ATOMIC OXYGEN EFFECTS ON HST-SA1 PROTECTIVE COATINGS

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ABSTRACT

When silicone based protective coatings are exposed to atomic oxygen a thin surface layer of silicon-dioxide is formed. On HST-SA1 large amounts of RTV-S 691 was used for the protection of atox susceptible materials. Depending on the substrate the RTV changed colour from light red to dark red. RTV-S 691 on the silver meander bar is lightly red coloured, while the RTV on the glass fibre stiffeners is coloured dark red. The surface composition of the atox exposed RTV surfaces will be investigated using Auger/XPS. Comparison will be made with unexposed RTV-S 691. Depth profiling will be used to investigated the change in composition and type of oxygen bond between the two different coloured coatings and the unexposed specimen.

Keywords: Atomic Oxygen, Silicone, SEM, Auger-XPS, Depth Profiling

1. INTRODUCTION

One of the protective coatings extensively used on the HST solar array is RTV-S 691. This red silicone from Wacker-Chemie was used to protect the silver busbars and meander bars and the glass fibre stiffeners from the attack of atomic oxygen. It is expected that the outer surface layer of this coating will change under the influence of the atomic oxygen exposure as was experienced on EURECA. Some oxidation of the silicone protection took place at relative low dose exposure.
On HST-SA1 two different surface morphologies of the RTV were seen as is displayed in figure 1. Dark red (almost brown) coloured RTV was found on the glass fibre stiffeners and lightly red coloured RTV was found on the silver busbars and meander bars. In some cases the silver meander bar went under the glass fibre and a gradual change in colour was observed.
Both appearances of the RTV are investigated. Visual inspection and scanning electron microscopy is used in order to determine differences in surface morphology, while Auger-XPS is utilised to determine the differences in the surface composition and ionic state between the two silicone surfaces.. Depth profiling was performed to measure the depth of oxidation. Comparison is made with non-exposed RTV-S 691. This non-exposed silicone was obtained by manually scraping the surface of the RTV to at least half of its thickness with a scalpel blade.

2. INSTRUMENTATION.

The visual inspection and detailed cutting of samples was performed using a Wild M8 stereozoom microscope up to magnifications of x50. These samples were either prepared for SEM investigation, EDX examination, microsectioning or Auger-XPS examination.
The samples for microsectioning were embedded in Caldofix epoxy resin from Struers. The embedded

samples were ground and polished down to 1 μm using standard methods and viewed on a Reichert MeF3a using magnifications up to x1500.
The SEM and EDX analysis were performed on a Cambridge S360 scanning electron microscope equipped with a four element solid state backscatter detector and a LINK AN10000 windowless X-ray analyser.
X-ray Photoelectron Spectroscopy was performed in a VG ESCALAB MkII system using un-monochomatised Mg K alpha radiation (1253.6 eV) operated at 12.5 keV and 20 mA emission (~250 W). Under these conditions the FWHM (Full Width Half Maximum of the C1s peak is ~1.5 eV. The multiplexed spectra were acquired with a CAE of 10 eV, and the wide survey scans with a CAE of 20 eV. The sputter depth profiling was performed with an argon ion wide area sputtering gun operated at 10 keV and delivering a current of ~1 μA as measured on a bare sample stub. The base pressure of the system with the X-ray anode operating was ~4 $.10^{-9}$ mbar, rising to 5. 10^{-8} during the depth profiling. The adventitious C1s peak at 284.8 ±0.2 eV was used to calibrate the binding energy scale when compensating for charging effects.

3. MATERIAL

Samples were cut from the solar array at the first occasion possible. These samples were stored in a anti-static bag filled with dry nitrogen and kept at low temperature in a refrigerator to avoid post flight changes as much as possible. Other samples were cut at a later date at British Aerospace Bristol and Estec clean rooms. The typical sample dimensions are 8 x 20 mm. The maximum width is given by the width of the busbar and also dictated by the sample holder of the Auger-XPS spectrometer.
The samples intended for SEM investigation were sputter coated with a gold layer of approx. 100 Ä to avoid surface charging. Samples intended for X-ray analysis and Auger-XPS analysis were used uncoated to avoid interference of the gold peaks from the sputter coating with the elemental peaks from the silicone.

4. RESULTS AND DISCUSSION

Optically a large difference is present between the RTV coating on the glass fibre and that on the silver busbars. As can be seen in figure 1, the colour of the RTV is almost brown, while the colour of the RTV from the silver busbars is light red.
Microsection as well as SEM photography did not show any differences between the light and dark regions. Figure 2 shows a microsection through the RTV on the silver meander bar and through the glass stiffener.
XPS surface analysis and depth profiling was used to distinguish between the two surfaces. For every surface (both colour and the fresh cut surface) an overall wide scan was taken with detailed scans around the carbon 1s, oxygen 1s and silicon 2p peaks. A fresh silicone surface is prepared by removing the exposed silicone surface to half its thickness with a sharp scalpel blade. On this fresh surface onlyä a surface analysis is performed to compare with the external surface measurements. This spectrum is used as baseline for the surface and depth analysis. See figure 3a..c for the fresh, light and dark RTV wide scan.
The position and the shape of the silicon and oxygen peaks give the ionic state of these elements. One clearly observes a shift in the silicon 2p peak position and shape from the fresh surface exposed surfaces. A shift to higher energies and a more a-symmetrical peak shape can be seen as is illustrated in figure 4a and b. This indicates that the exposed surfaces are almost completely oxidised to silicon-oxide. The light red surface is partly oxidised. Only the silicone peak can be seen on the fresh surface. Both peaks from the silicon-oxide and the silicone are present on the exposed surfaces. This is

confirmed by the position of the oxygen 1s peaks, also these shifts to higher energies when the silicone is oxidised to silicon oxide. The carbon 1s peak is almost absent in the spectrum of the dark red surface. The atomic oxygen bleached out completely the carbon from the surface, leaving only silicon and oxygen to form silicon-oxide.
The XPS-scan on the fresh surface shows clear C1s, O1s and the both Si (2p and 2s) peaks. The position of these peaks is listed in table I and indicates silicone bonds.
The spectrum of the fresh surface should be compared with those of the two exposed surfaces for the shift in energies and the change of the line shape. The results of that comparison is listed in table II.
A shifts towards higher energies is observed for the Oxygen and Silicon lines. The very small C1s peak for the dark red surface and the slightly larger C1s peak for the light red sample suggest a bond between Si and O. From the energies of these elements the bond type can be deduced and suggest a SiO_2 type. Asymmetry of the Si and O peaks hints to some smaller peaks at a lower energy. The peak positions tabulated in table III are used to decompose the measured silicon and oxygen shapes.

TABLE I
XPS line energies measured on fresh surface

Line	Energy(eV)	FWHM
C1s	284.8	1.66
O1s	532.5	1.7
Si2p	102.5	1.6

TABLE II
XPS energies from the light red and dark red surface.

	Light red		dark red	
Line	Energy(eV)	FWHM	Energy	FWHM
C1s	284.8	2.50	284.8	2.14
O1s	533.5	2.25	533.4	2.08
Si2p	103.9	2.85	103.8	2.53

TABLE III
Peak energies used to decompose the measured XPS peaks of C1s, O1s and Si2p

Line	Energy(eV)	Bond type
C1s	284.8	C-C, C-H
C1s	286.5	C-O
O1s	533.5	Si-O2
O1s	532.7	siloxanes
Si2p	103.5	Si-O2
Si2p	102.4	siloxanes

Peak deconvolutions according to this table gives the amount of the specific bonds in the overall spectrum

It is evident that on the dark red surface all Si and O manifests itself as SiO_2 with no further carbon present. The light red surface shows asymmetric peak shapes for both O1s and Si2p. The mean peak still indicates a major contribution of the SiO_2 bonds, but a certain amount of silicone bonds is still present on the surface. Also the small carbon peak indicates that. The deconvolution of the Si 2p peak into the contributions of Si in SiO_2 bonds and Si in siloxanes gives an 86% SiO_2 bonds for the dark red surface and 74% for the light red surface.

A small fluorine peak is present in both spectra. No fluorine is seen in the bulk silicone. This means that the fluorine originates form an outside source. The obvious source of fluorine is the MgF_2 from the coverglass of the solar cells.

Depth analysis was performed by sputtering the sample after each measurement with Ar^+ ions. The sputter time in between two measurements is 5 minutes which equates to approx. 150-160 Ä of removed silicone. From this data a depth profile for carbon, oxygen and silicon is constructed.

A depth profile of both surfaces is constructed and shows that after a first decrease of the C1s signal after the first etching (the adventitious carbon layer is removed by the first sputtering) that the carbon signal remains low and stable for a long time. Figure 5a gives the depth profile for the dark surface, figure 5b for the light surface. The Si and the O signals are also steady especially for the dark red surface. The calculated ratio between Si and O also suggests SiO_2. This is respectively 0.52 and 0.66 for the dark and the light surface.

5. CONCLUSIONS

The depth profiles of the light and the dark red surfaces are significantly different. After a sputter time of approx. 14 kseconds on the light red surface, the Si, O and C concentrations reach the bulk concentration. This time equates to a thickness of approx. 0.7 µm of SiO_2 on the light red surface.

The decrease in SiO_2 bonds and the trends of the Si, O and C profiles for the dark red surface tells us that even after 28 kseconds of etching, the bulk concentrations are not reached yet. It is estimated that the bulk concentration are reached after 60 kseconds of etching which equates to approx. 15 µm of SiO_2 layer on the dark red surface.

The reason for this difference is not clear to date. The temperatures experienced in orbit of both configurations are expected to be same. Another possible explanation could be that the silver busbars and meander bars are carrying an electrical load and that this changes locally the environment in suchä a way that the RTV on the silver conductors is much less affected than that on the glass fibre stiffeners.

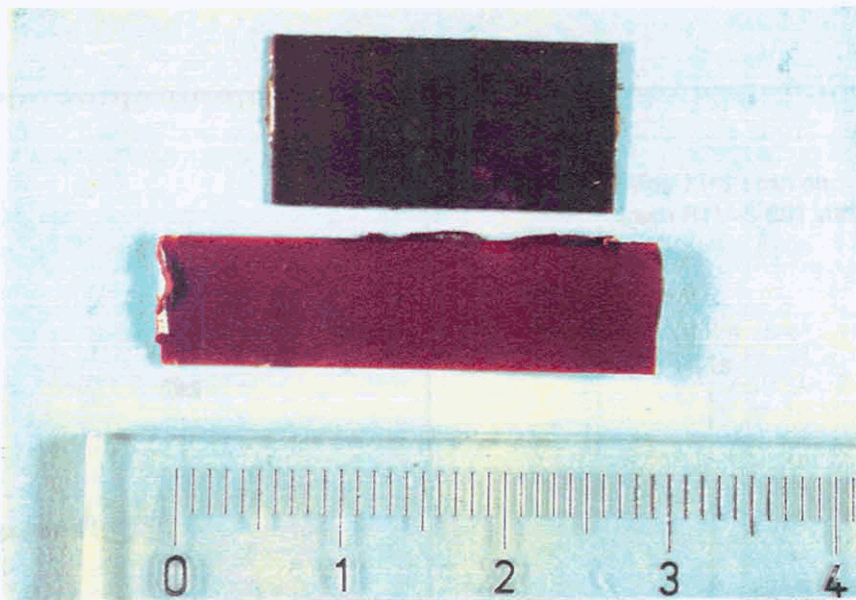

Figure 1. *Part of silver meander bar with the light RTV-S 691 coating at the bottom and part of the glass fibre stiffener with the dark RTV-S 691 coating at the top of the photograph. Magn. X2.2*

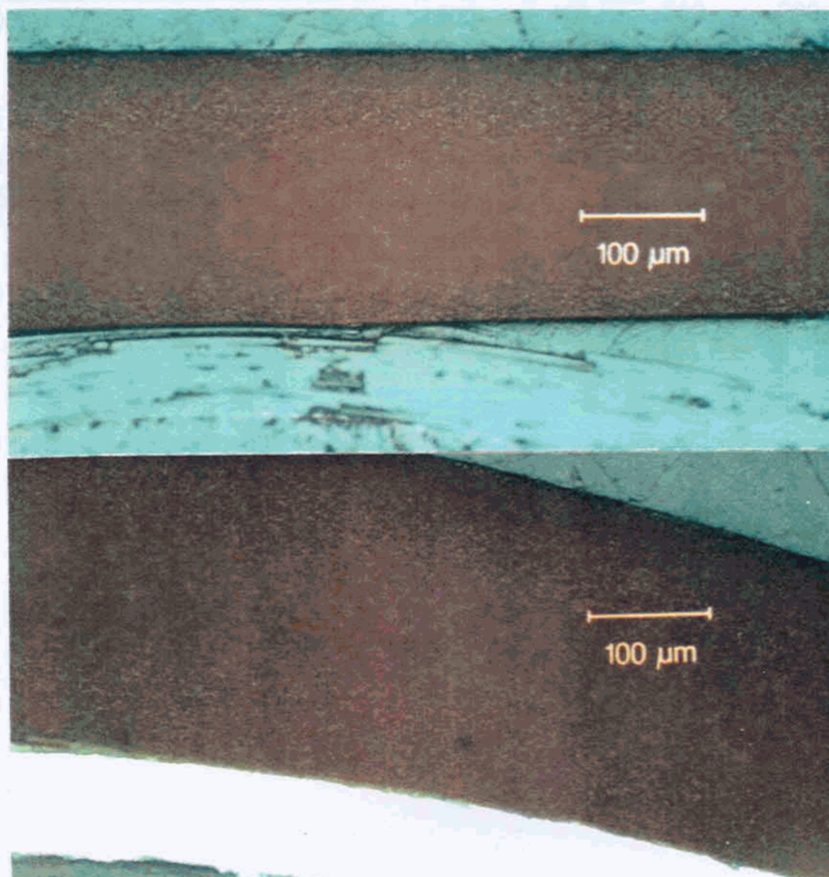

Figure 2. *Cross section through RTV layer on the silver meander bar (bottom) and through the RTV on the glass fibre stiffener (top). No internal differences are visible. Magn. X160.*

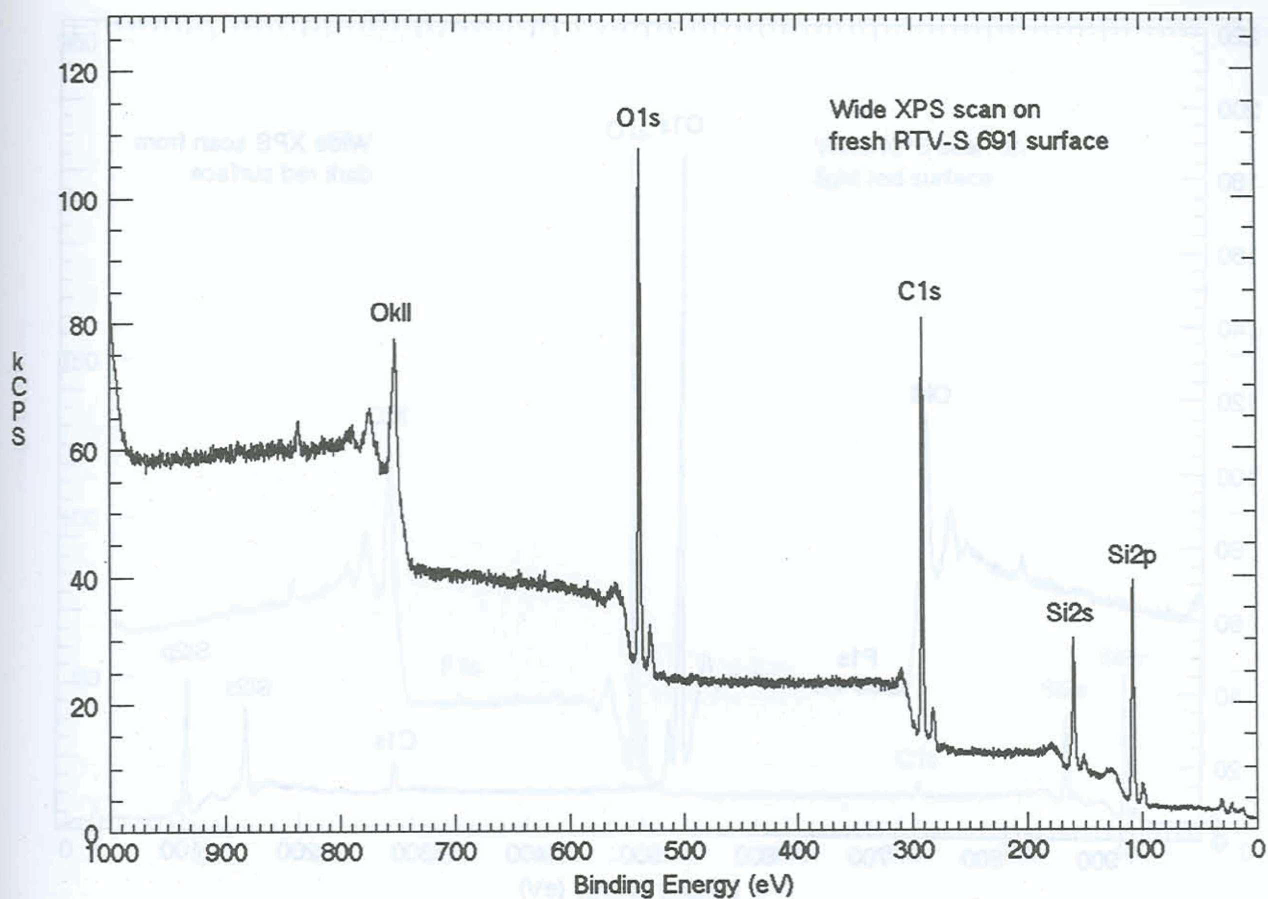

Figure 3a. *Wide XPS scan on a fresh RTV-S 691 surface, showing only carbon (C1s), Oxygen (O1s) and Si (Si2s and Si2p).*

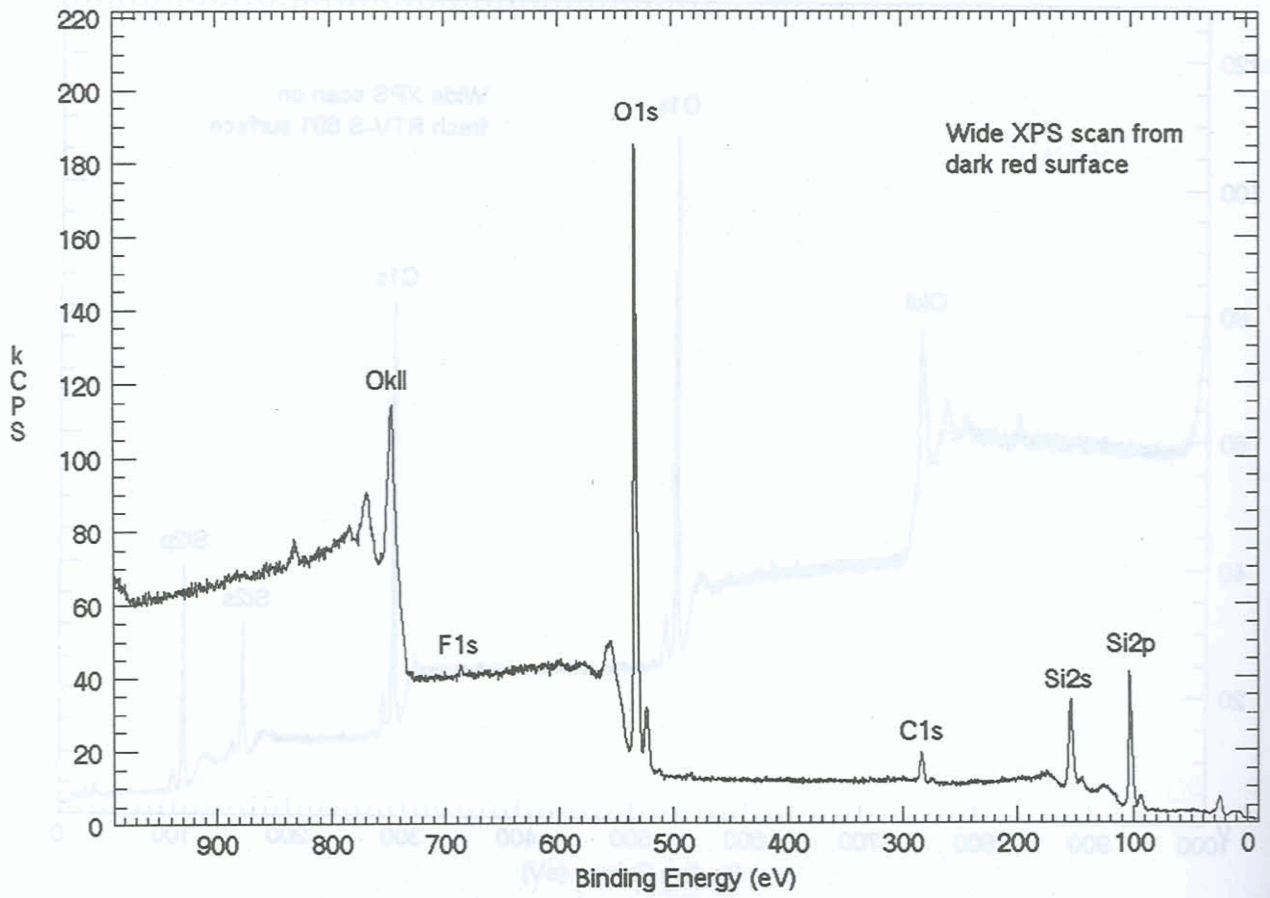

Figure 3b. *Wide XPS scan on the dark red surface on top of the glass fibre stiffener. The wide scan is after three etching in order to remove the adventitious carbon layer. The only major peaks present are the Silicon and the Oxygen*

Figure 3c. *Wide XPS scan on the light red surface on top of the silver meander bar. The wide scan is after three etching in order to remove the adventitious carbon layer. The only major peaks present are the Silicon and the Oxygen*

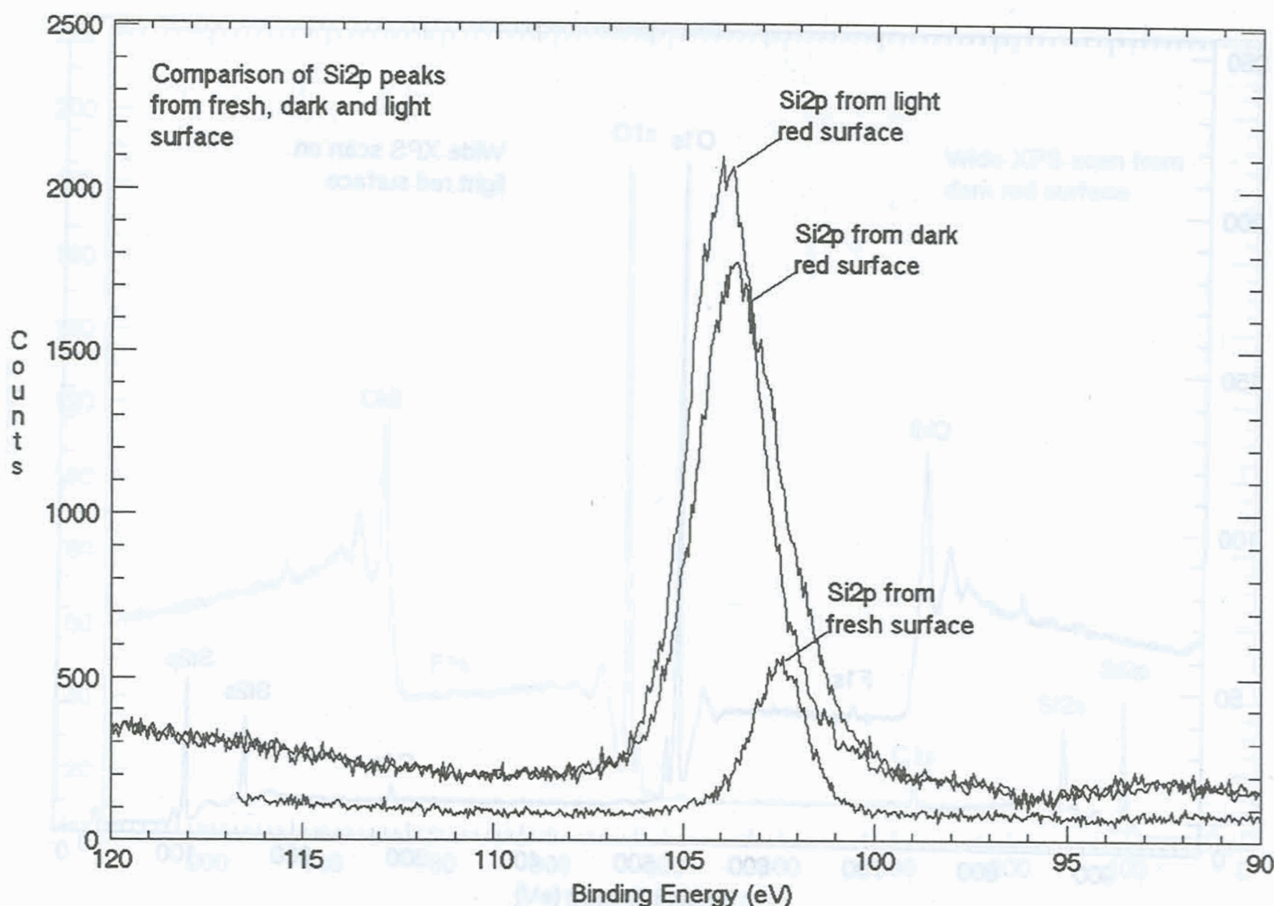

Figure 4a. *Comparison between the Si2p peaks from the fresh, dark red and light red RTV surface. An increase in Silicon concentration after LEO exposure is observed. This increase is due to depletion of the Carbon in the surface. The shift in peak energy form the fresh to the exposed surfaces indicate* SiO_2 *bonds.*

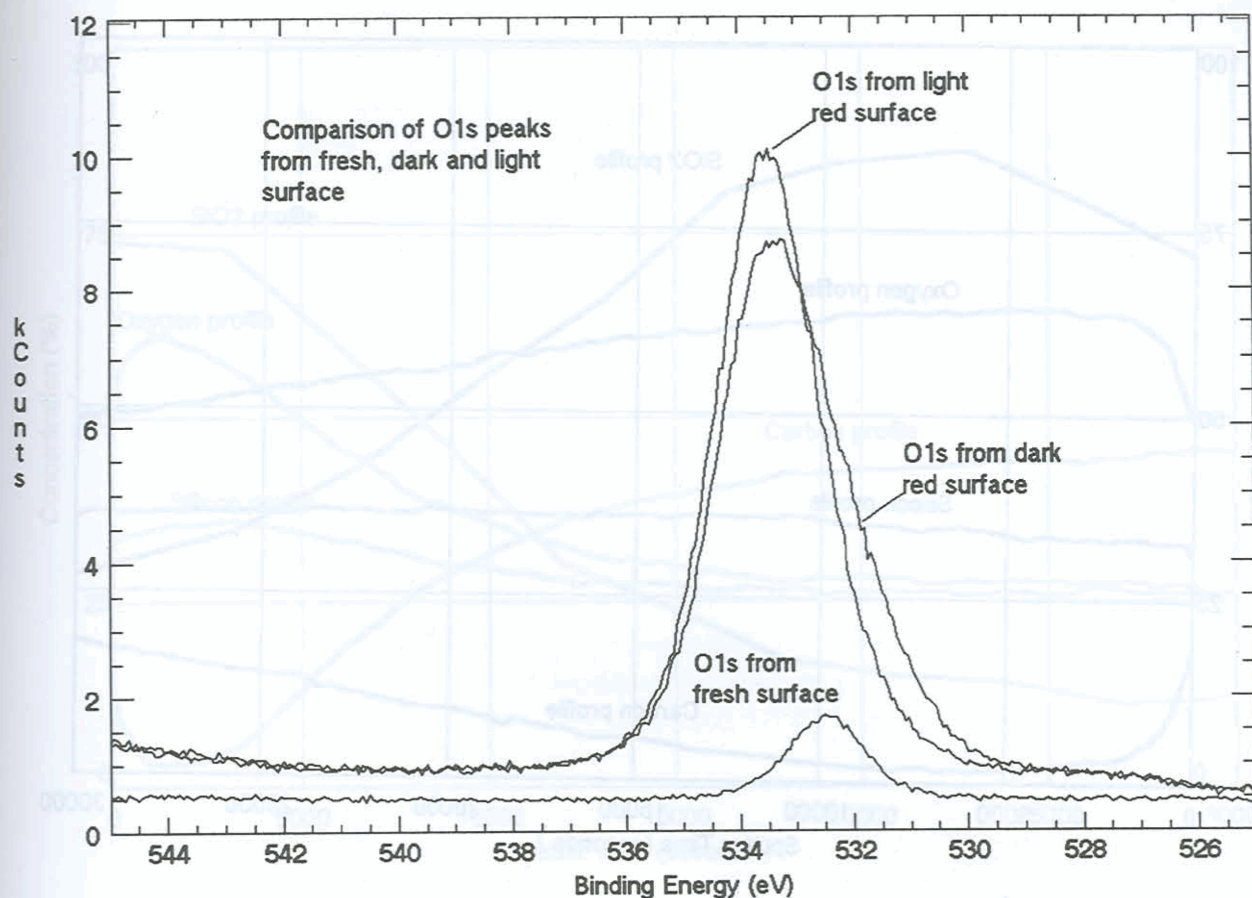

Figure 4b. *Comparison between the O1s peaks from the fresh, dark red and light red RTV surface. An increase in Oxygen concentration after LEO exposure is observed. This increase is due to depletion of the Carbon in the surface and atomic oxygen exposure. The shift in peak energy form the fresh to the exposed surfaces indicate SiO_2 bonds.*

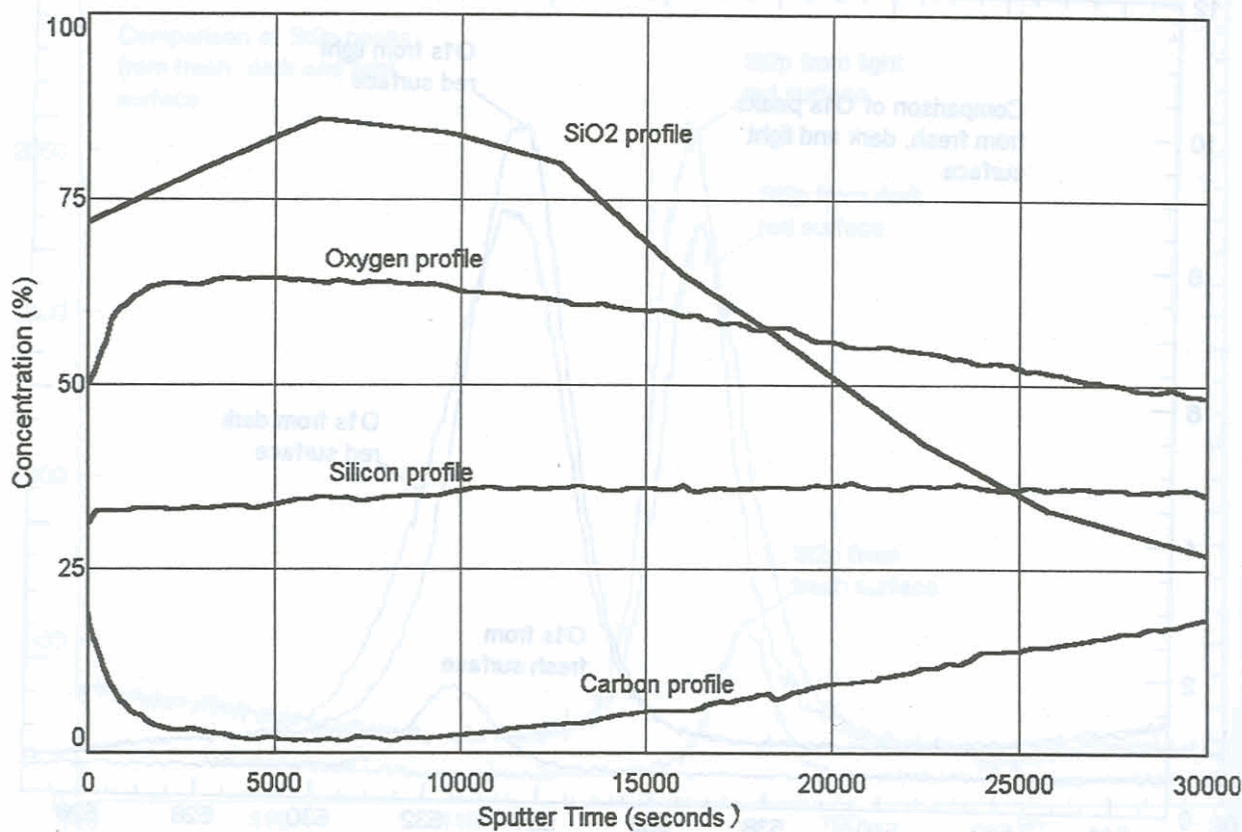

Figure 5a. *Depth profile of the dark red specimen showing a high oxygen and silicon concentration with a ratio Si/O of approx 0.52. The carbon concentration remains low. The SiO_2 profile, calculated from the Si2p a-symmetry, shows a thickness of over 30000 seconds of sputter time.*

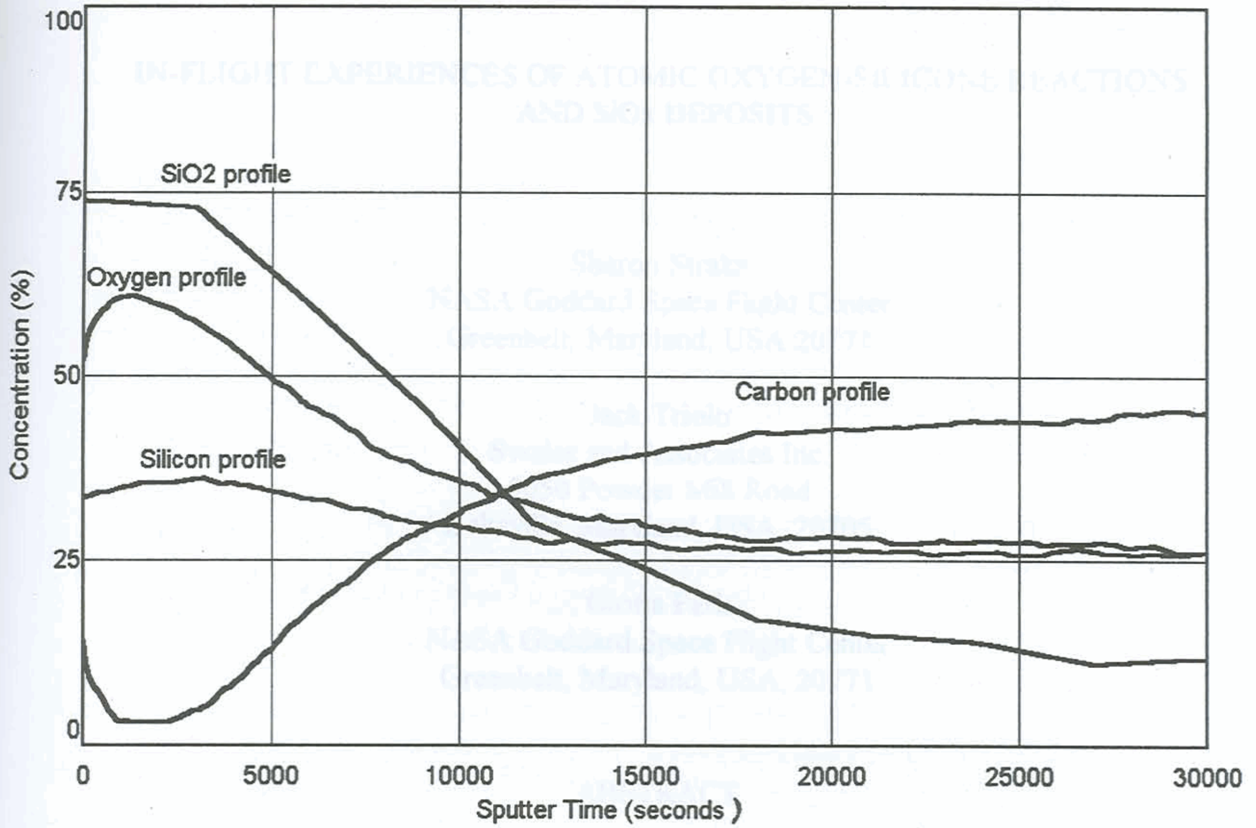

Figure 5b. *Depth profile of the light red specimen showing a high oxygen and silicon concentration with a ratio Si/O of approx 0.66. The carbon concentration remains low. After ca 5000 seconds the profile are changing towards the silicone bulk concentration. The SiO_2 profile, calculated from the Si2p a-symmetry, shows a thickness of over 10000 seconds of sputter time.*