Liquid repellent surfaces

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4.3.2.2. Experimental

Hexatriacontane, $C_{36}H_{74}$, (HTC) crystals (Fluka AG) were solvent cast onto glass slides from a 0.5 % w/v solution in hexane [50]. It was necessary to heat the solution slightly in order to fully dissolve all the crystals prior to casting. Several drops of the solution were dispensed onto glass slides via a Pasteur pipette and the solvent was left to evaporate. Once the crystals had formed they were subjected to a CF_4 (Air Products 99.7% purity) continuous wave plasma at varying powers and exposure times. These experiments were carried out in an inductively coupled cylindrical plasma reactor see Chapter 2. The CF_4 gas was introduced at a constant pressure of 0.2 mbar and allowed to purge the reactor for 15 min, followed by ignition of the glow discharge.

Sessile drop contact angle measurements using water were made as described in Chapter 2.

4.3.2.3. Results and Discussion

CF_4 plasma treatment time was fixed at 5 min and the continuous wave power was altered, Figure 4.6. Further experiments were carried out at a continuous wave power of 50 W for varying treatment times, Figure 4.7.

After solvent casting hexatriacontane crystals onto the glass substrate, a visibly rough surface resulted. There appeared to be several degrees of roughness present, depending on the scale being analysed. Optimum contact angle values will result from the superposition of surface roughness on various scales.

CF_4 plasma treatment of these crystals increased the contact angle of the water droplet for the 2 min, 50 W experiment. It is believed that the increase in contact angle results from fluorination of the crystal surface along with micro roughening for the short plasma treatment times, and additional increased micro-roughening effects of the fluorinated surface for the longer treatment times; explaining the very high contact angles in the latter case.

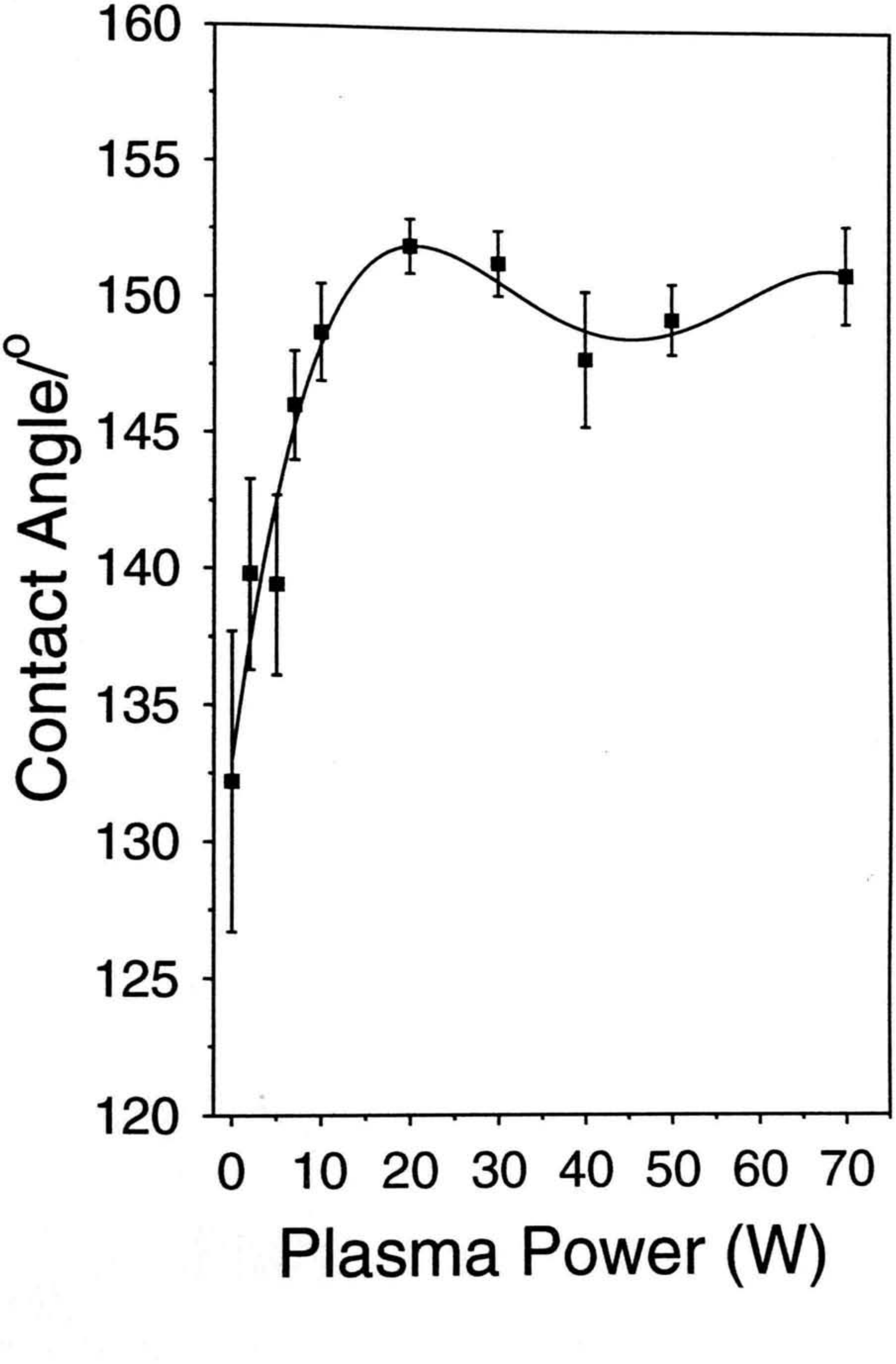

Figure 4.6 Plot of contact angle versus CF_4 plasma power for 5 min treatment times.

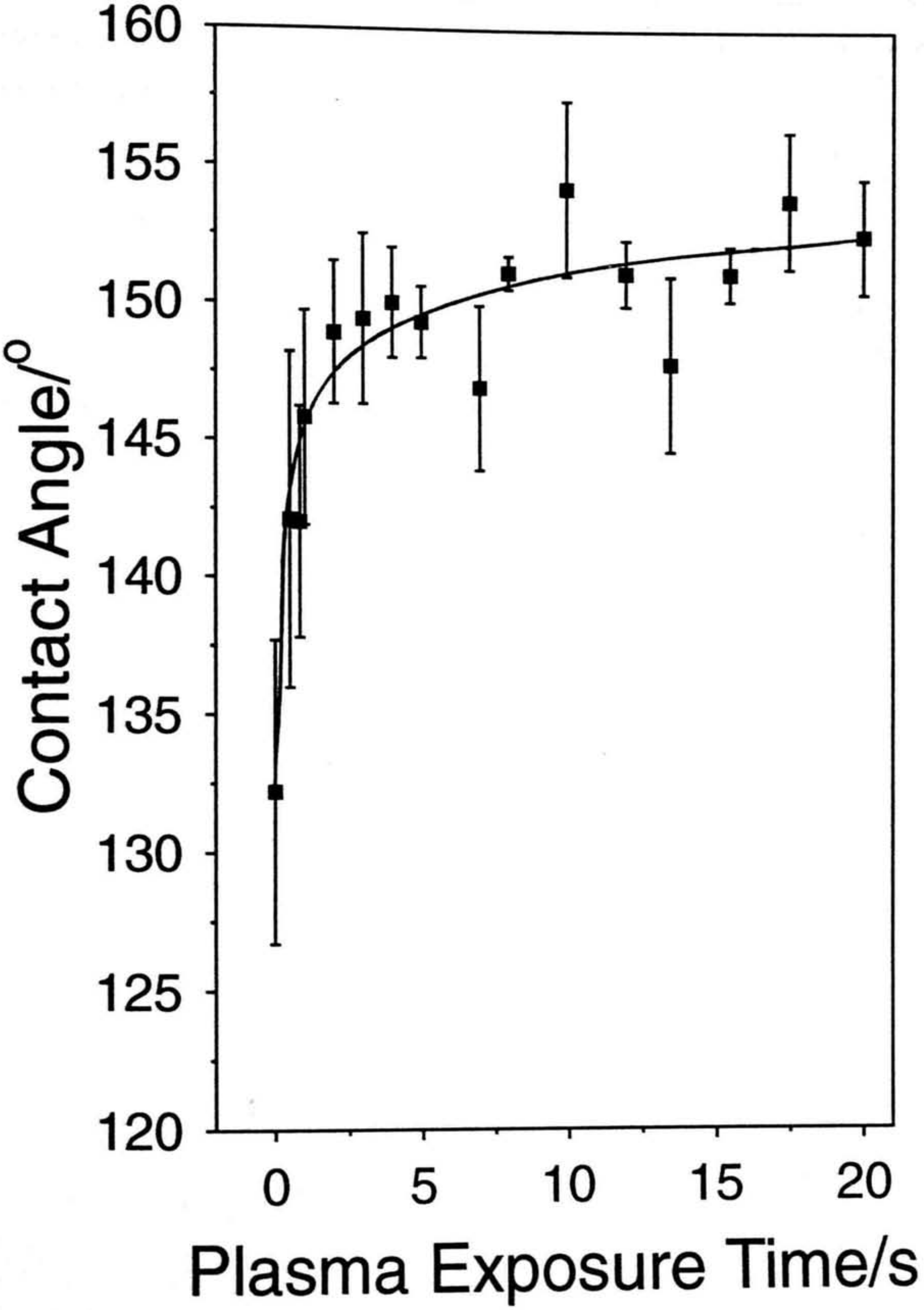

Figure 4.7 Plot of contact angle versus CF_4 plasma exposure time for 50 W power experiments.

The increase in contact angle due to increase in surface roughness of hydrophobic surfaces has been reported in an earlier paper [51] and arises due to the creation of aspirates and hence a composite surface [5].

4.3.2.4. Conclusions

CF_4 plasma treatment was effective for roughening an n-hexatriacontane surface, which led to an increase in water contact angles. However the values obtained were no greater than O_2 plasma treatment of PTFE.

4.4. *PART C*

4.4.1. Depositions onto Commercially available Sandpaper and Lapping Films

4.4.1.1. Introduction

Many papers to date have reported high contact angle and low surface energy values for various surface treatments [22], [52]. As mentioned earlier, wettability is dependent on both chemical and surface roughness factors [1], [2]. We believe the values we have obtained so far [35], [53], unlike others published, arise due to purely chemical effects resulting from the long perfluorinated chains at the solid-air interface. In order to achieve even lower surface energy values, our attention turns to using rough surfaces and depositing a pulsed plasma polymer of these desirable fluorinated moieties on top.

Commercially available rough samples were chosen to see if they possessed optimum roughness for repellency. Sandpaper samples were of varying degrees of roughness and the lapping films contained known particle sizes.

4.4.1.2. Experimental

Sandpaper and lapping film of varying degrees of roughness were taken and the repellent coating was pulsed plasma polymerised on top, using the experimental procedure reported in Chapter 2, in order to determine the effects of surface roughness on contact angle measurements. The sandpaper was obtained from Carbarundum (the letter P that proceeds the number indicates that the silicon carbide grit is backed by a paper substrate, and the letter after the number signifies the weight of the paper; A being the lightest and D the heaviest). The number of the paper refers to the quantity of grit particles per unit length and hence the coarseness of the finish. 80 and 120 are classed as fine, 240, 400 and 800 as very fine. Aluminium oxide lapping films were obtained from RS which are composed of 15-20 % Al_2O_3 and 80-85 % polyethylene terephthalate.

The substrates were placed into the reactor for the pulsed plasma deposition of 1H,1H,2H,2H-heptadecafluorodecyl acrylate for 5 min depositions. Sessile drop contact angle measurements were made as described in Chapter 2 using purified water (B.S. 3978 grade 1) on both the treated and untreated substrates and decane (Aldrich D90-1) on the treated. The oil contact angle is not shown for the untreated samples as the result is a zero contact angle.

4.4.1.3. Results and Discussion

Contact angles were obtained using both water and decane for the sandpaper and lapping films, Figure 4.8 and Figure 4.9 respectively.

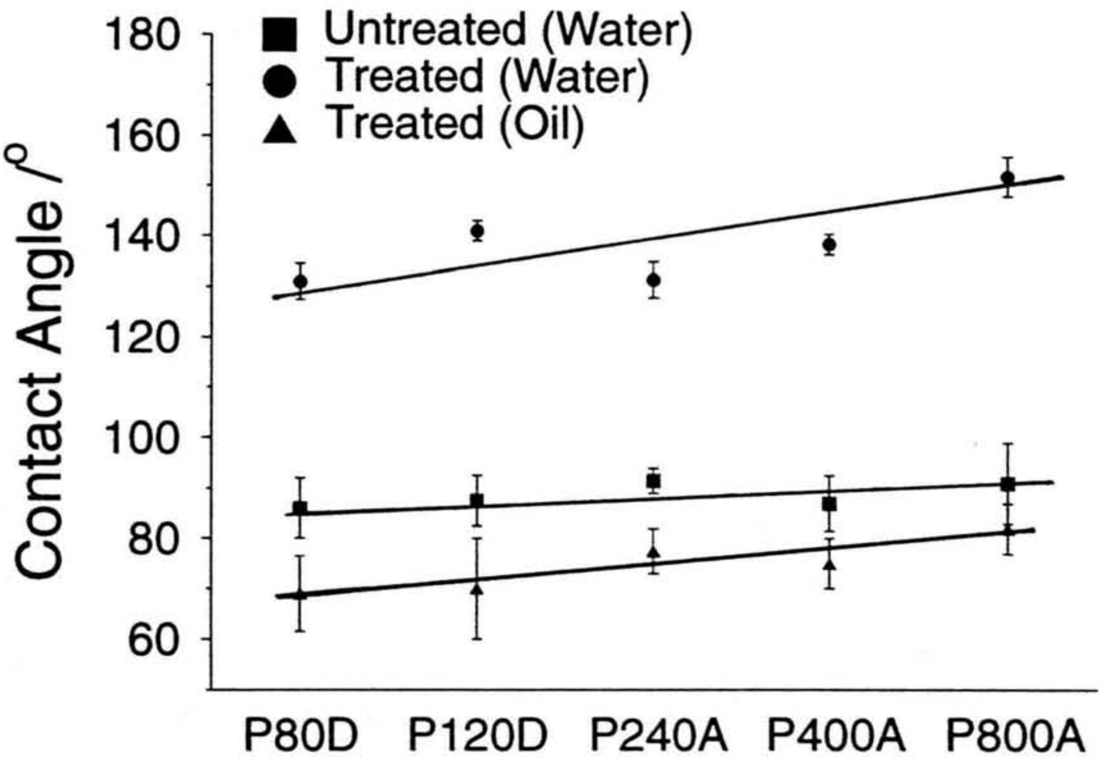

Figure 4.8 Contact angles of water and oil drops on treated and untreated grades of sandpaper.

It can be seen that there is an increase in contact angle as the degree of coarseness decreases for both water and decane on the treated sandpaper, because as the particles become finer the surface area increases [1]. The result of this, coupled with the low surface energy coating leads to the formation of a composite surface where the liquid

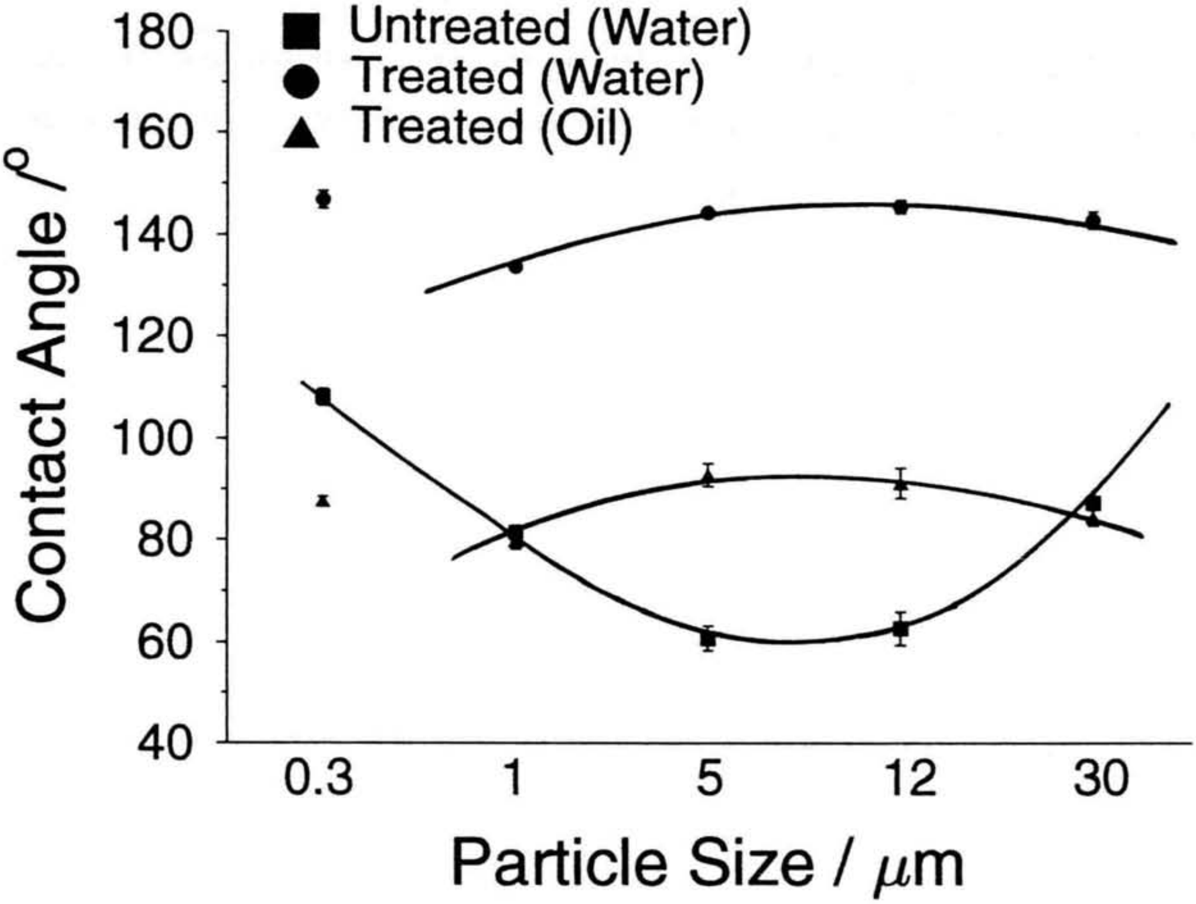

Figure 4.9 Contact angles for lapping films with different size Al_2O_3 particles.

droplets are now in contact with both air and the repellent substrate surface [5] (compare with contact angles formed on flat substrate surfaces, Chapter 2). As contact angle measurements are directly related to the surface energy (surface tension x surface area), the smaller the amount of surface the liquid is in contact with, the lower the interaction between the two and the higher the resulting contact angle.

Lapping films with particle sizes 1-30 μm show a good relationship between water contact angles of untreated and treated substrates. The larger water contact angle (>90°) for the untreated 0.3 μm lapping film could be due to a porous type structure, adopted by substrates containing very small particles.

4.4.1.4. Conclusions

The use of commercially pre-roughened substrates (sandpaper and lapping films) resulted in high water and decane contact angles; but none greater than those reported earlier.

4.5. REFERENCES

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CHAPTER 5

FLUOROCARBON LABELLING OF A FUNCTIONALISED PLASMA POLYMER LAYER

5.1. INTRODUCTION

Plasma polymerisation of fluorinated monomers has dominated the work in this thesis. However, there are other ways of fluorinating a surface, including direct plasma fluorination and free radical initiated polymerisation. Whilst the presence of long fluorinated chains at the surface remains a priority for low surface energy properties, these altenative methods present inherent drawbacks. The former tends to cause cross-linking and incomplete fluorination and the latter is strongly substrate dependent and so will be influenced by chemical groups present at the surface. A fourth method, functionalisation of a deposited plasma polymer layer, has the advantage that the fluorinated moiety will not be subjected to the plasma phase. This will prevent chain breakdown or cross-linking, allowing long perfluorinated groups to be retained at the surface.

Plasma polymerisation is a novel way of coating any solid substrate, regardless of its structure and chemical composition [1]. The glow discharge contains ions, radicals and excited molecules in the gas phase which then react via plasma-induced polymerisation [2]. Plasma processing of solid surfaces offers numerous advantages over conventional solution phase ("wet") chemistries for the production of polymeric films, see Chapter 1, however there are drawbacks. Plasma processing is extremely complex and variations in experimental parameters such as reactor volume, radio frequency, power level [3], gas flow rate, gas composition, monomer pressure [4], [5], substrate temperature [6], substrate position [7] and reactor geometry can all dramatically effect the physical and chemical properties of the polymer film [1], [8].

It has already been found that pulsed power experiments offer numerous advantages over continuous wave plasma polymerisation where conditions are often severe, causing monomer fragmentation [9], [10], [11]. Here we explain how the retention of precursor functionalities can be quickly optimised using a factorial (experimental) design technique for pulsed power polymerisation experiments. In this study, methacrylic anhydride was used as the organic precursor due to its high concentration of reactive anhydride group functionalities. These can subsequently be reacted with a nucleophile to provide, for example, long fluorocarbon chains at the surface which exhibit low surface energy properties [12]. Such layers have numerous everyday applications e.g. biocompatibility protection against environmental fouling and non-wettable surfaces, [13], [14], [15], [16]. Previous work has been carried out using maleic anhydride, which showed very good retention of the anhydride group functionality and has inspired our choice of precursor [11]. 1H,1H,2H,2H-perfluorooctan-1-ol was subsequently reacted with the methacrylic anhydride plasma polymer film in order to present perfluoroalkyl groups at the surface.

5.2. EXPERIMENTAL

Methacrylic anhydride, Figure 5.1, (Aldrich, 94% purity) is a liquid at room temperature.

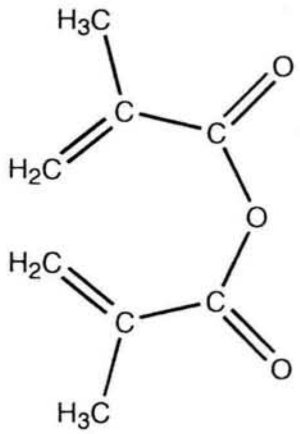

Figure 5.1 Methacrylic anhydride

The plasma treatment experiments were carried out as described in Chapter 2, at a pressure of 0.2 mbar. Depositions were carried out on glass slides and complete plasma polymer coverage was indicated by the absence of any Si(2p) XPS signals, from the underlying glass substrate.

To carry out a factorial design approach, 2 levels (high and low) were chosen for each of the three variables (factors) of the pulsed plasma polymerisation procedure: peak continuous wave power (P_P), pulse on time (t_{on}) and pulse off time (t_{off}). This gives rise to a 2^3 experimental design [17], Table 5.1.

	Low (-)	**High (+)**
P_P (W)	15	50
t_{on} (μs)	20	100
t_{off} (μs)	100	1200

Table 5.1 The 3 factors for pulsed plasma polymerisation experiments at 2 levels.

This method was employed in order to identify the factors, and the combination of factors, that maximise the percentage anhydride group within the plasma polymer film; this is known as the response function (r.f.) [17].

This then gives rise to 8 experiments as each combination of factor and level is examined, Table 5.2.

Experiment	P_P	t_{on}	t_{off}
1	-	-	-
2	+	-	-
3	-	+	-
4	+	+	-
5	-	-	+
6	+	-	+
7	-	+	+
8	+	+	+

Table 5.2 The experiments carried out to determine the effect of each parameter on the response function.

The average power $\langle P \rangle$ delivered to the system during pulsing can be calculated using the following formula:

$$\langle P \rangle = P_P \left\{ \frac{t_{on}}{t_{on} + t_{off}} \right\}$$

where $t_{on} / (t_{on} + t_{off})$ is defined as the duty cycle and P_P is the peak continuous wave power [18].

The deposited methacrylic anhydride plasma polymer layer was subsequently immersed in 1H,1H,2H,2H-perfluorooctan-1-ol, $CF_3(CF_2)_5CH_2CH_2OH$, (Fluorochem, 97% pure) and then evacuated down to base pressure to ensure no solution remained unreacted on the surface.

5.3. RESULTS AND DISCUSSION

Plasma deposition of methacrylic anhydride was found to give an "electrophilic" surface which was susceptible to attack by 1H,1H,2H,2H-perfluorooctan-1-ol, imparting fluorinated groups at the surface.

A 15 W continuous wave plasma polymerisation experiment did not completely cover the glass slide, as shown by the presence of silicon Si(2p) detected during XPS analysis. However a 10 W continuous wave plasma run for 10 min gave complete coverage, Figure 5.2. The C(1s) XPS envelope was fitted to different carbon environments with five components having equal full widths at half maximum corresponding to $\underline{C}_xH_y$ at 285.0 eV, $\underline{C}$-C(O)=O at 285.7 eV, $\underline{C}$-O at 286.6 eV, $\underline{C}$=O/O-$\underline{C}$-O at 287.9 eV and $\underline{C}$(O)=O at 289.4 eV environments [19]. Hydrocarbon / cross-linked carbon, $\underline{C}_xH_y$, is found to be the most abundant carbon centre in the C(1s) envelope, with smaller amounts of oxygenated functionalities.

For pulsed plasma polymerisation, the variation in percentage anhydride group present in the polymer film was investigated as a function of P_P, t_{on} and t_{off}. Using the experimental design method the important plasma parameters were isolated [17], Table 5.3. The effects, given at the bottom, indicate how important a particular factor is in generating a high response. A high positive effect means that if the level is high then a large r.f. (percentage anhydride group) will result. A high negative effect indicates a situation were decreasing the level will result in a high r.f. For experiment 4 a response function of 0 is given as analysis indicated the presence of silicon, because the pulsing conditions did not produce an even plasma polymer coverage.

From these results it is possible to list the main effects in order of magnitude:- (a) t_{off}, (b) t_{on}, (c) P_P. A further series of experiments were carried out, varying t_{on} and t_{off}, at a peak power of 15 W for 5 min in order to maximise the response, Tables 5.4a and 5.4b and Figures 5.3a and 5.3b. This is a form of simplex optimisation where only two parameters are altered in order to maximise the response.

The optimum conditions found were $P_p = 15$ W, $t_{on} = 20$ μs and $t_{off} = 1000$ μs, for a 5 min pulsed plasma polymerisation experiment, Figure 5.4. The C(1s) environment percentages for the optimum pulsed plasma polymer, along with the continuous wave experiment and the theoretical values have been compiled, Table 5.5. The greater level of structural retention in the case of pulsed plasma polymerisation can be attributed to conventional free radical assisted polymerisation processes occurring during the duty cycle off time [11].

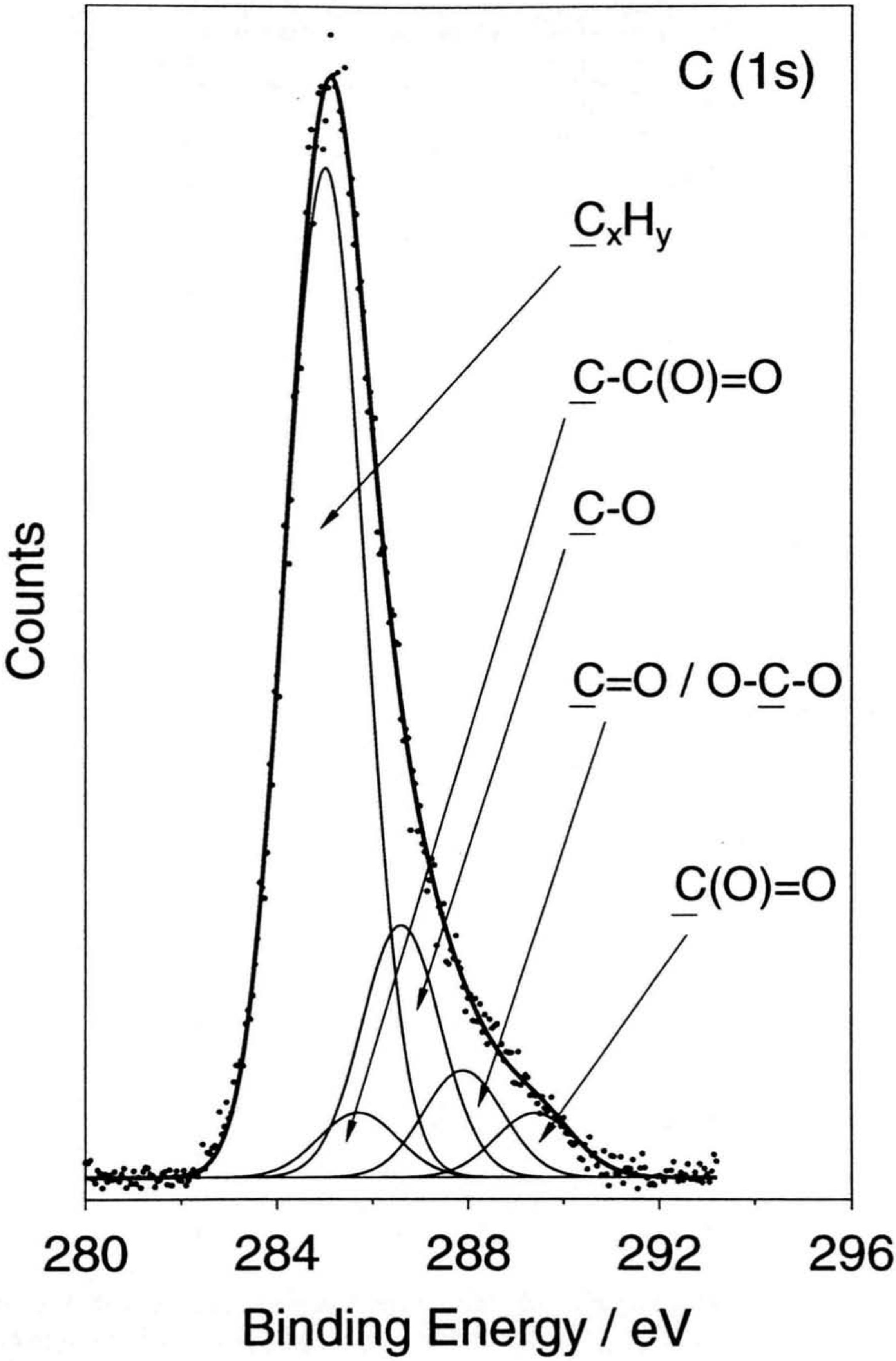

Figure 5.2 XPS C(1s) peak fit for a 10 W continuous wave plasma polymer of methacrylic anhydride for 10 min.

Exp.	P_P	t_{on}	t_{off}	*r.f.(%)*
1	-	-	-	2.6
2	+	-	-	3.7
3	-	+	-	4.3
4	+	+	-	0
5	-	-	+	16.4
6	+	-	+	15.8
7	-	+	+	8.4
8	+	+	+	2.9
Effect	*-2.33*	*-5.73*	*+8.23*	

Table 5.3 Response function and effects for different levels of pulsed plasma polymerisation.

Time On (μs)	**% Anhydride Group**
10	15.7 ± 1.7
20	16.4 ± 1.4
100	7.5 ± 1.5
150	3.5 ± 1.2
300	3.6 ± 1.4
500	4.1 ± 1.3
800	5.3 ± 1.4
1000	5.4 ± 1.5

Table 5.4a Percentage anhydride group obtained by varying the duty cycle on-time at a fixed off-time of 1200 μs and a peak power of 15 W.

Time Off (μs)	**% Anhydride Group**
20	5.3 ± 1.1
100	3.9 ± 0.9
500	12.4 ± 2.1
600	12.5 ± 2.8
800	14.4 ± 1.8
1000	17.1 ± 1.5
1200	16.4 ± 1.4
1400	16.0 ± 2.0
1500	16.2 ± 2.0
1600	15.7 ± 1.7
1800	15.2 ± 0.1
2000	15.5 ± 1.3
2300	5.9 ± 1.2

Table 5.4b Percentage anhydride group obtained by varying the duty cycle off-time at a fixed on-time of 20 μs and a peak power of 15 W.

The influence of t_{on} and t_{off} for a 15 W power pulsed plasma deposition was investigated in order to maximise the response function, Figure 5.5. The experiment with the shortest on-time and the longest off-time gave rise to the highest percentage of anhydride group retention.

1H,1H,2H,2H-Perfluorooctan-1-ol was used to functionalise the methacrylic anhydride pulsed plasma polymer film as shown in the reaction scheme, where R_f is $CF_3(CF_2)_5(CH_2)_2$-, Figure 5.6 [20], [21]. The polymer film was deposited using a P_P of 15 W, t_{on} of 20 μs and t_{off} of 1000 μs for 5 min and the solution phase labelling reaction was carried out at 20°C for 20 min, Figure 5.7. Two extra chemical environments, $\underline{C}F_2$ at 292.1 eV and $\underline{C}F_3$ at 294.3 eV, resulted from the addition of the fluorinated moiety to the plasma polymer film, Table 5.6 [19]. The experimentally measured CF_2:CF_3 ratio is 4.9:1, which is just below the theoretically expected value of 5:1, showing that the

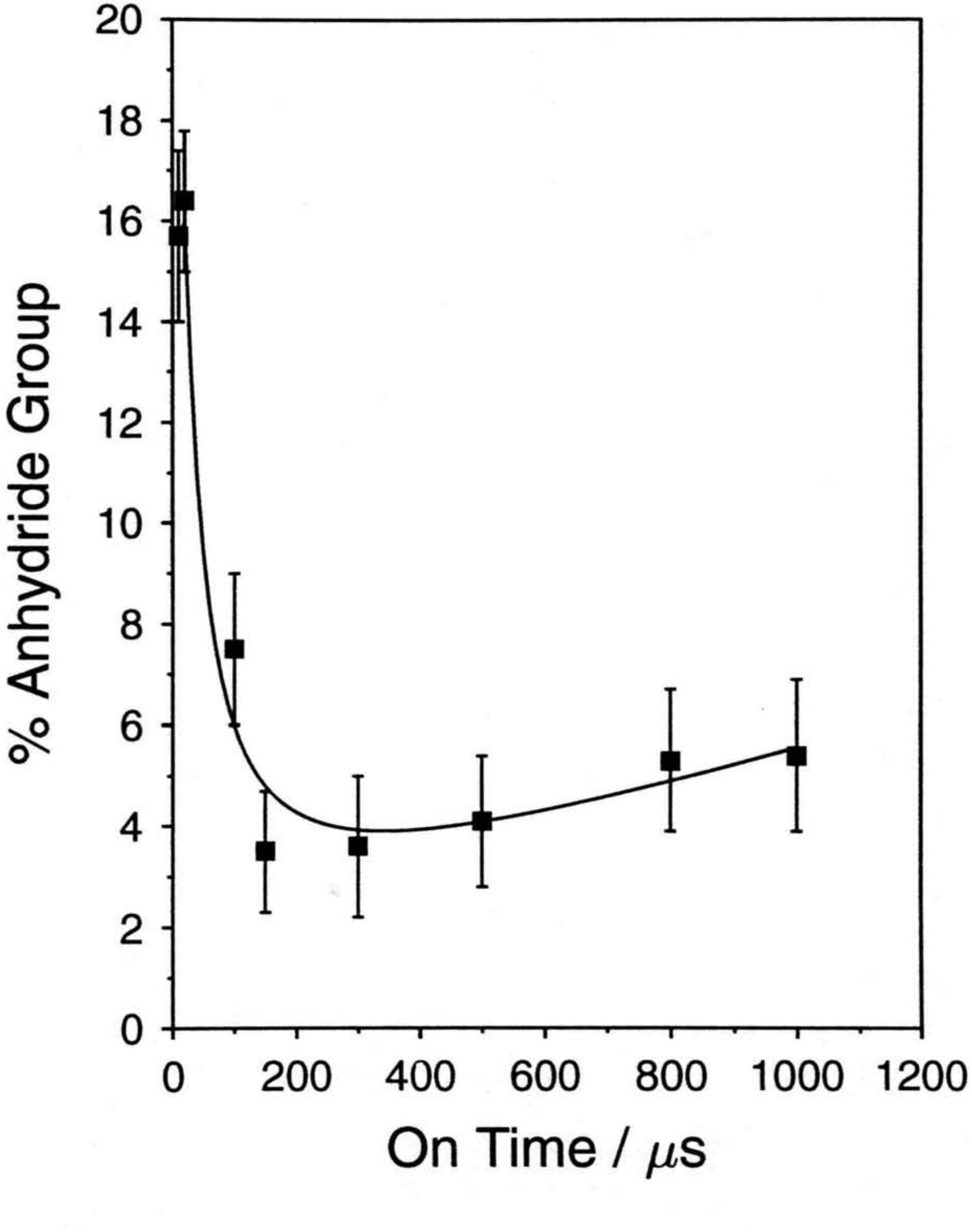

Figure 5.3a Percentage anhydride group functionality at varying on-times, with a fixed off-time of 1200 μs and a peak power of 15 W.

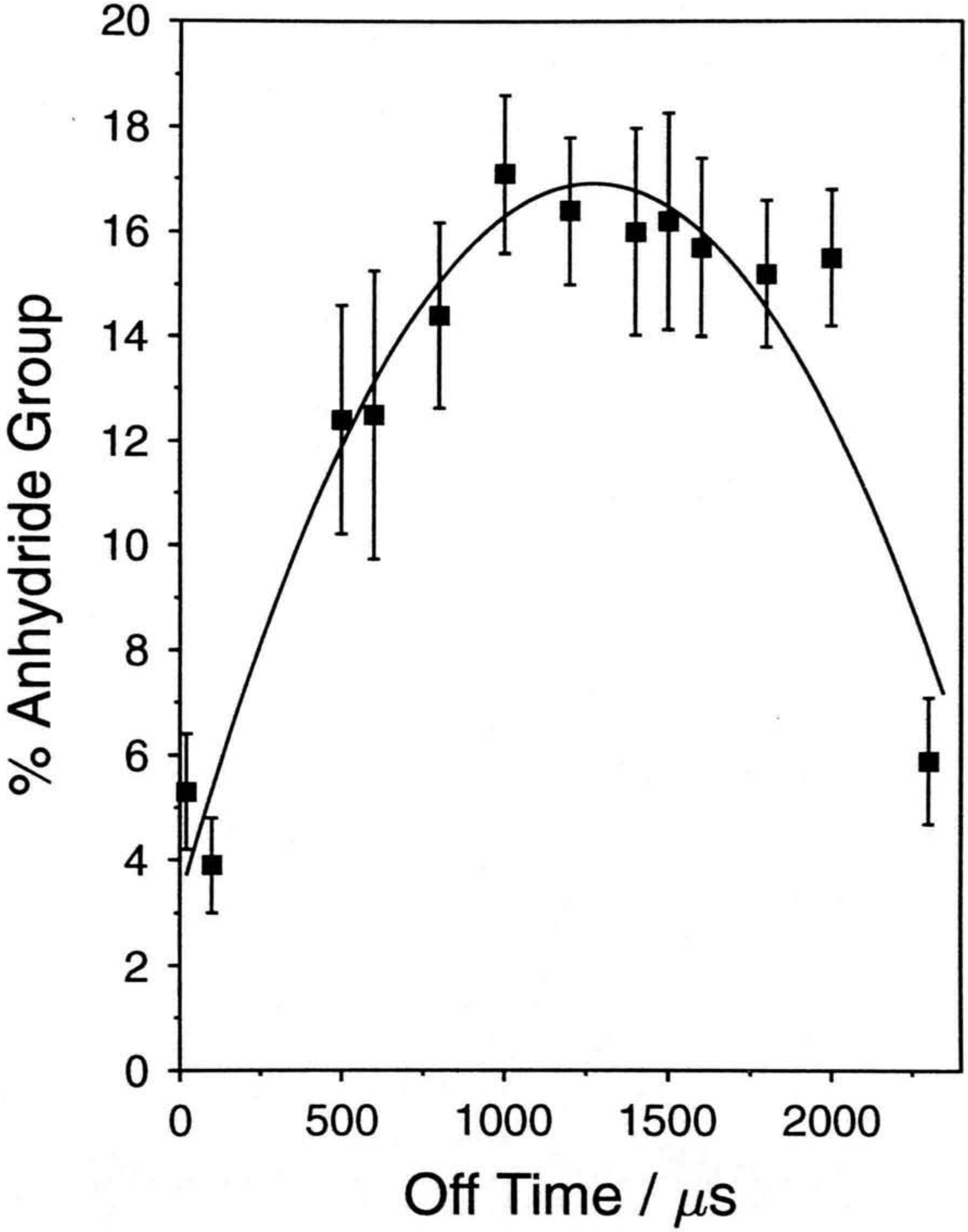

Figure 5.3b Percentage retention of anhydride group functionality at varying off-times, with a fixed on-time of 20 μs and a peak power of 15 W.

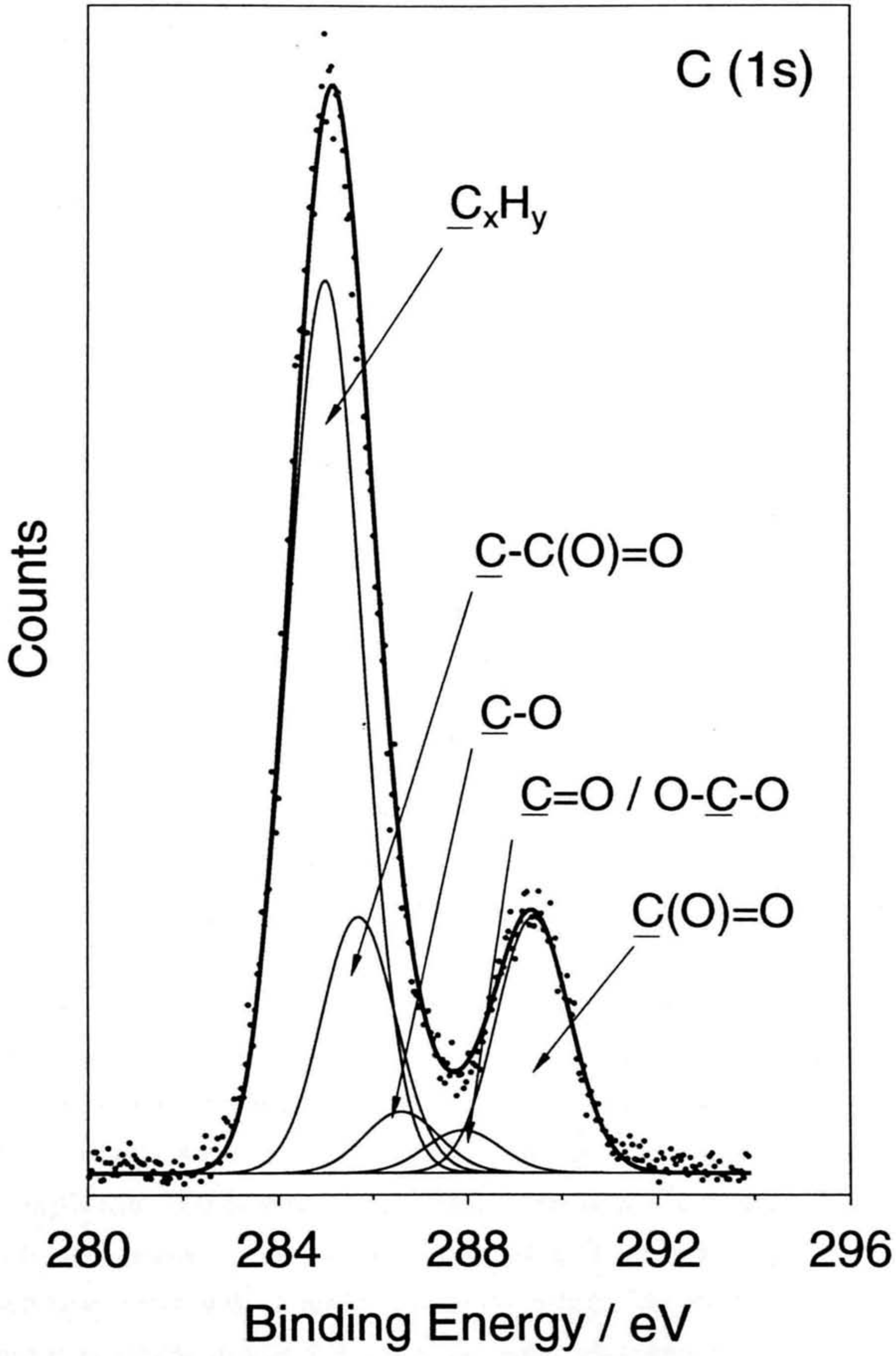

Figure 5.4 C(1s) spectrum of the optimised anhydride group retention for methacrylic anhydride at $P_P = 15$ W, $t_{on} = 20$ μs and $t_{off} = 1000$ μs for 5 min.

Environment	Theoretical (%)	10 W Continuous Wave Plasma Polymer (%)	Pulsed Plasma Polymer (%)
$\underline{C}_xH_y$	50	67.3	59.0
$\underline{C}$-C(O)=O	25	4.2	17.1
$\underline{C}$-O	-	17.1	4.1
$\underline{C}$=O / O-$\underline{C}$-O	-	7.3	2.7
$\underline{C}$(O)=O	25	4.1	17.1

Table 5.5 Experimental and theoretical environment percentages of a 10 W continuous wave plasma and pulsed plasma polymer of methacrylic anhydride.

perfluoroalkyl chain is present intact on the surface. The theoretically expected F:C ratio obtained is 0.81, assuming one alcohol group reacts with one anhydride functionality. The experimental ratio was 0.43 which can be attributed to incomplete reaction between the anhydride and the alcohol. The maximum F:C ratio attainable for a 17.1% anhydride group functionality would be 0.66.

The labelling reaction was carried out at a higher temperature, for different lengths of time, in order to obtain greater fluorine retention. However the presence of Si(2p) signals by XPS analysis indicated that the high temperatures were removing some of the deposited methacrylic anhydride plasma polymer film, Table 5.7.

After labelling the methacrylic anhydride with the alcohol at room temperature and washing with isopropyl alcohol (IPA), the CF_2 and CF_3 peaks completely disappeared. Therefore the IPA either reacts at the site where the fluoroalcohol was introduced, to bring about substitution, or it dissolves the fluorinated group. The plasma deposited methacrylic anhydride polymer washed with IPA was found to be stable, i.e. no Si(2p) signals were present. This experiment was repeated using a non-polar wash of cyclohexane, which did not modify the surface either. The methacrylic anhydride monomer is soluble in both IPA and cyclohexane, indicating that the methacrylic anhydride plasma polymer is well adhered to the glass substrate.

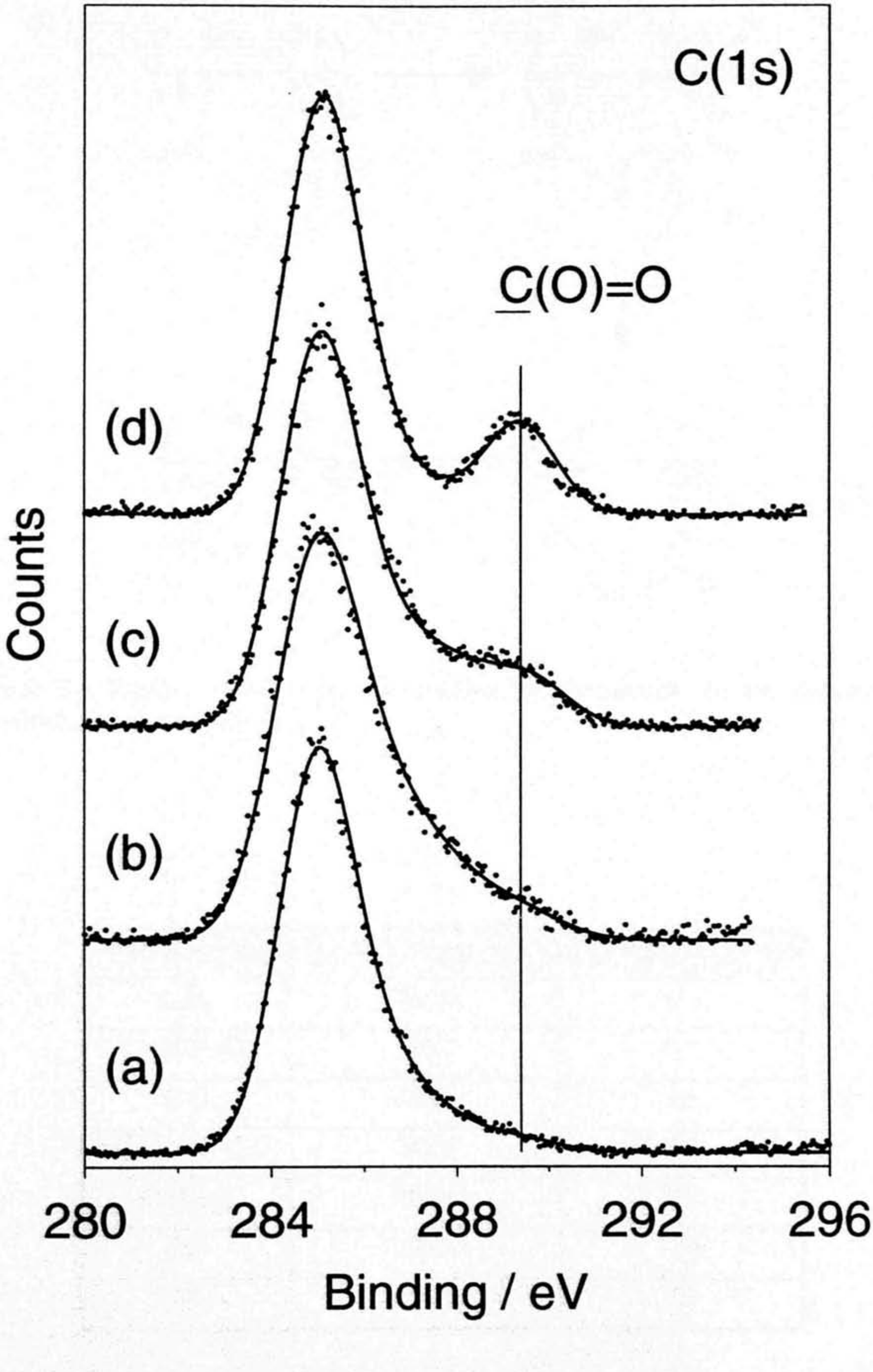

Figure 5.5 Stack plot of C(1s) spectra for 15 W pulsed plasma deposition of methacrylic anhydride for 5 min at (a) t_{on} = 20 μs, t_{off} = 100 μs, (b) t_{on} = 100 μs, t_{off} = 100 μs, (c) t_{on} = 100 μs, t_{off} = 1200 μs and (d) t_{on} = 20 μs, t_{off} = 1200 μs.

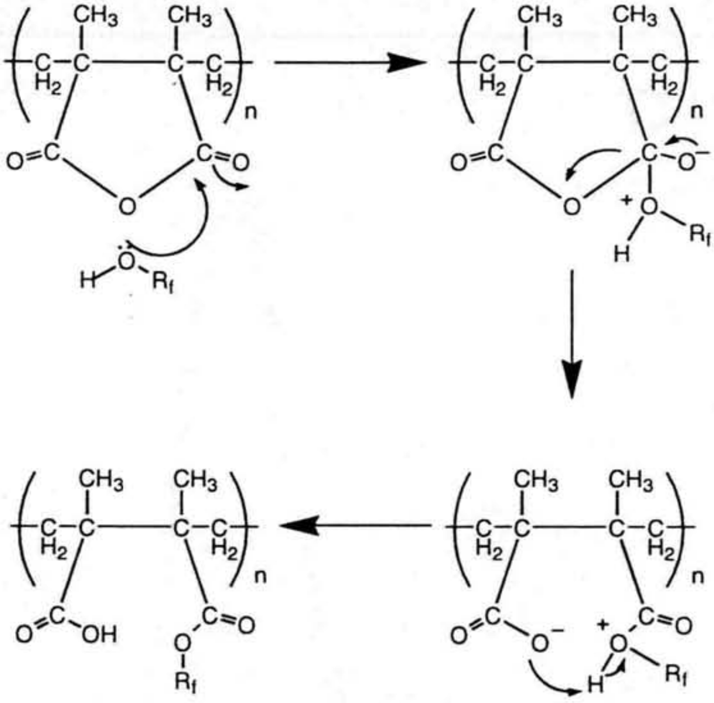

Figure 5.6 Reaction scheme for the addition of the alcohol to the methacrylic anhydride polymer layer [20], [21].

Functionality	Binding Energy (eV)	Percentage (%)
$\underline{C}_xH_y$	285.0	53.3
$\underline{C}$-C(O)=O	285.7	6.3
$\underline{C}$-O	286.6	6.5
>$\underline{C}$=O / O -$\underline{C}$-O	287.9	8.8
$\underline{C}$(O)=O	289.4	6.3
$\underline{C}F_2$	292.1	15.6
$\underline{C}F_3$	294.3	3.2

Table 5.6 Carbon environment percentages for the pulsed plasma polymer layer of methacrylic anhydride, labelled with 1H,1H,2H,2H-perfluorooctan-1-ol.

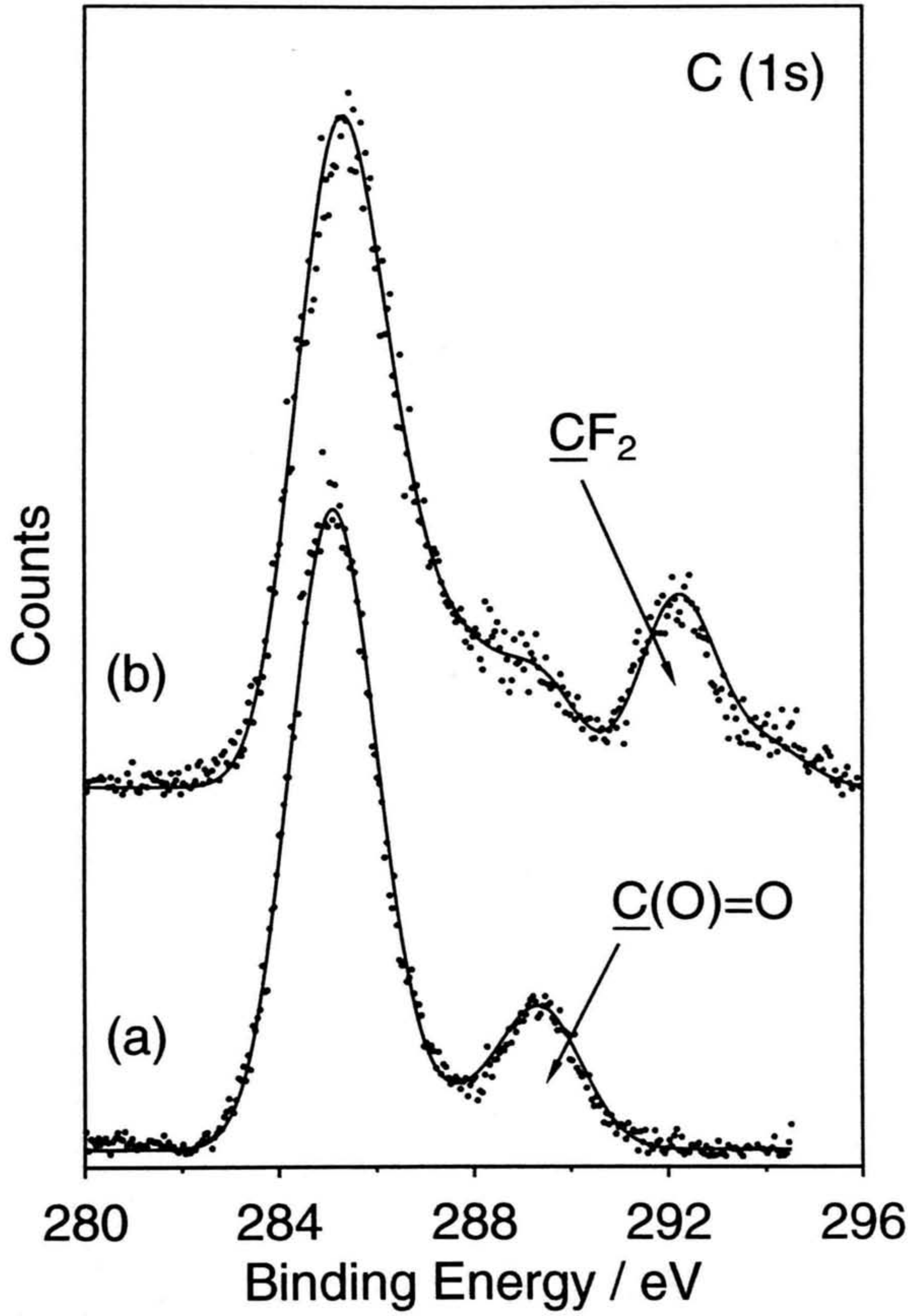

Figure 5.7 C(1s) stack plot of (a) pulsed plasma polymer of methacrylic anhydride and (b) 1H,1H,2H,2H-perfluorooctan-1-ol labelled pulsed plasma polymer of methacrylic anhydride.

Time (min)	Temperature (°C)	F:C ratio	Silicon (%)
10	20	0.25	0
20	20	0.43	0
10	56	0.50	4

Table 5.7 Change in F:C ratio with respect to the alcohol temperature and reaction time.

5.4. CONCLUSIONS

A plasma polymer film of reactive anhydride groups has been successfully polymerised onto a glass surface, which can be subsequently labelled with a fluorinated alcohol. Due to the nature of the condensation reaction leading to the fluorinated surface, the fluoroalkyl chain remains intact. However the flurinated moiety can be removed with isopropyl alcohol.

5.5. REFERENCES

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CHAPTER 6

CONCLUSIONS

This thesis has been primarily aimed at the vapour phase deposition of low surface energy films. It has been shown that pulsed plasma polymerisation of long perfluorinated chain precursors can achieve this objective.

Current methodologies for the production of repellent films are organic or aqueous based and require the addition of cross-linking agents, surfactants and pH adjusters. The method of pulsed plasma polymerisation adopts a solvent-less approach which is carried out at ambient temperatures with little waste product formation. Other advantages of this technique include the ability to coat any solid object, regardless of shape or material, the formation of pin-hole free films and deposition conditions which leave bulk properties unperturbed.

PTFE (teflon) is the benchmark low surface energy solid which gives rise to good water repellency. In order to achieve greater repellency long perfluorinated chains need to be attached to the solid surface which present terminal -CF_3 groups at the solid / air interface. Traditional plasma polymerisation at relatively high continuous wave powers has led to the production of many novel coatings, but suffers from precursor structure fragmentation due to the high powers involved. Pulsed plasma polymerisation has the advantage of modulating the input power which can result in monomer vapour being subjected to very low average powers. This will result in little precursor fragmentation, leading to retention of monomer functional group properties on the solid surface. The polymer films produced have been characterised using XPS, contact angle, IR and AFM and indicate that structural retention has occurred with little substrate damage.

Pulsed plasma polymer films of 1H,1H,2H,2H-heptadecafluorodecyl acrylate were successfully deposited onto flat surfaces. Structural retention was quickly optimised using experimental design techniques giving rise to surface energy values of 9-10 mN m^{-1} and critical surface tension values as low as 4.3 mN m^{-1} (P_P = 40 W, T_{on} = 20 μs, T_{off} = 20,000 μs for 5 min).

Greater deposition rates for unsaturated, as opposed to saturated, perfluorinated anologues indicated that polymerisation was occurring during the duty-cycle off-period. As the monomer gas will not be exposed to an excitation source during the plasma off-time, functional group retention can occur within the growing plasma polymer film via conventional free radical polymerisation of the double bond.

Another major influence on repellency is surface roughness. By increasing the underlying surface roughness of repellent films, it is possible to decrease the area of contact between a liquid and a solid medium by the production of a composite interface. As surface energy is a function of surface area, the lower the contacting area, the lower the interactions and the greater the repellency. By initially roughening PTFE surfaces using an O_2 plasma followed by the pulsed plasma polymerisation of the perfluorinated acrylate, extremely high repellency towards water and decane resulted.

In summary, this thesis has shown that pulsed plasma polymerisation of monomers containing long perfluorinated chains can give rise to liquid repellent films on flat surfaces, with precursor structure retention. With additional surface roughening, super liquid repellency can be obtained.

APPENDIX

COLLOQUIA, SEMINARS, PRESENTATIONS AND LECTURE COURSES

UNIVERSITY OF DURHAM

BOARD OF STUDIES IN CHEMISTRY

COLLOQUIA AND SEMINARS FROM INVITED SPEAKERS

1996

October 22	Prof. B. J. Tighe, Aston University *Polymers for Biomedical Applications*
October 23	Prof. H. Ringsdorf, Johannes Gutenberg-Universitat *Function Based on Organisation*
November 6	Dr. Reid, Nottingham University *Probing Dynamic Processes with Photoelectrons*
November 18	Prof. Olah *Crossing Conventional Lines in my Chemistry of the Elements*
November 20	Prof. J. Earnshaw, Belfast University *Surface Light Scattering: Ripples and Relaxation*
December 4	Prof. K. Muller-Dethlefs, York University *Very High Resolution ZEKE Spectroscopy*

1997

February 6	Prof. P. Bartlet, Southampton University *Integrated Chemical Systems*
February 19	Brian E. Hayden *Dynamics of Dissociation at Surfaces*

March 3	Dr. M. Owen and Dr. D. Gravier, Dow Corning *Siloxanes at Surfaces*
March 6	Prof. Toth *Advances in Scanning Electrochemical Microscopy*
October 15	Dr. R. Mark Ormerod, Keele University *Studying Catalysis in Action*
October 22	Prof. R. J. Puddephatt, University of Western Ontario *Organoplatinum Chemistry and Catalysis*
October 23	Prof. M. R. Bryce, University f Durham *New Tetrathiafulvalene Derivatives in Molecular, Supramolecular and Macromolecular Chemistry. Controlling the Electronic Properties of Organic Solids*
November 12	Dr. Jeremy Frey, Southampton University *Spectroscopy of Liquid Interfaces: From Bio-organic Chemistry to Atmospheric Chemistry*
November 26	Prof. R. W. Richards, University of Durham *A Random Walk in Polymer Science*
1998	
January 14	Prof. David Andrews, University of East Anglia *Energy Transfer and Optical Harmonics in Molecular Systems*
February 18	Prof. Gus Hancock, Oxford University *Suprises in the Photochemistry of Tropospheric Ozone*

	them
October 21	Dr. Patrick Unwin, Warwick University *Dynamic Electrochemistry: Small is Beautiful*
October 23	Prof. J. C. Scaiano, University of Ottawa *In Search of Hypervalent Free Radicals*
October 28	Prof. J. P. S. Badyal, University of Durham *Tailoring Solid Surfaces*
November 18	Dr. Ruth Cameron, Cambridge University *Biodegradable polymers*
December 9	Dr. M. E. Smith, Warwick University *Multinuclear Solid-State Magnetic Resonance Studies of Noncrystalline Oxides and Glasses*
1999	
January 27	Prof. K. Wade, Durham University *Foresight or Hindsight? Some Borane Lessons and Loose Ends*
February 10	Dr. C. D. Bain, Oxford University *Surfactant Adsorption and Marangoni Flow at Expanding Liquid Surfaces*
February 17	Dr. B. R. Horrocks, Newcastle University *Microelectrode Techniques for the Study of Enzymes and Nucleic Acids at Interfaces*

PRESENTATIONS ATTENDED

April 1999	North-Eastern Universities Graduate Symposium *"Super Repellent Surfaces"*

CONFERENCES ATTENDED

December 1998	MRS Fall Meeting Boston

EXAMINED LECTURE COURSES

Spectroscopies (Dr. Halliday)

Electron Microscopy (Dr. Durose)

Experimental Design (Prof. Badyal)

Mass Spectroscopy (Dr. Jones)