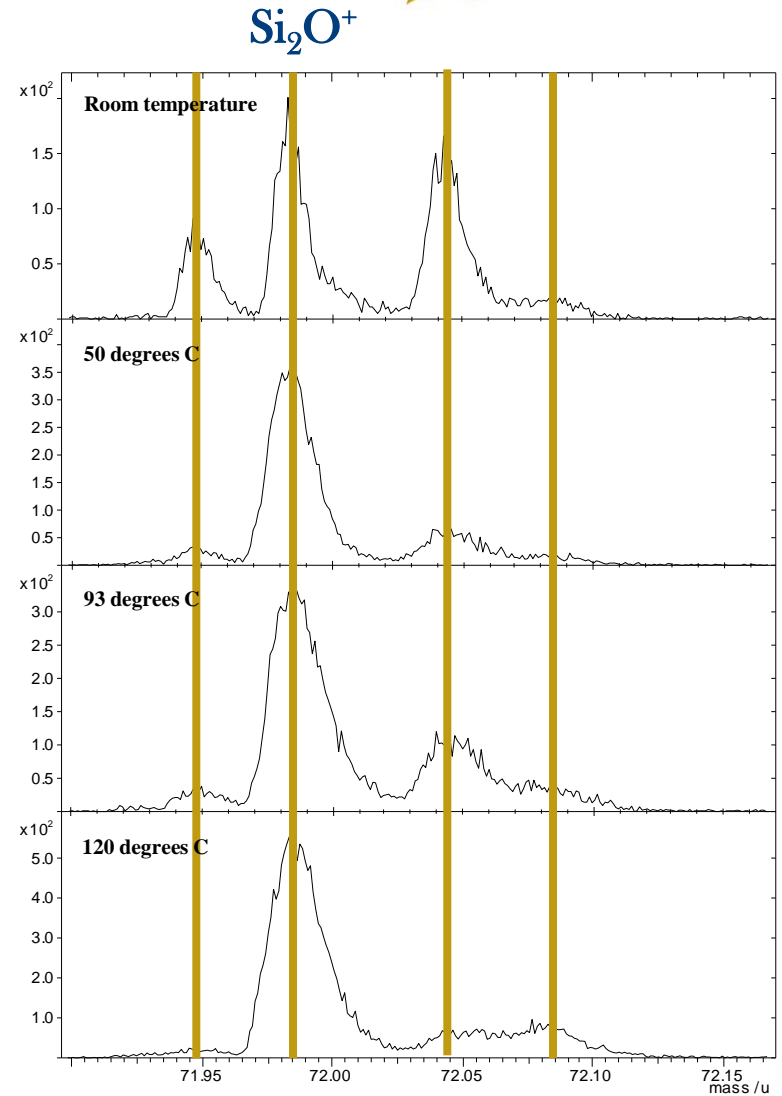
APS Thin Films examined with ToF-SIMS

- The fragment $\text{Si}(\text{OH})_3^+$ is present at all temperatures but decreases with temperature increasing
- We postulate that this is related to increase of crosslinking of APS within the thin film



APS Thin Films examined with ToF-SIMS

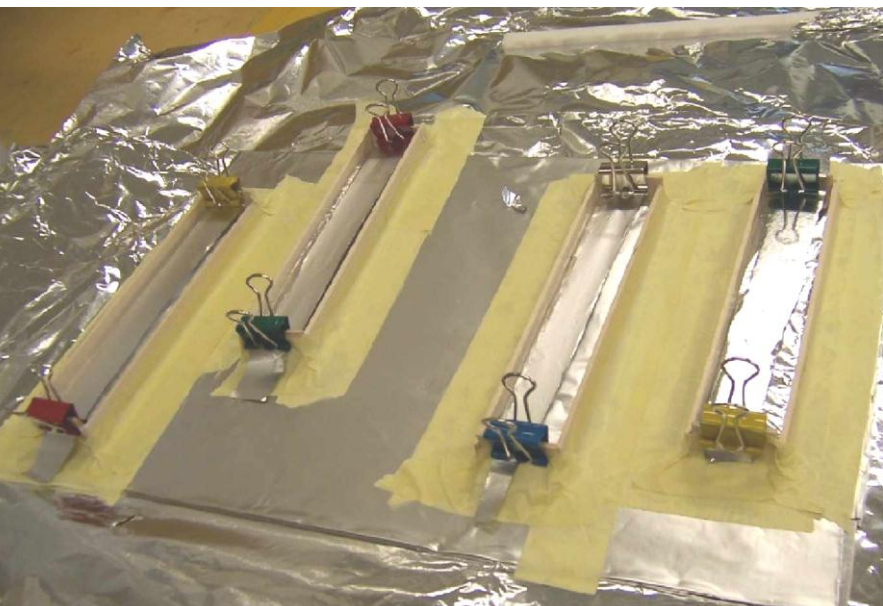
- Similarly to GPS thin films, APS has crosslinked
- It has however increased in intensity with temperature
- This may be due to the self catalysing nature of nitrogen containing silanes on such reactions



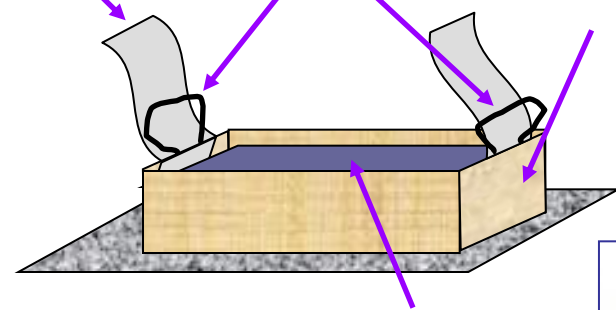
Silanes Incorporated in Adhesive Formulations



Sample Preparation: Model Samples (“sandwich”)



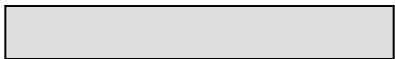
Aluminium foil
Clips to keep Al foil taught
Trough is made from wooden mixing spatulas



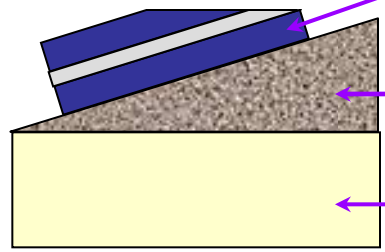
Adhesive mixture (contains APS or GPS)



Microtome Knife



Sandwich sample

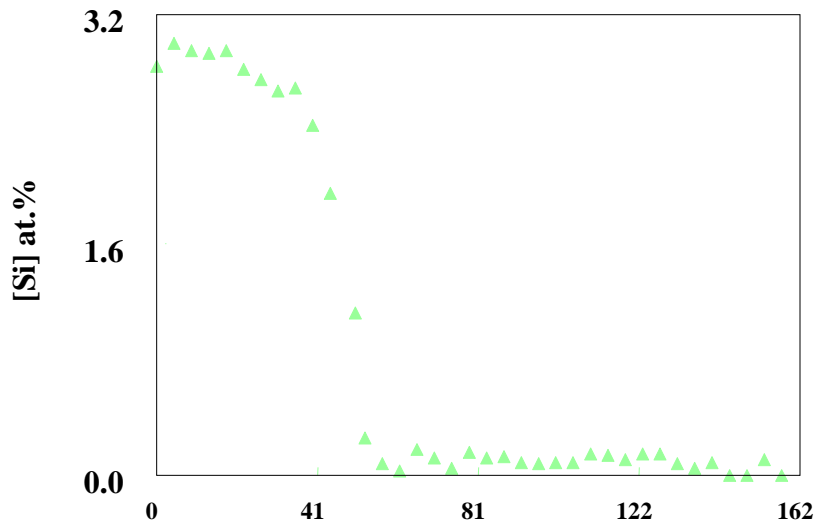


Angled Sectioning Block (2 or 0.33 degrees)

Polypropylene Block

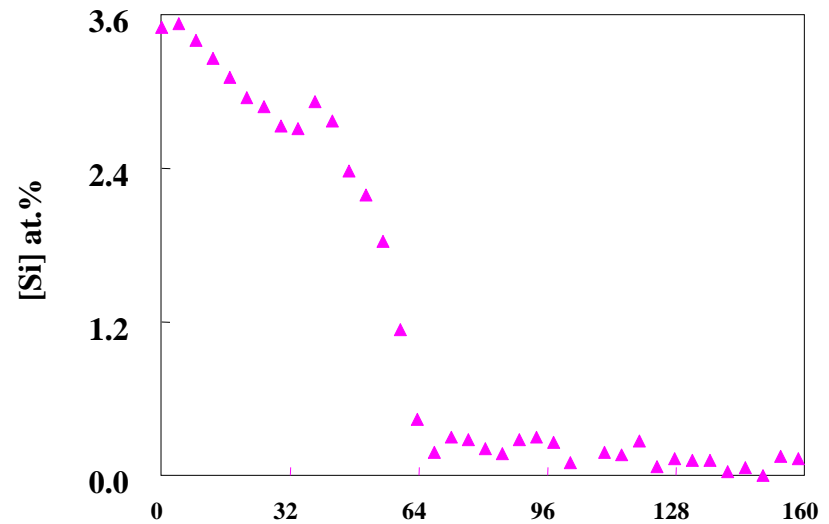
XPS of Sandwich Samples: GPS

Linescan for epoxy adhesive
0.5% GPS silane 2 degrees



Depth (um) interface to bulk

Linescan for epoxy adhesive
2% GPS silane 2 degrees

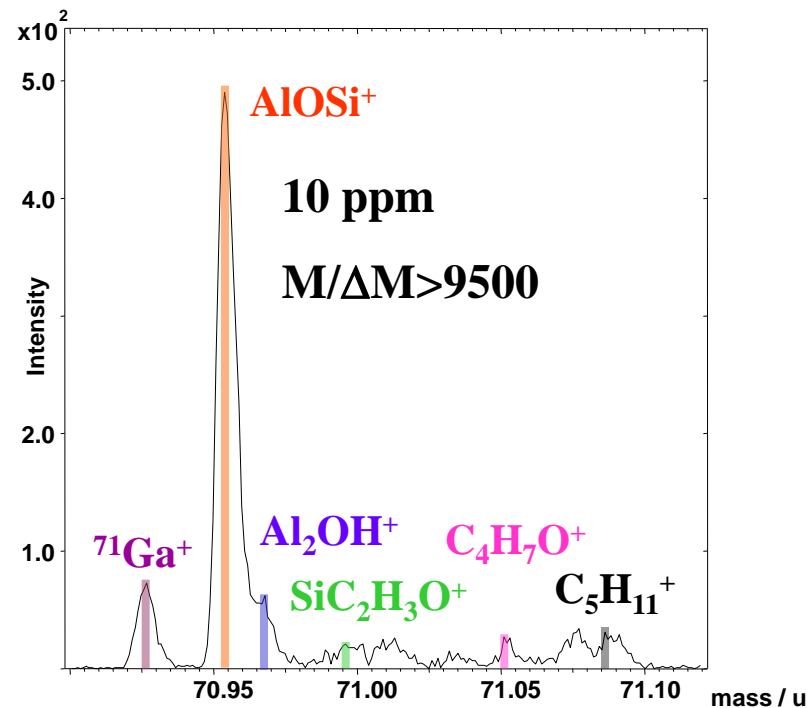
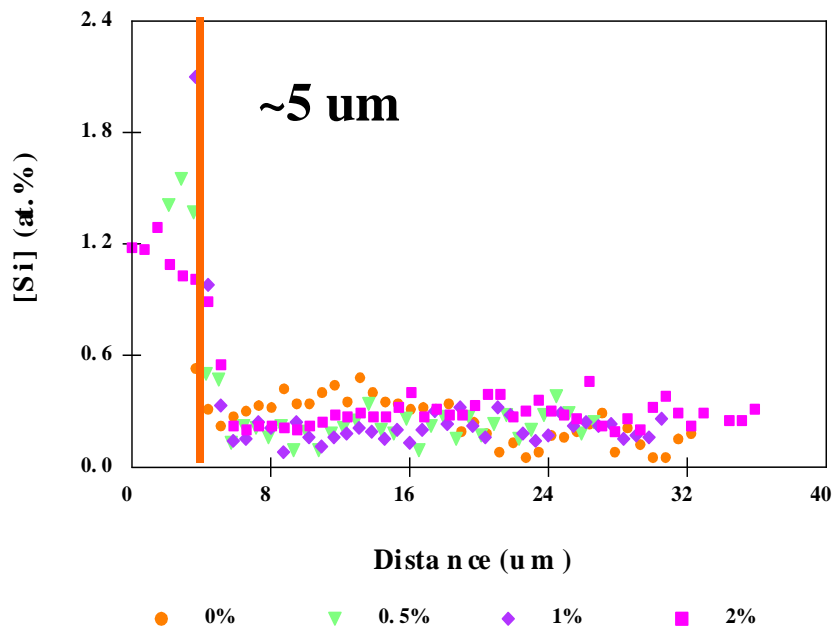


Depth (um) interface to bulk

- Concentrations of silicon similar
- Front of diffusion different at 50 and 55 microns
- Two fronts of diffusion??



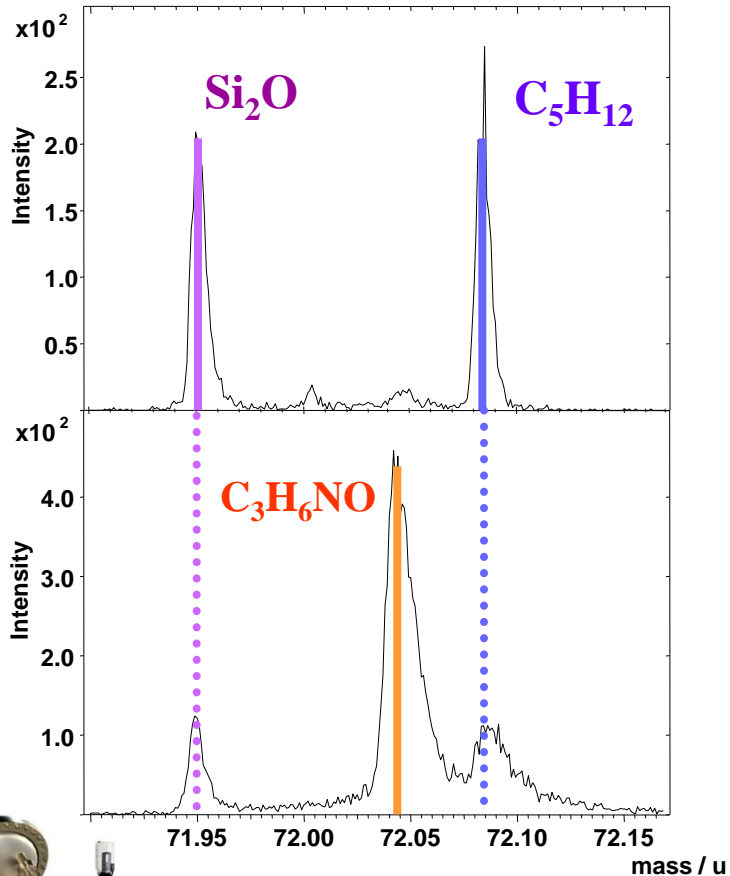
XPS of Sandwich Samples: APS



- APS diffuses towards interface but much closer than GPS
- There exist a pure layer of APS
- Bonding occurs at interface
- Phenomena are neither temperature nor concentration dependant

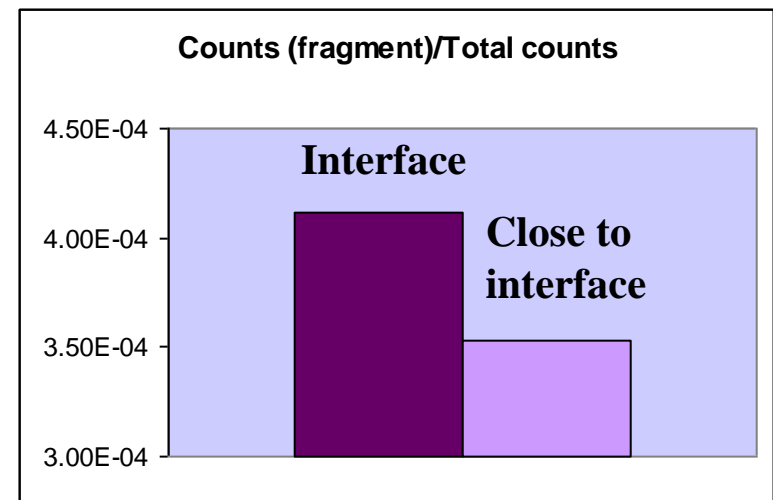


Condensation within Formulation: APS

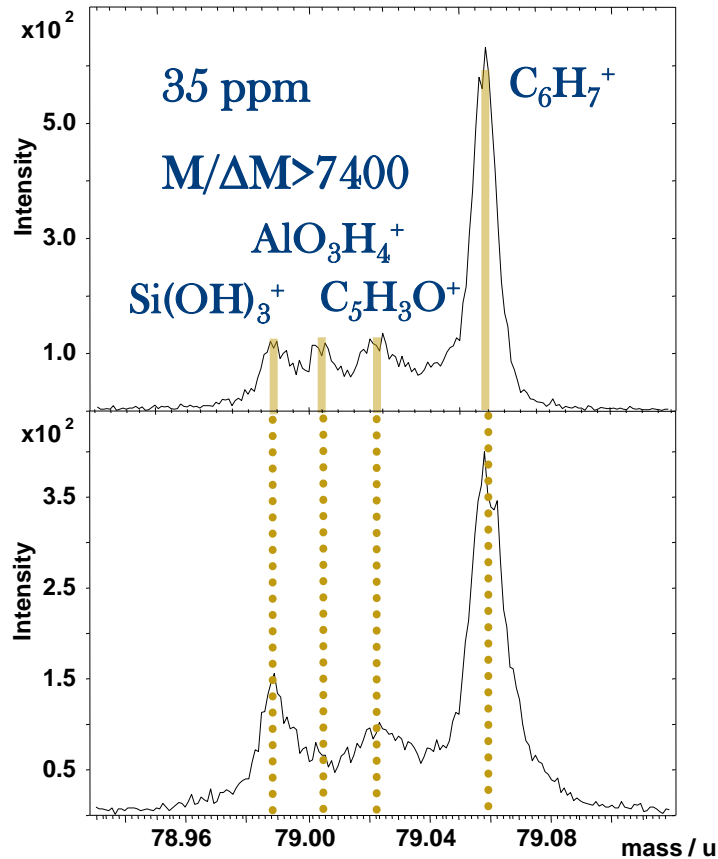


Mass interval = 0.27 u

- Crosslinking can be demonstrated with fragments containing at least two silicon atoms
- Simple quantification procedure indicates that Si₂O is more intense for top spectrum
- This may become a convenient way to show that crosslinking is present within films

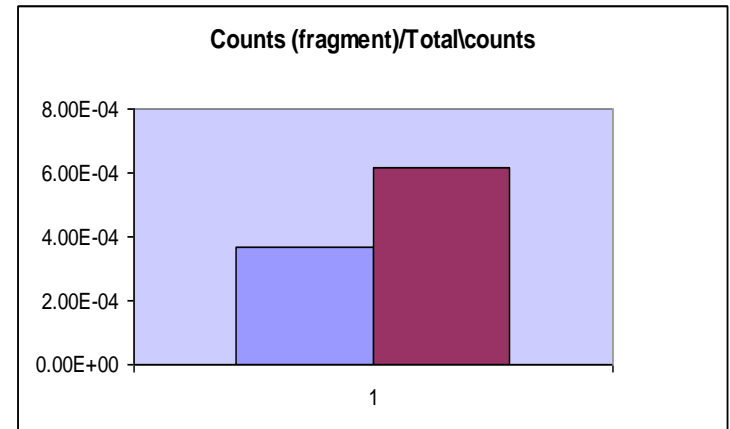


Hydrolysis within Formulation

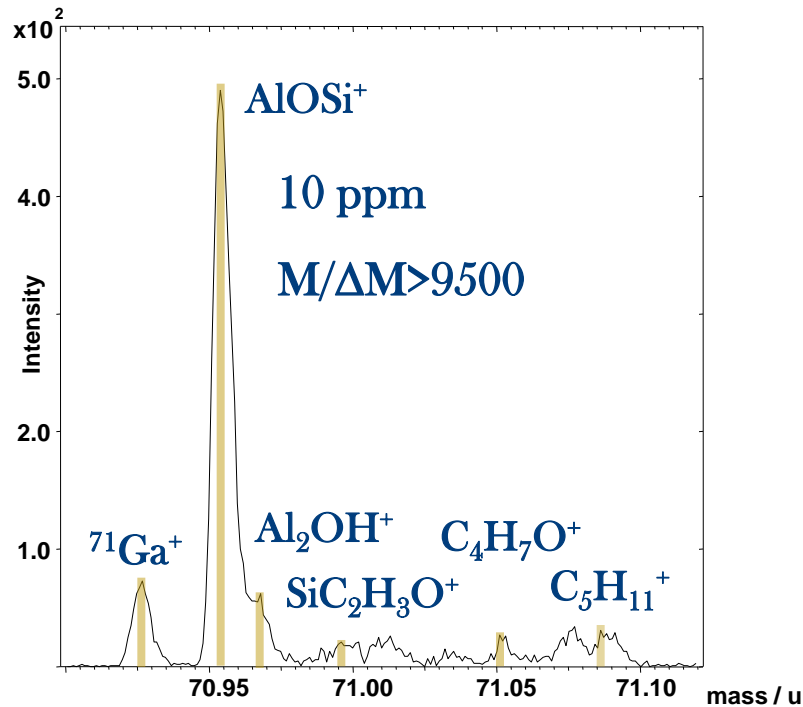


- Hydrolysis occurs even within the formulation
- With only water within material or adsorbed on substrate
- APS autocatalysis
- Favourable for covalent bond formation at interface

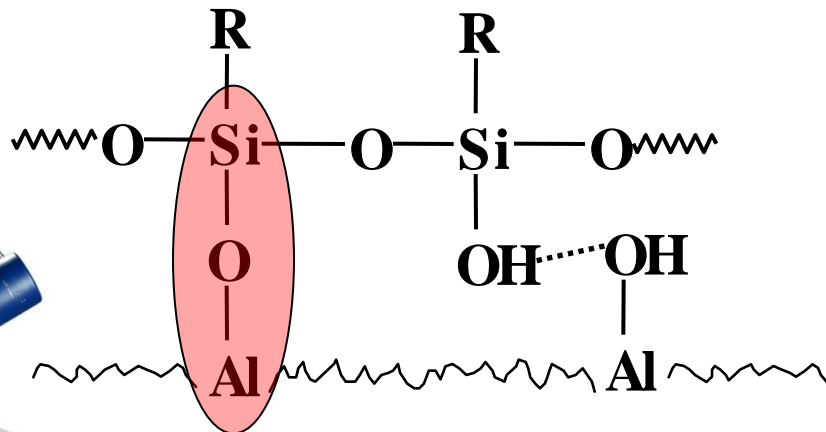
- Mass interval = 0.19 u



Bonding at Interface of Model Samples



- ToF-SIMS at high mass resolution
- 71 nominal mass signal for an interface prepared with 0.5% (w/w) APS: covalent bond formation
- Mass interval = 0.22 u



Conclusions

- The main silane reactions as described previously behave in a different way for APS and GPS. APS shows a behaviour versus temperature, GPS less so
- Silanes diffuse to the interface between adhesive and aluminium but the front of diffusion is closer for APS (5 μ m) than for GPS (\sim 50 μ m)
- Within a formulated system, it is possible to show that hydrolysis, covalent bonding and crosslinking occurs



Acknowledgements



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