

# An X-ray photoelectron spectroscopic investigation into the chemical structure of deposits formed from hexamethyldisiloxane/oxygen plasmas

M. R. ALEXANDER, R. D. SHORT, F. R. JONES

*Laboratory for Surface and Interface Analysis, Department of Engineering Materials, University of Sheffield, P.O. Box 600, Sir Robert Hadfield Building, Mappin Street, Sheffield S1 4 DU, UK*

M. STOLLENWERK, J. ZABOLD, W. MICHAELI

*Institut Für Kunststoffverarbeitung, RWTH Aachen, D-52056 Aachen, Germany*

The effect of oxygen addition to microwave-sustained plasmas of hexamethyldisiloxane (HMDSO) has been investigated. Attention was directed to the solid products formed on aluminium substrates (plasma deposits). To enable a quantitative analysis of these, X-ray photoelectron spectroscopy (XPS) of standard silicon-containing materials was carried out. When suitable charge correction is applied to the XP spectra of HMDSO/O<sub>2</sub> plasma deposits, a number of very clear trends emerge. From changes in elemental composition, core line binding energies (Si 2p, C 1s, and O 1s) and widths, we show how oxygen addition to the plasma affects the chemical nature of the plasma deposit. The data reported also provide (some limited) information on the reactions taking place in the plasma.

## 1. Introduction

The use of microwaves to sustain “non-equilibrium” plasmas of volatile organic compounds has proved a popular means to fabricate coatings. Deposition rates of the order of several tens of nanometres per second have been achieved, making the process an industrially attractive coating technology. The chemistry and structure of these materials may be controlled through choice of monomer and/or co-reactants, the substrate temperature, and power density of the plasma [1–5]. A number of potential applications for these coatings have been described, including protection (*e.g.* anti-corrosion) [4], adhesion promotion [4, 6], optical modifiers [7] and diffusion membranes [8].

It is believed that the plasma polymerization process involves bond scission and the addition reactions of free-radical species which condense on a substrate to form a solid from the vapour phase. The actual mechanisms involved are not fully understood. The interested reader is referred to books by Yasuda [9] and d’Agostino [10].

Previous reports describe the preparation of coatings from organosilicon compounds using either radio-frequency (r.f.), or microwave sources to sustain the plasma [1–5, 11–15]. The products have been analysed by elemental analysis [1], infrared spectroscopy [3–5, 8, 12, 15, 16], pyrolysis and gas chromatography mass spectrometry [2, 3, 13–15], nuclear magnetic resonance [11, 16] and X-ray photoelectron spectroscopy

(XPS) [8, 16]. The nature of the product is influenced by the energy source, power, monomer, use of co-reactants, and substrate temperature employed. In general, low-power r.f. plasmas produce polymeric products that have been likened to polysiloxanes. These may contain an oligomeric (soluble) fraction [14, 16], which is not seen at higher power in r.f. systems and only at particularly low powers with microwave sources.

Hexamethyldisiloxane (HMDSO) has proved a popular organosilicon compound for study. Tkachuk *et al.* [1] described the range of structures that may be obtained in plasma deposits from this monomer. These are presented in Fig. 1. It is well known that more “inorganic”-like deposits can be obtained from plasmas of this monomer, and the following have been investigated: use of oxygen (O<sub>2</sub>) as a co-reactant [3]; deposition on to heated substrates [2, 4]; post-heat-treatment [5, 11]; and use of high plasma powers [3–5]. Precise control over coating properties (organic to inorganic) is highly desirable. Interestingly, the effect of addition of O<sub>2</sub> to plasmas of HMDSO has only been followed qualitatively, by infrared spectroscopy [3], which shows that O<sub>2</sub> promotes the formation of a “silica-like” deposit. This paper provides a useful qualitative indication of the changes in deposit chemistry resulting from different oxygen flows into the HMDSO plasma. However, the relative (quantitative) importance of O<sub>2</sub> flow was not ascertained.

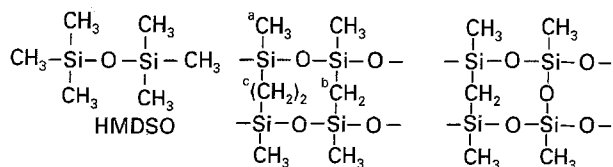


Figure 1 HMDSO and the structures proposed for HMDSO plasma polymers, after Tkachuk [1].

Here, we describe the XPS analyses of a series of flat HMDSO/O<sub>2</sub> plasma-deposited coatings. XPS has the advantage over many conventional analytical techniques in that it provides quantitative elemental and chemical state information (and is therefore ideally suited to this type of analysis). While the technique is specific to the top few nanometres of a material, we argue that the data presented here also provide a measure of the bulk chemistry of the films.

In order to obtain an accurate interpretation of the XPS results, it was necessary to perform analyses on some standards [poly(dimethylsiloxane) (PDMS), poly(phenylmethylsiloxane) (PPMS) and silica (SiO<sub>2</sub>)] to determine exact binding energies and peak widths for silicon, carbon and oxygen. Employing these data, we show quantitatively how O<sub>2</sub> flow changes the deposit chemistry, and identify some aspects that have not previously been observed.

## 2. Experimental procedure

### 2.1. Plasma polymerization

All samples were produced and analysed as 5 μm thick films on aluminium plate (≈ 1 mm thick). In the plasma apparatus the total pressure, *P*, was fixed at 50 Pa, the power, *W*, at 200 W, and the HMDSO flow at 20 standard cm<sup>3</sup> min<sup>-1</sup>. The O<sub>2</sub> flow rate was varied from 0–200 standard cm<sup>3</sup> min<sup>-1</sup>. The microwave generator operated at 2.45 GHz. Presented in Fig. 2 is a schematic drawing of the apparatus.

### 2.2. XPS

All XPS analyses were carried out using a VG CLAM 2 electron analyser and MgK<sub>α</sub> X-radiation. For the purpose of elemental quantification we have used sensitivity factors experimentally determined from a PDMS polymer standard (Aldrich).

A take-off angle of 30° was used throughout the study: assuming a value for λ (C 1s) of 1.4 nm (based on work in [17]), the sampling depth (3λ sin 30) is calculated to be ≈ 2.1 nm (~ 14 Si–O bonds, estimated from its length in [SiO]<sup>+</sup> which is 0.15 nm).

The X-ray source was run at 10 kV with a 10 mA emission current, i.e. a power of 100 W. This was chosen as a compromise between possible X-ray-induced sample damage and signal intensity. Widescans were acquired in Constant analyser energy (CAE) using a pass energy of 100 eV, a dwell time of 50 ms (per channel), and a step size (channel width) of 0.55 eV. Three scans were made and added together. From these, quantification was effected, using a linear background subtraction. Narrow scans (pass energy

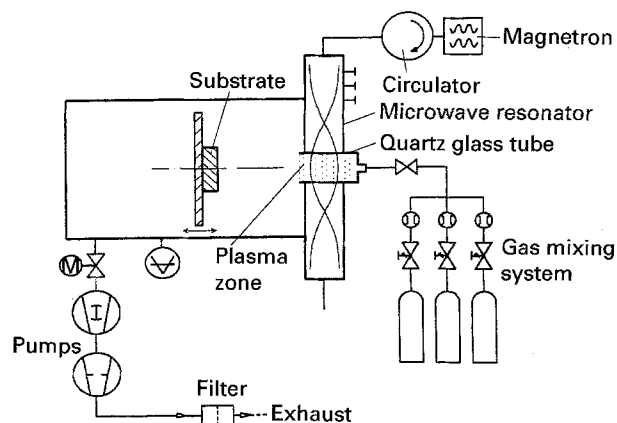


Figure 2 Schematic drawing of the plasma-deposition unit.

of 20 eV and channel width of 0.05 eV) were also acquired to monitor chemical state changes.

### 2.3. Instrument calibration

The energy scale of the instrument was calibrated using a gold standard, chosen because it does not form a stable oxide on its surface under ambient conditions. The binding energy for the Au 4f<sub>7/2</sub> core level peak (84.00 eV) was verified along with the separation of the C 1s and F 1s peaks from PTFE (measured as 397.2 eV). This compares well with a value of 397.19 eV in the literature [18], indicating that the binding energy scale is reliable between 84 eV (Au 4f<sub>7/2</sub>) and 689 eV (F 1s). All core levels considered in this study appear within this range of binding energies.

## 3. Results

### 3.1. XPS

#### 3.1.1. Elemental quantification

**3.1.1.1. Analysis of standards.** There are significant discrepancies amongst the published experimental (and theoretical) sets of sensitivity factors (SFs) [19], and for this reason we chose to determine our own for the C 1s, O 1s, and Si 2p core level peaks. Five measurements were made on PDMS and from the stoichiometry of the repeat unit of the polymer, SFs were calculated. This approach gave SF (O 1s) = 3.14 (σ<sub>n-1</sub> = 0.10) and SF (Si 2p) = 1.40 (σ<sub>n-1</sub> = 0.06), where carbon is set to 1. The complication of cyclic oligomers in PDMS [20] will not affect these SFs, as these have the same stoichiometry as the polymer repeat unit. The level of hydrocarbon contamination in the spectrometer was low, contributing (typically) no more than 3% to the C 1s core line.

**3.1.1.2. Plasma deposits.** Within the detection limits of XPS, the only elements seen were carbon, silicon, and oxygen. A representative widescan spectrum is illustrated in Fig. 3. Changes in the elemental atomic composition of the plasma deposits, with oxygen flow rate, are presented in Table I. From the atomic concentrations, it is difficult to appreciate trends in the

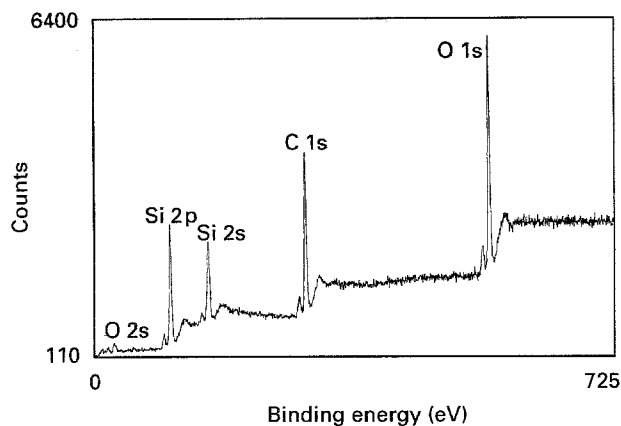


Figure 3 An XPS wide scan of an HMDSO/O<sub>2</sub> plasma deposit ( $p = 50$  Pa,  $P = 200$  W,  $d = 30$  mm, HMDSO flow = 20 standard  $\text{cm}^3\text{min}^{-1}$ , film thickness = 5  $\mu\text{m}$ ) with no oxygen flow.

TABLE I Elemental atomic concentrations from HMDSO/O<sub>2</sub> plasma polymer films for varying oxygen flow rates (pressure = 50 Pa).

Oxygen flow/(standard $\text{cm}^3\text{min}^{-1}$ )	C	O	Si	C/O	C/Si	O/Si
0	50.31	22.89	26.8	2.12	1.88	0.85
10	39.93	32.33	27.74	1.24	1.44	1.17
20	35.57	35.56	28.88	1.00	1.23	1.23
40	29.94	41.43	28.63	0.72	1.05	1.45
100	22.66	47.57	29.77	0.48	0.76	1.60
200	18.74	50.76	30.50	0.37	0.61	1.66

film compositions, and therefore the atomic ratios C/O, C/Si, and O/Si have been calculated; changes in these with O<sub>2</sub> flow rate are shown in Fig. 4.

Samples exposed to ambient conditions for between 3 h and 14 d prior to analysis showed no distinct difference in elemental composition.

### 3.1.2. Chemical state determination

Insulating specimens, such as the samples in this study, develop a net positive charge during X-ray irradiation (as a result of photoemission). The positions of the core lines are therefore shifted to a higher binding energy. To obtain accurate chemical state information, a peak with which to charge-correct is therefore required. This peak is selected from the analysis of model compounds, as set out below.

**3.1.2.1. Analysis of standards.** The structure of the HMDSO molecule is illustrated in Fig. 1. To obtain a measure of the binding energy of  $\text{CH}_3\text{-Si}$  we have adopted the procedure used elsewhere [18].

(a) The binding energy of the C 1s peak in phenyl carbon (284.7 eV) was taken from [18]. This was determined with a high-resolution spectrometer on polystyrene (PS).

(b) We charge-correct the spectra of PPMS using the C 1s position of 284.7 eV, see Table II. The assumption made here is that the carbon atoms within

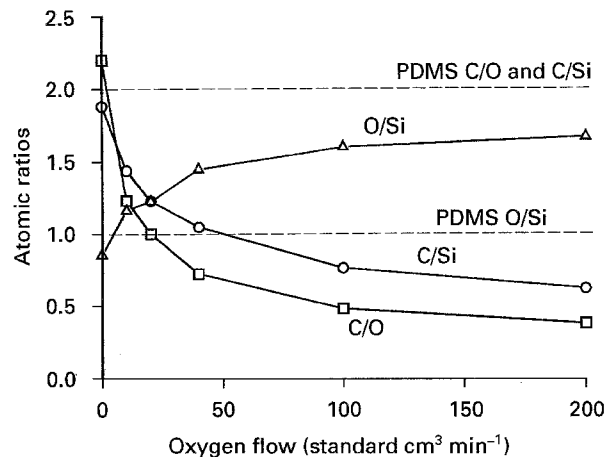


Figure 4 XPS-determined elemental ratios versus oxygen flow for HMDSO/O<sub>2</sub> plasma deposits ( $p = 50$  Pa,  $P = 200$  W,  $d = 30$  mm, HMDSO flow = 20 standard  $\text{cm}^3\text{min}^{-1}$ , film thickness = 5  $\mu\text{m}$ ).

TABLE II Binding energy of XPS peak centroids (average of five samples) from poly(dimethylsiloxane) (PDMS), poly(phenylsiloxane) PPMS, and quartz (SiO<sub>2</sub>). The figures in parentheses are the observed standard deviations ( $\sigma_{n-1}$ )

	Binding energy (eV)		
	C 1s	O 1s	Si 2p
PPMS	284.7 <sup>a</sup>	532.4(0.05)	102.0(0.06)
PDMS	284.4(0.11)	532.4 <sup>a</sup>	102.1(0.07)
Quartz	285.0 <sup>a</sup>	532.6(0.25)	103.4(0.19)

<sup>a</sup>Peaks to which the spectra were charge-referenced.

the phenyl ring (not directly attached to the polymer backbone) are not significantly influenced by the different nature of the polymer backbones in PS and PPMS. Without high-energy resolution capabilities, the C 1s peak centre from PPMS provides only an estimate of the binding energy of carbon in the phenyl state. However, the majority of the carbon atoms (5/7) in PPMS are not bonded directly to the silicon atom. These will therefore represent the majority of the C 1s peak and provide an estimate of C 1s<sub>phenyl</sub>. A small overestimation of the C 1s<sub>phenyl</sub> binding energy may be introduced by this approximation. We estimate this to be less than 0.1 eV (calculated from the difference in binding energy between the environments  $\text{CH}_x\text{-Si}$  and C<sub>phenyl</sub> (ca. 0.3 eV) and the stoichiometry and structure of PPMS).

(c) The O 1s binding energy obtained from PPMS provides a measure of the binding energy (O 1s) for the oxygen atoms within the siloxane environment (Si-O-Si: 532.4 eV). We then use this to charge-correct the spectra of PDMS. This reveals that the C 1s peak from a  $\text{CH}_3\text{-Si}$  environment appears at 284.4 eV. This is in good agreement with a value obtained by Beamson and Briggs [18] of 284.38 eV using the same procedure.

It should be noted, however, that while these are in good agreement, a discrepancy exists in the O 1s peak position determined by us for the O 1s peak from a siloxane environment (532.4 eV), compared with that obtained by Beamson and Briggs of 532.00 eV. We do not have an explanation for this. However,

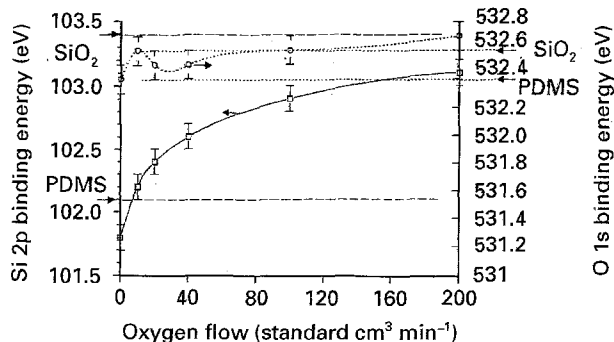


Figure 5 XPS peak binding energies, charge corrected to the C 1s peak at 284.4 eV, from HMDSO/O<sub>2</sub> plasma deposits ( $p = 50$  Pa,  $P = 200$  W,  $d = 30$  mm, HMDSO flow = 20 standard cm<sup>3</sup>min<sup>-1</sup>, film thickness = 5  $\mu$ m) versus oxygen flow.

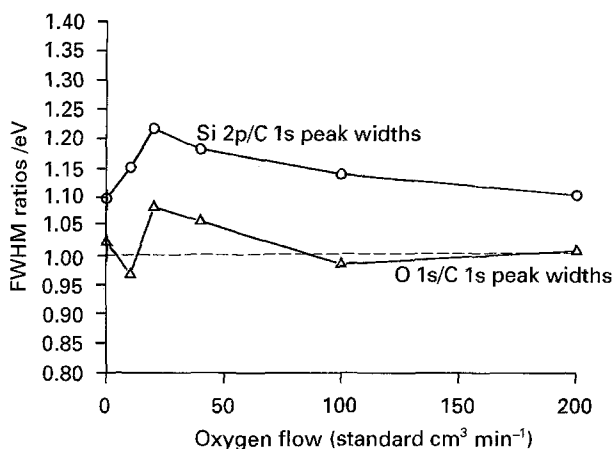


Figure 6 XPS peak width ratios from HMDSO/O<sub>2</sub> plasma deposits ( $p = 50$  Pa,  $P = 200$  W,  $d = 30$  mm, HMDSO flow = 20 standard cm<sup>3</sup> min<sup>-1</sup>, film thickness = 5  $\mu$ m) versus oxygen flow per standard cm<sup>3</sup> min<sup>-1</sup>.

because all our spectra have been acquired on the same instrument, we are confident in the correlation between spectra from standards and plasma deposits made within this work.

To determine the binding energy of the Si 2p and O 1s peaks from SiO<sub>2</sub>, quartz powder was analysed. The binding energies of the O 1s and Si 2p peaks were determined by charge-correcting the spectra to the C 1s peak from adventitious hydrocarbon contamination at 285.0 eV (Table II). It is notable that the standard deviations obtained on these powder samples were greater than those obtained from PPMS and PDMS smeared on to aluminium foil. We assume that this is related to the different roughnesses of the samples. PDMS and PPMS are fluids which we assume produce a smooth surface (in comparison with quartz powder). The binding energies of the O 1s and Si 2p peaks from PDMS and SiO<sub>2</sub> have been incorporated into Figs 5 and 6 to facilitate comparison with the peak positions determined from the plasma deposits.

**3.1.2.2. Plasma deposits.** Within the plasma deposits it is assumed that the chemical state of the silicon atoms will vary according to the extent of oxygen incorporation into the plasma deposits. The Si 2p peak position will change as a result, through the range of samples. Hence, the Si peak cannot be used

for charge-correction, which leaves the choice of O 1s or C 1s core lines. Although the dynamic range of chemical shifts seen in the O 1s core line is smaller than that seen within the C 1s, we have selected the latter for charge correction. Our justification for this is set out below.

Previous work [1] indicates that there are three main carbon environments within HMDSO plasma polymers (these are illustrated in Fig. 1). In addition to these, carbon-oxygen environments have been reported on the basis of infrared data [3, 5, 12]. In the C 1s core line, the presence of C-O<sub>x</sub> groups would manifest as asymmetry or as a shoulder (to high binding energy). This was not seen in any of the C 1s narrow scans (across the entire O<sub>2</sub> range). This leads us to discount the presence of significant quantities of carbon-oxygen functionalities ( $\lesssim 5\%$ ) in these deposits, and we assume that either their relative importance is overestimated by infrared spectroscopy, or that their formation only takes place in r.f., rather than microwave sustained plasmas.

From Fig. 1, it is evident that there are two carbon environments that we could use to correct the C 1s peak. The C 1s peak from both environments "a" and "c" would be expected at  $\sim 284.4$  eV and from "b" at  $\sim 283.8$  eV (a difference of 0.6 eV). We are helped here by the analysis of standards. If we were to correct all the spectra obtained from HMDSO plasma deposits using C 1s at 283.8 eV (corresponding to the Si-CH<sub>2</sub>-Si environment, "b" in Fig. 1), then at all oxygen flow rates, the O 1s peak position would appear well below the binding energy determined for silica and PDMS. This is not a realistic result, as in plasma deposits of this type (Fig. 1) we expect to find oxygen in exactly these environments. Therefore, we have chosen to charge correct all of the C 1s spectra to 284.4 eV (which corresponds to environments "a" and "c" in Fig. 1).

When the spectra have been charge-corrected, we observe a distinct upward trend in the Si 2p peak position (Table III and Fig. 5). From Table III it is apparent that the amount of charging increases with O<sub>2</sub> flow. This result may be explained by the increased oxygen content of the deposits. Oxygen has a photoemission cross-section two to three times that of silicon and carbon and the overall flux of electrons from

TABLE III XPS peak binding energies from HMDSO/O<sub>2</sub> plasma deposits:  $p = 50$  Pa,  $P = 200$  W,  $d = 30$  mm, HMDSO flow = 20 standard cm<sup>3</sup> min<sup>-1</sup>, film thickness = 5  $\mu$ m. Charge-corrected to a C 1s peak at a binding energy of 284.4 eV of the environment CH<sub>3</sub>-Si obtained from PDMS. Figures in parentheses refer to the as-acquired (non-charge-corrected) peak centroids

Oxygen flow (standard cm <sup>3</sup> min <sup>-1</sup> )	C 1s	O 1s	Si 2p
0	284.4(286.70)	532.4(534.65)	101.8(104.05)
10	284.4(287.75)	532.6(535.90)	102.2(105.55)
20	284.4(289.35)	532.5(537.40)	102.4(107.30)
40	284.4(289.70)	532.5(537.80)	102.6(107.90)
100	284.4(290.60)	532.6(538.75)	102.9(109.10)
200	284.4(290.80)	532.7(539.10)	103.1(109.45)

the sample therefore increases. Although a general upward trend is observed in the O 1s BE this is not as marked as that of the Si 2p. This is indicative of similar, or equivalent, oxygen environments throughout the range of oxygen flow.

Although the resolution of the spectrometer was not sufficient to allow for sensible curve fitting of the C 1s, O 1s or Si 2p core lines, the core-line widths may be used to provide a qualitative measure of the diversity of states within any one peak. Examination of a system where each element is in only one chemical environment, PDMS, indicates that the C 1s: O 1s: Si 2p full width half-maximum (FWHM) ratio is 1.00: 1.02: 1.01 (i.e. the X-ray line width and spectrometer are contributing most of the FWHMs). The presence of several (non-equivalent) environments (within a core line) will result in a change in this ratio. However, no trend was found in the peak widths. We assume that this is because chemical inhomogeneity is not the only factor that affects the peak width. (For example, roughness will result in subtle differential charging). Normalizing the Si 2p and O 1s peak widths using the C 1s peak width revealed the trends shown in Fig. 6. This figure indicates that O<sub>2</sub> flow has an appreciable effect on the Si 2p peak width, and at 20 standard cm<sup>3</sup> min<sup>-1</sup> the Si 2p contains the maximum diversity of chemical states. From the Si 2p binding energy (Fig. 5) we know that this material is approximately half-way between the two silicon environments of our standards (namely PDMS and silica).

Samples exposed to ambient conditions for between 3 h and 14 days prior to analysis showed no change in peak shape or position.

#### 4. Discussion

There is a number of similarities between the HMDSO plasma deposit (no O<sub>2</sub>) and conventional PDMS. The O 1s and Si 2p binding energies of both materials are of the same order, as are their stoichiometries (Tables II and III, Fig. 5). However, close examination reveals that in PDMS, the Si 2p binding energy is 0.3 eV higher than in the plasma deposit, whilst the O 1s binding energies are exactly the same. This suggests that oxygen is in the same environment in both, namely Si–O–Si, but a (contribution from a) more electropositive environment influences the Si 2p core line. This is consistent with at least partial retention of the trimethyl siloxyl ((CH<sub>3</sub>)<sub>3</sub>Si–O–) structure of the monomer. Examination of the normalized Si 2p width (Fig. 7) indicates that there is more than one chemical state present within this peak. Taken together, these pieces of data suggest that both (CH<sub>3</sub>)<sub>2</sub>SiO<sub>2</sub> and (CH<sub>3</sub>)<sub>3</sub>Si–O environments exist within the deposit, a conclusion consistent with other work. The slightly lower O/Si and C/Si ratios, in this plasma deposit (compared with those of PDMS), may be rationalized if we consider that there may also be Si–H and CH<sub>2</sub>–Si–CH<sub>2</sub> arrangements present. The existence of these has been postulated elsewhere on the basis of infrared data [3].

The excellent correlation in the Si 2p and O 1s peak positions from the deposits, with the binding energies

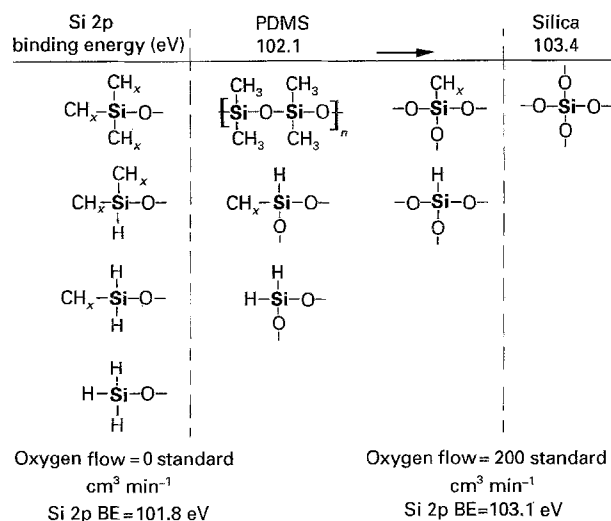


Figure 7 Possible silicon chemical environments and the corresponding Si 2p binding energies as determined from PDMS and SiO<sub>2</sub>. (---) The approximate positions of the samples at the extremes of oxygen flow into the plasma, where  $x = 2$  or  $3$ . Note, the CH<sub>3</sub>–Si and H–Si groups will result in different Si 2p binding energies; however, this difference is too small to be detected by our instrument.

of accepted HMDSO plasma polymer structures gives us confidence in the C 1s binding energy to which we charge-corrected our spectra (284.4 eV representing environments “a” and “c” in Fig. 1). This suggests that the concentration of the Si–CH<sub>2</sub>–Si arrangement (environment “b”) within the plasma deposits is low.

The effect of increased oxygen flow into the plasma (0–200 standard cm<sup>3</sup> min<sup>-1</sup>) is to more than double the atomic oxygen concentration in the deposit (Table I). From Fig. 3 it can be seen that the O/Si ratio reaches a plateau at a value of  $\approx 1.7$  (200 standard cm<sup>3</sup> min<sup>-1</sup>). Pure silica (SiO<sub>2</sub>) would provide an O/Si ratio of 2, and our material is, therefore, some way short of silica. This is consistent with the retention of 19% carbon, which is probably bonded to the silicon. This observation is also consistent with the chemical state information provided by the Si 2p peak position (Fig. 5), where the Si 2p binding energy at 103.1 eV is about 0.3 eV lower than that determined for silica (103.4 eV).

The trend in the Si 2p core-line binding energy is consistent with increased oxygen incorporation into the product; the data also suggest that this oxygen is almost entirely associated with the silicon atom. It is worth noting that while infrared studies suggest that silica is formed [3], the XPS data (chemical state, line width and stoichiometries) show that this is not the complete picture. The range of possible silicon environments (and binding energies) is given in Fig. 7. At higher oxygen flow rates, more highly oxidized silicon environments are formed. (In this instance the term “oxidized” refers to the number of oxygen atoms bonded to the silicon atom.) The line-width data tell us that there is always more than one type of silicon functionality (in any deposit), and that the maximum number of (different) chemical states formed occurs at an O<sub>2</sub> flow rate of 20 standard cm<sup>3</sup> min<sup>-1</sup>. At the highest O<sub>2</sub> flow, it is likely that most of the silicon atoms are bonded to three and four oxygen atoms.

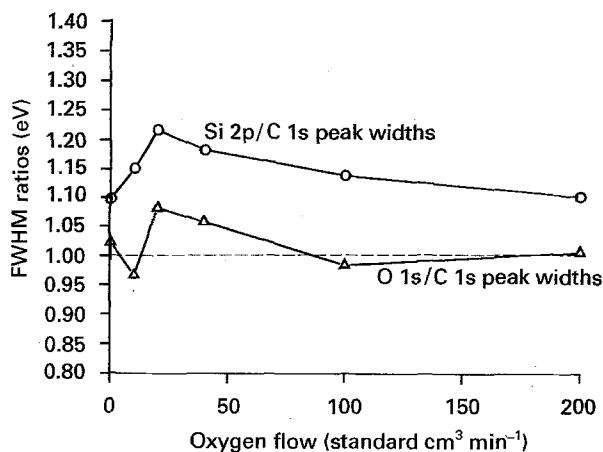


Figure 8 XPS peak width ratios from HMDSO/O<sub>2</sub> plasma deposits ( $p = 50$  Pa,  $P = 200$  W,  $d = 30$  mm, HMDSO flow = 20 standard cm<sup>3</sup>min<sup>-1</sup>, film thickness = 5  $\mu$ m) versus oxygen flow.

From infrared and mass spectroscopic investigations [3], it has been postulated that along with the trimethyl and dimethyl structures (discussed above), the addition of oxygen also introduces other structures; CH<sub>2</sub>-OH, C=O and Si-O-C. These have been linked to ageing phenomena [15]. No features in the C 1s narrow scans were seen to substantiate these earlier studies at any time after production. Our observation is consistent with that of Hays [3] who determined that as power input into plasma increased, the concentration of these functionalities decreased using infrared spectroscopy. We believe that our plasmas are within this region of high power. We also point out that infrared spectroscopy may over-estimate the relative importance of these groups.

The absence of any carbon-oxygen functionalities, and the decrease in carbon content (with increasing oxygen flow rate), have important implications. The data reveal that in the plasma, stable, condensable carbon-oxygen moieties are not formed. This draws attention to the propensity of HMDSO methyl group to react (in the plasma) with oxygen to produce volatile reaction products. This is supported by the fact the carbon concentration decreases with oxygen addition. The form of the curve indicates, however, that any further increase in the oxygen flow will not completely remove the carbon from the deposit. Mass spectral analysis of HMDSO/O<sub>2</sub> plasma has shown that OH, H<sub>2</sub>O, CO, CO<sub>2</sub>, HOSiCH<sub>3</sub>CH<sub>3</sub> and (HO)<sub>2</sub>SiCH<sub>3</sub> are produced on addition of oxygen. The presence of these volatile reaction products is consistent with our inability to detect C-O<sub>x</sub> species in these materials.

Finally, it is worth comparing the effect of oxygen introduction into the plasma with the effects of power and substrate heating. Krishnamurthy *et al.* [5] reported the formation of a silica network with higher power inputs, whilst Assink *et al.* [11] described the same result through heat treatment. Both of these observations are consistent with the changes in chemistry that we have described above.

## 5. Conclusion

Solid deposits (5  $\mu$ m thick) were fabricated from low-temperature microwave HMDSO/O<sub>2</sub> plasmas. Quantitative analysis of these has been carried out by XPS. We show that it is appropriate to charge-correct XP spectra of these deposits using the C 1s core line. As the oxygen flow rate (into the plasma) was increased, the chemistry of the deposits changed from that of a siloxane, with a high proportion of trimethyl siloxyl groups, to a material closer to silica. Increased oxygen flow resulted in higher levels of oxygen incorporation, as reflected both in the stoichiometry of the deposits, and in the binding energies of the Si 2p core line. However, we show that pure silica deposits are not formed, nor would they be by further increasing the O<sub>2</sub> flow rate.

Increased oxygen flow reduces the carbon content of the deposits. However, it is not possible to remove all of the carbon from the deposits simply through the addition of oxygen. From the C 1s binding energies we show that this residual carbon is not present as simple hydrocarbon, but that it is (mostly) associated with the silicon. The absence of any carbon-oxygen functionalities in the deposits indicates that (within the plasma) there is a preferential formation of small volatile carbon-oxygen species and of condensable/solid silicon-oxygen species.

## Acknowledgements

This work was funded as a Brite EuRam project under the title "Plasma polymerised coatings and interphases for improved performance carbon fibre composites", Contract BRE2-0453. In addition to the named authors, this collaboration also involves groups within the Department MTM Metallurgy and Materials Engineering, KU Leuven, Belgium, and the Department of Materials and Production Engineering, Luleå University of Technology, Sweden.

## References

1. B. V. TKACHUK, V. V. BUSHIN, V. M. KOLOTYRKIM and V. M. SMETANKINA, *Polym. Sci. USSR* **9** (1967) 2018.
2. A. M. WRÓBEL, J. E. KLEMBERG, M. R. WERTHEIMER and H. P. SCHREIBER, *J. Macromol. Sci. Chem. A* **15** (1981) 197.
3. A. K. HAYS, *Proc. Electrochem. Soc.* **82-6** (1982) 75.
4. M. R. WERTHEIMER, J. E. KLEMBERG-SAPIEHA, H. P. SCHREIBER, *Thin Solid Films* **115** (1984) 109.
5. V. KRISHNAMURTHY, I. A. KAMEL and Y. WEI, *J. Appl. Polym. Sci.* **38** (1989) 605.
6. Y. M. TSAI, F. J. BOERIO, W. J. VAN OOIJ, G. K. KIM and T. RAU, *Surf. Inter. Anal.*, **23** (1995) 261.
7. P. K. TIEN, G. SMOLINSKY and R. J. MARTIN, *Appl. Opt.* **11** (1972) 637.
8. J. SAKATA, M. YAMAMOTO and M. HIRAI, *J. Appl. Polym. Sci.* **31** (1986) 1999.
9. H. YASUDA, (ed.), "Plasma Polymerisation", (Academic Press, London, 1985).
10. R. d'AGOSTINO (ed.), "Plasma deposition, treatment, and etching of polymers" (Academic Press, 1990).
11. R. A. ASSINK, A. K. HAYS, R. W. BILD and B. L. HAWKINS, *J. Vac. Sci. Technol.* **A3** (1985) 2629.
12. A. M. WRÓBEL, *J. Macromol. Sci. Chem.* **A22** (1985) 1089.

13. M. GAZICKI, A. M. WRÓBEL and M. KRYSZEWSKI, *J. Appl. Polym. Sci. Appl. Polym. Symp.* **38** (1984) 1.
14. *Idem*, *J. Appl. Polym. Sci.* **21** (1977) 2013.
15. A. M. WRÓBEL, M. KRYSZEWSKI and M. GAZICKI, *J. Macromol. Sci. Chem.* **A20** (1983) 583.
16. I. TAJIMA and M. YAMAMOTO, *J. Polym. Sci. Polym. Chem. Edn* **23** (1985) 615.
17. D. T. CLARKE and H. R. THOMAS, *ibid.* **15** (1977) 283.
18. G. BEAMSON and D. BRIGGS, "High Resolution XPS of Organic Polymers—The Scienta ESCA300 Database" (Wiley, Chichester, 1992) p. 72.
19. R. J. WARD and B. J. WOOD, *Surf. Interface Anal.* **18** (1992) 679.
20. P. V. WRIGHT and M. S. BEEVERS, in "Cyclic Polymers", edited by J. A. Semlyen (Elsevier Applied Science, Amsterdam 1986) p. 85.

*Received 6 February  
and accepted 19 September 1995*