

Surface studies of model chemisorption systems

Author:

Paris, Nathan

Publication Date:

2004

DOI:

<https://doi.org/10.26190/unsworks/4352>

License:

<https://creativecommons.org/licenses/by-nc-nd/3.0/au/>

Link to license to see what you are allowed to do with this resource.

Downloaded from <http://hdl.handle.net/1959.4/54933> in <https://unsworks.unsw.edu.au> on 2024-04-30

SURFACE STUDIES OF MODEL CHEMISORPTION SYSTEMS

A thesis submitted in partial fulfilment of the requirements for the
degree of Doctor of Philosophy

Nathan James PARIS

Supervisor: Dr Nagindar Singh

17th May 2004



U N S W

2 SEP 2005

LIBRARY

ABSTRACT

A study of surface reactions to better understand industrial processes forms the focus of this research. Reactions of Cl_2 on a chemical vapour deposited (CVD) diamond surface, $\text{CF}_3\text{CH}_2\text{SH}$ (TFET) and $\text{CF}_3\text{CH}_2\text{I}$ (TFEI) on GaAs(100) and TiCl_4 on Pt(111) were investigated. The adsorption systems studied are relevant in CVD diamond growth, alkyl catalytic chemistry and TiN deposition. The techniques used were X-ray Photoelectron Spectroscopy (XPS)^{*, †, ‡, §}, Temperature Programmed Desorption (TPD) spectroscopy^{†, ‡, §}, Low Energy Electron Diffraction (LEED)[†], Auger Electron Spectroscopy (AES)[†] in conjunction with deuterium exchange experiments[†].

Molecular chlorine adsorbs dissociatively on CVD diamond at 300 K, occupying two states, a covalent and semi-ionic state. The covalent state is thermally more stable and remains on the surface up to 676 K (clean surface) and 575 K (hydrogen-terminated surface) while the semi-ionic state desorbs by 400 K for both surfaces. Etching of the chlorine layer by atomic hydrogen results in depletion of the chlorine from both states with the semi-ionic state more readily etched. Etching experiments show a dependency on the H_2 flux with higher pressures resulting in greater etching rates.

Techniques used for

- * Cl_2 on CVD diamond
- † $\text{CF}_3\text{CH}_2\text{SH}$ on GaAs(100)
- ‡ $\text{CF}_3\text{CH}_2\text{I}$ on GaAs(100)
- § TiCl_4 on Pt(111)

Surface studies of TFET show that it adsorbs on GaAs(100) at 111 K with complete dissociation of the S-H bond to form the thiolate species ($\text{CF}_3\text{CH}_2\text{S}^-$) and partial C-S bond scission to form CF_3CH_2^- species. The surface species undergo several competing reaction pathways to form $\text{CF}_3\text{CH}_2\text{SH}$ (recombination), $\text{CF}_2=\text{CH}_2$ (β -fluoride elimination), CF_3CH_3 and H_2 (hydrogen reduction) and $\text{CF}_2=\text{CHCH}_2\text{CH}_3$ (olefin insertion). Furthermore, fluorine (from β -fluoride elimination) migrates into the sub-surface forming GaF_x species. The GaF_x species etches spontaneously from the surface and displaces arsenic to the surface which desorbs as As_2 .

Partial dissociation of the C-I bond in TFEI occurs on GaAs(100) at 107 K to form CF_3CH_2^- and I species. These species react to form $\text{CF}_2=\text{CH}_2$ (β -fluorine elimination), $\text{CF}_3\text{CH}_2\text{CH}_2\text{CF}_3$ (alkyl reduction) and $\text{CF}_2=\text{CHCH}_2\text{CF}_3$ (olefin insertion). Atomic F and I etch the surface similarly to TFET.

TiCl_4 adsorbs dissociately on Pt(111) at 107 K to form TiCl_3 and Cl. Heating the surface results in disproportionation/dissociation of TiCl_3 to desorb atomic Ti and Cl.

ACKNOWLEDGEMENTS

The following research could not have been possible without the assistance and guidance of a multitude of people, some of them listed below.

Dr Nagindar Singh for her time and effort in providing me with the necessary knowledge and skills which will form the foundations of a successful scientific career.

Prof. John Foord at the University of Oxford, UK and Dr Andrew Wee at NUS, Singapore for the use of their instrumentations and invaluable support during my stay in their respective countries.

To the other members in my research group, Mr Patrick Gatland and Ms Debbie Giveen and especially Mr Esteban Austidillo who initially showed me how to use the instrumentation.

The various technicians who have repaired or constructed instrumentation, whose efforts are most appreciated and without whose skilled assistance this research would not been possible. Mr Barry Ward for his invaluable assistance. Mr Paul Hallahan and Mr Mitch Davis from the UNSW mechanical workshop for the construction of many of the major components of the XPS chamber. Mr Richard Burgess for the speedy repair of glass ampoules. Mr John Morgan for diagnosing and repairing the electronic equipment, when it failed. Mr Chen for the guidance in the use of several pieces of equipment. The Electronics workshop at University of Oxford, UK for repairing the XPS instrument on several occasions. Also Prof. Rob Lamb's and A/Prof. Gary Willett's research group for the lending of equipment.

Mr Doug Lawes, Dr Spili Geftakis and Dr Scott Watkins for help in transferring of air sensitive samples.

Dr Ron Haines for his assistance in all things computers.

The team of editors who took the time to read my thesis. Dr Ron Haines, Ms Susan Lorenzo, Mrs Denise Paris and Dr. Garth Jones. Each provided a different but pertinent prospective that was invaluable and this thesis would not have been to the standard it is today without their input.

My friends at UNSW who made the time there enjoyable including Garth, David, Doug, Susan, Antonella and Scott.

And a special thank you to my parents, Arthur and Denise Paris, whose loving support has been immeasurable.

TABLE OF CONTENTS

	pg #
ABSTRACT	ii.
ACKNOWLEDGEMENT	iv.
TABLE OF CONTENTS	vi.
LIST OF FIGURES	xii.
LIST OF TABLES	xxi.
ACRONYMS	xxii.
LIST OF PUBLICATIONS	xxiv
CHAPTER I	
INTRODUCTION	1
1.1 Background Information	1
1.2 Objectives and Issues	2
1.3 Thesis Outline	4
1.4 References	4
CHAPTER II	
EXPERIMENTAL THEORY	5
2.1 Temperature Programmed Desorption (TPD)	6
2.2 Surface Spectroscopic Techniques and Surface Specificity	8
2.2.1 <i>X-ray Photoelectron Spectroscopy (XPS)</i>	9
2.2.2 <i>Chemical Information from XPS</i>	11
2.2.3 <i>Auger Electron Spectroscopy (AES)</i>	12
2.2.4 <i>Low Energy Electron Diffraction (LEED) and Surface Structure</i>	13

2.3	References	14
------------	-------------------	-----------

CHAPTER III

EXPERIMENTAL	15
---------------------	-----------

3.1	Ultra-High Vacuum (UHV) Chambers	15
------------	---	-----------

3.1.1	<i>The Temperature Programmed Desorption (TPD) Chamber</i>	15
-------	--	----

3.1.2	<i>Evacuation of the TPD chamber</i>	18
-------	--------------------------------------	----

3.1.3	<i>The X-ray Photoemission Spectroscopy (XPS) Chamber</i>	18
-------	---	----

3.1.4	<i>Pumping of the XPS Chamber</i>	21
-------	-----------------------------------	----

3.2	Single Crystals and Chemicals Used	21
------------	---	-----------

3.2.1	Surface Structure of GaAs(100) - (4x1) and Pt(111)	21
-------	--	----

3.2.2	<i>TPD Chamber</i>	23
-------	--------------------	----

3.2.3	<i>XPS Chamber</i>	27
-------	--------------------	----

3.2.4	<i>Liquid and Gas Samples</i>	28
-------	-------------------------------	----

3.3	Experimental Procedures	29
------------	--------------------------------	-----------

3.3.1	<i>Dosing Experiments</i>	29
-------	---------------------------	----

3.3.2	<i>TPD Experiments</i>	29
-------	------------------------	----

3.3.3	<i>XPS and AES Experiments</i>	30
-------	--------------------------------	----

3.3.4	<i>LEED Experiments</i>	32
-------	-------------------------	----

3.4	References	32
------------	-------------------	-----------

CHAPTER IV

THE EFFECT OF CHLORINE ON CVD DIAMOND GROWTH	33
---	-----------

4.1	Introduction	33
------------	---------------------	-----------

4.1.1	<i>CVD Diamond Growth</i>	34
-------	---------------------------	----

4.1.2	<i>Low Temperature CVD Diamond Deposition</i>	36
4.1.3	<i>Halogen Precursors</i>	42
4.1.4	<i>Technique</i>	43
4.1.5	<i>Aims</i>	43
4.2	Experimental	44
4.2.1	<i>Chamber Description</i>	44
4.2.2	<i>Diamond CVD Sample and Gases</i>	45
4.2.3	<i>XPS Experiments</i>	47
4.2.4	<i>Saturation Experiments</i>	48
4.2.5	<i>Temperature Desorption Experiments by XPS</i>	48
4.2.6	<i>Reactions on Hydrogenated CVD Diamond</i>	49
4.2.7	<i>Chlorinated CVD Diamond Reactions with Atomic Hydrogen</i>	49
4.3	Results	51
4.3.1	<i>XPS Survey Spectra</i>	51
4.3.2	<i>Adsorption of Chlorine on Diamond Films</i>	51
4.3.3	<i>Thermal Desorption of Chlorine on CVD Diamond</i>	57
4.3.4	<i>Hydrogen Etching of the Chlorinated Diamond Film</i>	60
4.4	Discussion	63
4.5	Conclusions and Future Work	74
4.6	References	76

CHAPTER V

REACTIONS OF $\text{CF}_3\text{CH}_2\text{SH}$ AND $\text{CF}_3\text{CH}_2\text{I}$ ON GaAs(100)		79
5.1	Introduction	79
5.1.1	<i>The Effect of the Co-Adsorbed Species on Alkyl Chemistry</i>	80

5.1.2	<i>Alkyl Reactions on Industrial Catalytic and Single Crystal Surfaces</i>	81
5.1.3	<i>Ziegler-Natta Catalysis and Olefin Insertion</i>	82
5.1.4	<i>Fischer-Tropsh synthesis, Methylene Insertion and Alkyl Termination</i>	83
5.1.5	<i>The Effect of Fluorine Substitution on the Alkyl Chemistry</i>	88
5.1.6	<i>Aims</i>	92
SECTION B		
	SURFACE REACTIONS OF 2,2,2-TRIFLUOROETHANETHIOL ON GaAs(100)	93
5.2	Results	93
5.2.1	<i>TPD Studies of 2,2,2-Trifluoroethanethiol</i>	93
5.2.2	<i>LEED and AES Studies</i>	100
5.2.3	<i>Uptake of TFET Observed Using XPS</i>	103
5.2.4	<i>Thermal Desorption of TFET Multi-Layers Studied Using XPS</i>	110
5.2.5	<i>Electron Irradiation of TFET Monitored by XPS</i>	114
5.3	Discussion	117
5.4	Conclusion	124
SECTION C		
	CF₃CH₂I ADSORPTION ON GaAs(100)	125
5.5	Results	125
5.5.1	<i>TPD Analysis of 1,1,1-Trifluoroethane Iodide</i>	125
5.5.2	<i>Adsorption of TFEI Monitored Using XPS</i>	129
5.5.3	<i>Thermal Desorption of TFEI Observed Using XPS</i>	132
5.6	Discussion	136

5.7	Conclusion	141
SECTION D		
	THE IMPORTANCE OF THE CO-ADSORBED SPECIES	142
5.8	References	144
 CHAPTER VI		
	XPS AND TPD STUDIES OF TiCl_4 ADSORPTION ON Pt(111)	147
6.1	Introduction	147
6.1.1	<i>Adsorption of Titanium Tetrachloride</i>	148
6.1.2	<i>Aims</i>	149
6.2	Results	151
6.2.1	<i>TPD Study of TiCl_4 on Pt(111)</i>	151
6.2.2	<i>XPS Thermal Desorption Studies</i>	157
6.3	Discussion	161
6.4	Conclusions	165
6.5	References	166

APPENDIX A

XPS DATA FOR Cl_2 ADSORPTION ON CVD DIAMOND	A1
--	-----------

APPENDIX B

ANALYSIS OF XPS DATA FOR TFET AND TFEI ON GaAs(100)	B1
B1 TPD Fragmentation Spectra	B1
B2 Mass Spectra of the Different Products Detected in Chapter 5	B3
B3 XPS Peak Fitting	B4
B4 Unshifted XPS Data	B10
B5 References	B23

APPENDIX C

ANALYSIS OF XPS DATA FOR TiCl_4 ON Pt(111)	C1
References	C3

LIST OF FIGURES

Fig.		pg #
2.1	A schematic representation of the four techniques described in this chapter and a summary of the information provided by each technique.	5
2.2	The “universal curve”: demonstrates the mean free paths for inelastic scattering of electrons in solids. ⁴	9
2.3	Energy level diagram for a. the XPS process and b. the emission of an Auger electron. ⁶	10
3.1	A schematic overview and photograph of the TPD chamber.	16
3.2	A photograph of the XPS chamber.	19
3.3	A schematic representation of a. the c(8x2) reconstructed GaAs(100) surface ⁵ and b. the LEED pattern for the (4x1) reconstruction of the GaAs(100) surface.	22
3.4	A model of a. the LEED pattern of Pt(111) and b. the Pt(111) surface.	23
3.5	A diagram of the TPD chamber depicting the sample set-up in detail when the platinum crystal is attached and a detailed illustration of GaAs(100) sample mount.	25
3.6	An illustration of the microcapillary array doser and mass spectrometer arrangement.	27
4.1	A schematic of the reactions during diamond thin film formation when using a CH ₄ /H ₂ precursor mixture.	35
4.2	A schematic of CVD diamond growth mechanism using a CX _y H _z /H ₂ mixture, where X = F or Cl.	37
4.3	Schematic of the sample mount.	45
4.4	Survey scan of the CVD diamond film after heating to 1270 K.	51
4.5	The XP spectra of Cl 2p region as a function of molecular chlorine exposure on CVD diamond at 298 K.	52
4.6	The peak area as a function of increasing chlorine exposure for the two different chemical states, state 1 (○) and state 2 (■).	53
4.7	The C 1s Region at 3 different periods during the experiment. 1. Clean surface, 2. diamond surface saturated with chlorine and 3. after annealing the surface to 1200 K. The insert shows the plasmon loss spectra of C 1s expanded.	54

4.8	A comparison of the uptake of chlorine on a pre-annealed surface (○) and a hydrogen-terminated surface (■) for state 1.	55
4.9	A comparison of the uptake of chlorine on an initially clean surface (○) and a hydrogenated surface (■) for state 2.	56
4.10	The thermal stability of the chlorine layer (Cl_2 exposure is 23 L at 298 K) on a pre-annealed diamond surface observed using the Cl 2p XPS region.	57
4.11	The Cl 2p peak area as a function of increasing temperature for the state 1 (○) and state 2 (■) on a pre-annealed diamond surface.	58
4.12	The Cl 2p peak area as a function of increasing temperature for the state 1 (○) and state 2 (■) on a hydrogen-terminated diamond surface.	59
4.13	The Cl 2p peak area as a function of increasing temperature for the analysis of the thermal stability of surface chlorine (23 L at 298 K) on the pre-annealed (○) and hydrogenated (■) diamond surface for state 2.	60
4.14	The thermal stability of the chlorine layer (23 L at 298 K) on the pre-annealed (○) and hydrogenated (■) diamond surface for state 1, studied using the Cl 2p XPS region.	60
4.15	The plot of the Cl 2p peak area as a function of hydrogen exposure time at four different pressures for state 1: $P_{\text{H}_2} = 10^{-7}$ mbar (□), 10^{-6} mbar (◇), 10^{-5} mbar (○) and 10^{-4} mbar (△).	61
4.16	The plot of the Cl 2p peak area as a function of hydrogen exposure time at two different pressures for state 2: $P_{\text{H}_2} = 10^{-7}$ mbar (□) and 10^{-6} mbar (◇).	62
4.17	The kinetic analysis of chlorine etched by atomic hydrogen ($P_{\text{H}_2} = 10^{-4}$ mbar) for both first and second order analysis. First order analysis (left axis) shows the plot of the log of the chlorine concentration [Cl] divided by the saturated coverage, $[\text{Cl}]_0$ as a function of hydrogen exposure time (□). Second order analysis (right axis) shows the plot of the saturated coverage, $[\text{Cl}]_0$ divided by the chlorine concentrate, [Cl] as a function of hydrogen exposure time [○].	70
4.18	The second order kinetic analysis of chlorine etched by atomic hydrogen at a H_2 pressure of 10^{-4} mbar [△], 10^{-5} mbar [◇] and 10^{-6} mbar [○]. Second order analysis was determined by plotting the saturated coverage, $[\text{Cl}]_0$ divided by the chlorine concentrate, [Cl] as a function of hydrogen exposure time.	71

5.1	The olefin insertion reaction observed in the Ziegler-Natta catalyst.	82
5.2	β -Hydride elimination of an alkyl group to generate an alkene - a proposed termination mechanism in the Fischer-Tropsch process. ⁷	85
5.3	Hydrogen reduction of an alkyl group to form an alkane – a proposed termination mechanism in the Fischer-Tropsch process. ⁷	85
5.4	The three possible transition states for the formation of ethene from ethyl species on a undefined surface. ¹⁷	86
5.5	The temperature programmed desorption (TPD) spectra of the uptake of TFET on GaAs (100) - (4x1) monitoring $m/z = 116$ amu ($\text{CF}_3\text{CH}_2\text{SH}$) at 300 K. The temperature ramp is 10 K s^{-1} .	94
5.6	The temperature programmed desorption (TPD) spectra monitoring the desorption of TFET ($m/z = 116$ amu) from GaAs (100) - (4x1) at 300 K and at a higher temperature of 390 K where the first state does not populate. The temperature ramp is 10 K s^{-1} .	94
5.7	The temperature programmed desorption (TPD) spectra of H_2 ($m/z = 2$ amu), CF_3 (69 amu) CF_3CH_3 ($m/z = 84$ amu) and CF_2CH_3 ($m/z = 65$ amu) monitored after adsorption of TFET on GaAs (100) - (4x1) at 300 K. The temperature ramp is 10 K s^{-1} .	95
5.8	The temperature programmed desorption (TPD) spectra monitoring desorption of CF_2CH_3 ($m/z = 65$ amu) and $\text{CF}_2\text{CH}_2\text{D}$ ($m/z = 66$ amu) from GaAs (100) - (4x1) observed after adsorption of 40 L of TFET on a clean (<i>i.e.</i> CF_2CH_3) surface and 100 L of TFET on a partially deuterated (<i>i.e.</i> $\text{CF}_2\text{CH}_2\text{D}$) surface at 300 K. The temperature rate is 10 K s^{-1} .	97
5.9	The TPD spectra of the uptake of TFET on GaAs (100) - (4x1) monitoring the desorption of $\text{CF}_2=\text{CH}_2$ ($m/z = 64$ amu) from GaAs (100) - (4x1) at 300 K. The temperature ramp is 10 K s^{-1} .	98
5.10	The TPD spectra of the uptake of TFET on GaAs (100) - (4x1) monitoring the coupling fragment ($m/z = 77$ amu) at 300 K. The temperature ramp is 10 K s^{-1} .	98
5.11	The TPD spectra of the uptake of TFET on GaAs (100) - (4x1) monitoring $m/z = 150$ amu (As_2) at 300 K. Between each experiments, the surface was heated to 710 K, instead of the usual annealing temperature of 770 K to prevent the reordering of the surface. The exposure values represent the overall exposure of TFET on the surface. The temperature ramp is 10 K s^{-1} .	100

5.12	The LEED pattern of the clean GaAs(100)-(4x1) surface. (Supplied from D. Doran honours thesis, although photos were taken of the LEED patterns in this study, poor exposure times resulted in underdeveloped pictures) ³⁵	101
5.13	(a) The AES spectra before and after adsorption of TFET (25 L) onto GaAs(100) – (4x1) and (b) the AES peak area of S (165 eV) divided by the peak area of Ga (57 eV) and plotted as a function of TFET exposure.	102
5.14	The thermal stability of TFET (20 L at 300 K) on GaAs(100) – (4x1) monitored using AES.	103
5.15	The XPS spectra of the C 1s region as a function of TFET exposure on GaAs(100) – (4x1) at 111 K. — spectra are referenced either to the Ga 3d peak at 19.5 eV (0 – 20 L) or C[F] 293.0 eV peak (30 – 80 L).	104
5.16	The XPS spectra of the S 2p region as a function of TFET exposure on GaAs(100) – (4x1) at 111 K. — spectra are referenced either to the Ga 3d peak at 19.5 eV (0 – 20 L) or C[F] 293.0 eV peak (30 – 80 L).	106
5.17	The uptake of TFET on GaAs(100) – (4x1) monitored using the F 1s XPS region at 111 K. — spectra are referenced either to the Ga 3d peak at 19.5 eV (0 – 20 L) or C[F] 293.0 eV peak (30 – 80 L).	108
5.18	The XPS spectra of the As and Ga 3d region as a function of TFET uptake on GaAs(100) – (4x1) at 111 K. The difference between the As and Ga 3d peaks is included in parentheses. — spectra are referenced either to the Ga 3d peak at 19.5 eV (0 – 20 L) or C[F] 293.0 eV peak (30 – 80 L).	109
5.19	The thermal stability of TFET (100 L at 111 K) while monitoring the C 1s XPS region. — spectra are referenced to the C[F] 293.0 eV peak (111 & 165 K). — spectra remain unshifted (213 – 323 K).	110
5.20	The thermal stability of TFET multi-layers (100 L at 111 K) while monitoring the S 2p XPS region. — spectra are referenced to the C[F] 293.0 eV peak (111 & 165 K). — spectra are unshifted (213 – 774 K)	111
5.21	Monitoring of S 2p and Ga 3s XPS region for the clean GaAs (100) – (4x1) surface and a surface treated with three cycles of 100 L exposure of TFET followed by annealing to 670 K to deposit a layer of sulphur.	111
5.22	The thermal stability of TFET (100 L at 111 K) while monitoring the F 1s XPS region. — spectra are referenced to the C[F] 293.0 eV peak (111 & 165 K). — spectra remain unshifted (213 – 573 K)	113

5.23	The thermal stability of TFET multi-layers (100 L at 111 K) while monitoring the As and Ga 3d XPS region. The difference between the As and Ga 3d peaks is included in parentheses. — spectra are referenced to the C[F] 293.0 eV peak (111 & 165 K). — spectra are unshifted (213 – 774 K).	114
5.24	The XPS of the thermal stability of TFET (100 L at 105 K) on GaAs(100) – (4x1) after electron irradiating the surface for 10 minutes while observing (a) the C 1s region, (b) the S 2p region and (c) the F 1s region. — spectra are referenced to the C[F] 293.0 eV peak (107 K, e-beamed & 273 K). — spectra are unshifted (371 – 751 K).	115
5.25	The reaction scheme of TFET adsorption on GaAs (100)-(4x1).	117
5.26	The TPD spectra of the molecular ion, $\text{CF}_3\text{CH}_2\text{I}$ ($m/z=210$) as a function of TFEI exposure on GaAs(100) – (4x1) at 100 K. The temperature ramp is 10 K s^{-1} .	125
5.27	The TPD spectra of the uptake of TFEI on GaAs(100) – (4x1) monitoring $\text{CF}_2=\text{CH}_2$ ($m/z = 64$) at 300 K. The temperature rate is 10 K s^{-1} .	126
5.28	The TPD spectra of the uptake of TFEI on GaAs(100) – (4x1) monitoring As_2 ($m/z=150$). Between each experiment, the surface was heated to 710 K, instead of the usual annealing temperature of 770 K to allow the accumulation of etch species on the surface. The exposures represent the overall amount of TFEI used. The temperature ramp is 10 K s^{-1} .	128
5.29	The uptake of TFEI on GaAs(100) – (4x1) monitoring the C 1s XPS region. All spectra are referenced to either the Ga 3d peak at 19.5 eV (0 – 10 L) or C[F] 293.0 eV peak (40 - 200 L).	129
5.30	The XPS spectra of TFEI on GaAs(100) – (4x1) monitoring the F 1s region. All spectra are referenced to either the Ga 3d peak at 19.5 eV (0 – 30 L) or C[F] 293.0 eV peak (40 - 200 L).	130
5.31	XPS study of TFEI on GaAs(100) – (4x1) monitoring the I 3d region. All spectra are referenced to either the Ga 3d peak at 19.5 eV (0 – 30 L) or C[F] 293.0 eV peak (40 - 200 L).	131
5.32	The XPS study of the uptake of TFEI on GaAs(100) monitoring the Ga and As 3d regions. The difference between the As and Ga 3d peaks is included in parentheses. All spectra are referenced to either the Ga peak 3d at 19.5 eV (0 – 30 L) or C[F] 293.0 eV peak (40 - 200 L).	132

5.33	The thermal stability of TFEI (100 L at 107 K) on GaAs(100) – (4x1) monitored using the C 1s XPS region. The spectra are left unshifted.	133
5.34	The thermal desorption study of TFEI (100 L at 107 K) on GaAs(100) – (4x1) observed using the F 1s XPS region as a function of substrate temperature. The spectra remain unshifted.	133
5.35	The XPS spectra of the I 3d region monitoring the thermal stability of TFEI (100 L at 107 K) on GaAs(100) – (4x1). The spectra remain unshifted.	134
5.36	The thermal stability of TFEI (100 L at 107 K) on GaAs(100) – (4x1) monitoring the Ga and As 3d XPS region. The difference between the As and Ga 3d peaks is included in parentheses. The spectra remain unshifted.	135
5.37	The reaction mechanism for TFEI adsorbed on GaAs(100) – (4x1).	136
6.1	The TPD spectra of the adsorption of TiCl_4 on Pt(111) whilst monitoring Ti ($m/z = 48$) for 1 L and TiCl ($m/z = 93$), TiCl_2 ($m/z = 118$), TiCl_3 ($m/z = 153$), and TiCl_4 ($m/z = 188$) for 4 L at 130 K. The surface was heated to 196 K before each TPD experiment to remove the physisorption peak with the exception of the TiCl_4 where it is included for clarity. Heating rate is 10 K s^{-1} .	151
6.2	The TPD spectra of the uptake of TiCl_4 on Pt(111) whilst monitoring TiCl ($m/z = 93$). The surface was heated to 196 K before each TPD experiment to remove the physisorption peak. Heating rate is 10 K s^{-1} .	152
6.3	The TPD spectra of Ti ($m/z = 48$) monitored after the adsorption of TiCl_4 on Pt(111) at 130 K followed by heating to 196 K to remove the physisorption peak. Heating ramp is 10 K s^{-1} .	153
6.4	The TPD spectra of TiCl_4 adsorbed on Pt(111) at an elevated temperature of 300 K whilst monitoring Ti ($m/z = 48$). Heating rate is 10 K s^{-1} .	154
6.5	The TPD spectra of the uptake of TiCl_4 on Pt(111) monitoring Cl_2 ($m/z = 70$) at 130 K. Heating ramp is 10 K s^{-1} .	155
6.6	The uptake of TiCl_4 on Pt(111) at 150 K monitoring Cl ($m/z = 35$) using TPD spectroscopy. Heating rate is 10 K s^{-1} .	155
6.7	The thermal stability of a multi-layer coverage of titanium tetrachloride (100 L at 113 K) observed using the Pt 4f XPS region. Spectra are referenced to the Pt $4f_{5/2}$ peak at 71.0 eV.	157

6.8	The thermal desorption study of TiCl_4 (100 L at 113 K) on Pt(111) monitoring the Ti 2p XPS region as a function of temperature with the line indicating the positions of the TiCl_4 and TiCl_3 species. Spectra are referenced to the Pt $4f_{5/2}$ peak at 71.0 eV.	158
6.9	The total XPS Ti [O] signal for the XPS thermal desorption experiments plotted as a function of temperature.	159
6.10	The thermal stability of TiCl_4 (100 L at 113 K) on Pt(111) observed using the Cl 2p XPS region.	159
6.11	The total Cl XPS [O] signal for the XPS thermal desorption experiments plotted as a function of temperature.	160
6.12	The thickness of the TiCl_4 layer as a function of temperature.	160
6.13	Reaction scheme proposed for titanium tetrachloride adsorption on Pt(111).	161
A1	The Cl 2p XPS spectra monitoring the uptake of molecular chlorine on CVD diamond surface.	A1
A2	The uptake of Cl_2 on a hydrogen-terminated ($P_{\text{H}_2} = 1.0 \times 10^{-4}$ for 20 minutes) CVD diamond surface observed using the Cl 2p XPS region.	A1
A3	The thermal stability of a saturated chlorinated diamond surface (Cl_2 exposure is 23 L at 298 K) monitored using the Cl 2p XPS region.	A2
A4	The thermal desorption of chlorine (Cl_2 exposure is 23 L at 298 K) from a hydrogen-terminated CVD diamond surface ($P_{\text{H}_2} = 1.0 \times 10^{-4}$ for 20 minutes) observed using the Cl 2p XPS region.	A2
A5	The etching of the chlorine layer (Cl_2 exposure is 23 L at 298 K) on CVD diamond as a function of atomic hydrogen exposure time using a constant H_2 pressure of 1.0×10^{-7} mbar and monitoring the Cl 2p XPS region.	A3
A6	The Cl 2p XPS spectra showing the saturation chlorine layer (Cl_2 exposure is 27 L at 298 K) as it is exposed to atomic hydrogen ($P_{\text{H}_2} = 1.0 \times 10^{-6}$ mbar) for the periods indicated.	A3
A7	Etching of the chlorine coverage (Cl_2 exposure is 23 L at 298 K) on CVD diamond by atomic hydrogen ($P_{\text{H}_2} = 1.0 \times 10^{-5}$ mbar) for the times indicated and observed using the Cl 2p XPS region.	A4
A8	Cl 2p XPS spectra for surface chlorine (Cl_2 exposure is 30 L at 298 K) on CVD diamond after it is exposed to atomic hydrogen ($P_{\text{H}_2} = 1.0 \times 10^{-4}$ mbar) for the times indicated.	A4

B1	The TPD spectra of the uptake of TFET on GaAs (100) - (4x1) monitoring $m/z = 47$ amu (CH_2SH), a fragment of the parent ion $\text{CF}_3\text{CH}_2\text{SH}$ at 300 K. The temperature ramp is 10 K s^{-1} .	B1
B2	The TPD spectra of the uptake of TFET on GaAs (100) - (4x1) monitoring $m/z = 45$ and 31 amu, fragments of the parent ion $\text{CF}_2=\text{CH}_2$. The temperature ramp is 15 K s^{-1} . There is a slight discrepancy between the T_{max} from Figure 5.9 (500 K) and one's above (475 K) which may due may factors such as a different GaAs sample, heating rate and/or position of the thermocouple. This is confirmed when compared to the spectrum of $\text{CF}_2=\text{CH}_2$ using the same conditions. Regardless, all three spectra are consistent in peak shape and T_{max} , confirming that 45 and 31 are fragments of $\text{CF}_2=\text{CH}_2$.	B2
B3	Literature mass spectrum of 1,1,1-difluoroethene. ²	B3
B4	Literature mass spectrum of 1,1,1-trifluoroethane. ²	B3
B5	Literature mass spectrum of 1,1,1-trifluoro-2-iodoethane. ²	B4
B6	The Ga and As 3d XPS regions (a) before and (b) after internally referencing the peaks to Ga 3d (19.5 eV).	B8
B7	The XPS spectra of the As and Ga 3d regions as a function of TFET exposure on GaAs(100) – (4x1) at 111 K.	B10
B8	The uptake of TFET on GaAs(100) – (4x1) at 111 K monitored using the C 1s XPS region.	B11
B9	The F 1s XPS region as a function of TFET exposure on GaAs(100) – (4x1) at 111 K.	B11
B10	The uptake of TFET on GaAs(100) – (4x1) at 111 K observed using the S 2p XPS region.	B12
B11	The thermal stability of TFET (100 L at 111 K) on GaAs(100) – (4x1) monitored using the As and Ga 3d XPS region.	B12
B12	The XPS spectra of the C 1s region observing the thermal stability of TFET layer (100 L at 111 K) on GaAs(100) – (4x1).	B13
B13	The thermal stability of TFET (100 L at 111 K) on GaAs(100) – (4x1) observed using the F 1s XPS region.	B13
B14	The S 2p XPS region monitoring the thermal stability of TFET layer (100 L at 111 K) on GaAs(100) – (4x1).	B14

B15	Monitoring of the As and Ga 3d XPS spectra for the thermal stability of TFET (100 L at 105 K) on GaAs(100) – (4x1) after electron irradiation of the surface for 10 minutes.	B14
B16	The thermal stability of TFET (100 L at 105 L) on GaAs(100) – (4x1) after electron irradiating the surface for 10 minutes, observed using the C 1s XPS region.	B15
B17	The F 1s XPS spectra monitoring the thermal stability of the TFET layer (100 L at 105 K) on GaAs(100) – (4x1) after electron irradiation for 10 minutes.	B15
B18	The thermal stability of TFET (100 L at 105 L) on GaAs(100) – (4x1) after electron irradiating the surface for 10 minutes, monitored using the S 2p XPS region.	B16
B19	The XPS spectra of the As and Ga 3d regions as a function of TFEI exposure on GaAs(100) – (4x1) at 123 K. Note: The absence of some lines in the I 2p peak. There was a spike that occurred at the missing values. Instead of replacing the points, the points were removed and have no bearing on the results since I 3d peaks showed no such spike and iodide analysis is based on the I 3d rather than the I 2p peaks.	B16
B20	The C 1s XPS region as a function of TFEI exposure on GaAs(100) – (4x1) at 123 K.	B17
B21	The uptake of TFEI on GaAs(100) – (4x1) monitored using the F 1s XPS region at 123 K.	B17
B22	The XPS spectra of the I 3d region as a function of TFEI exposure on GaAs(100) – (4x1) at 123 K.	B18
B23	The XPS spectra of the Ga and As 3d regions observing the thermal stability of TFEI (100 L at 107 K) on GaAs(100) – (4x1).	B18
B24	The thermal stability of TFEI (100 L at 107 K) on GaAs(100) – (4x1) observed using the C 1s XPS region.	B19
B25	The F 1s XPS spectra monitoring the thermal stability of TFEI (100 L at 107 K) on GaAs(100) – (4x1).	B19
B26	The thermal stability of TFEI (100 L at 107 K) on GaAs(100) – (4x1) monitored using the C 1s XPS region.	B20
C1	The XPS spectrum of the Pt 4f region as a function of temperature after exposing a Pt(111) surface with titanium tetrachloride (100 L at 113 K).	C2
C2	The thermal stability of titanium tetrachloride layer (100 L at 113 K) adsorbed on Pt(111) monitored using the Ti 2p XPS region.	C2

C3	Monitoring of the Cl 2p XPS region as a function of temperature after exposing the Pt(111) surface with titanium tetrachloride (100 L at 113 K).	C3
-----------	--	----

LIST OF TABLES

Table		Pg #
B1	Peak fitting parameters for the XPS analysis of the Ga 3d, As 3d, C 1s, F 1s and S 2p regions.	B9
B2	The XPS values for the Ga 3d, As 3d, C 1s, F 1s and S 2p regions as a function of TFET coverage	B21
B3	The XPS values for the Ga 3d, As 3d, C 1s, F 1s and I 3d regions as a function of TFEI coverage	B22
C1	Peak fitting parameters for XPS analysis of the Pt 4f and Ti 2p regions.	C1

ACRONYMS

AES	Auger Electron Spectroscopy
amu	atomic mass unit
BE	Binding Energy
C[F]	fluorinated carbon in the C 1s region (XPS)
C[H]	hydrogenated carbon in the C 1s region (XPS)
CF 70	Conflat Flange with an outer diameter of 70 mm
CVD	Chemical Vapour Deposition
FAT	Fixed Analyser Transmission
FWHM	Full Width Half Maximum
HPHT	High-Pressure and High-Temperature
IC	Integrated Circuits
KE	Kinetic Energy
LEED	Low Energy Electron Spectroscopy
ML	Monolayer
MS	Mass Spectrometer
PVD	Physical Vapour Deposition
RFA	Retarding Field Analyser
S.O.S.	Separation of State
SS	Stainless Steel
TDS	Thermal Desorption Spectroscopy
TFEI	1,1,1-trifluoroethyl iodide
TFET	2,2,2-trifluoroethanethiol
TPD	Temperature Programmed Desorption
UHV	Ultra-High Vacuum

XPS

X-ray Photoelectron Spectroscopy

LIST OF PUBLICATIONS

1. Donev, S.; Brack, N.; Paris, N. J., Pigram, P. J., Singh, N. K.; Usher, B. F. *Surface Reactions of 1-Propanethiol on GaAs(100)*. **Langmuir (In press)**
2. Singh, N. K.; Kemp, N. T.; Paris, N.; Balak, V. *Coupling Reaction of trifluoroethyl iodide on GaAs(100)*. **Journal of Vacuum Science & Technology A (2004), 22(4), 1659-1666**
3. Proffitt, S.; Thompson, C. H. B.; Gutierrez-Sosa, A.; Paris, N.; Singh, N. K.; Jackman, R. B.; Foord, J. S. *Understanding the chemistry of low temperature diamond growth: an investigation into the interaction of chlorine and atomic hydrogen at CVD diamond surfaces*. **Diamond and Related Materials (2000), 9(3-6), 246-250.**
4. Paris, N.; Singh, N. *Surface studies of Cl₂ chemisorption on CVD diamond*. **Proceedings - Australian Conference on Nuclear Techniques of Analysis (1999), 11th 51-54.**

CHAPTER I

INTRODUCTION

1.1 Background Information

Surface studies of model systems under UHV conditions are used by surface scientists to mimic industrial processes such as catalysis and chemical vapour deposition (CVD) and hence improve the activity of a catalyst or the quality of deposited films. These processes involve gaseous vapours interacting with a surface to grow solid-state advanced material or to form industrially important products by catalysis. Industrial conditions generate intermediates with short life spans and low concentrations, making spectroscopic identification difficult.¹ Hence, the mechanisms and problems associated with the growth and reactions that occur for either process can be elucidated by surface studies carried out under ultra-high vacuum conditions using single crystal surfaces.

Single crystal surfaces are well-defined and reactions of precursors on these surfaces can lead to the elucidation of elementary reaction steps. This information can be used to determine the deposition temperature, reaction pathways, competing pathways and overall reaction mechanisms. The mechanisms this elucidates can be used to identify problems that may exist in industrial processes, for example, low growth rates in diamond deposition or incorporation of undesirable reactive species in the growing films, leading to corrosion of surface layers. In the case of catalysis, the reaction mechanisms could account for reaction product distribution, selectivity and the conversion rates of reactants to products.

A combination of several techniques such as X-ray Photoelectron Spectroscopy (XPS), Temperature Programmed Desorption (TPD), Auger Electron Spectroscopy (AES) and Low Energy Electron Spectroscopy (LEED) provides a complete picture of the adsorption and decomposition pathways of a precursor.

1.2 Objectives and Issues

The work presented in this thesis aims to widen the understanding of the role that halogens play in a number of systems by studying precursors on three different surfaces: GaAs(100), Pt(111) and CVD diamond thin films on Si(100). These studies undertaken in a controlled environment provide chemical information that can model catalytic activity or CVD growth. This fundamental knowledge may then be applied to the improvement of industrial processes.

Halogens have been reported to lower the growth of diamond thin films yet there are few reports on the mechanism. Previously, extensive studies have been undertaken on chlorine reacting with natural diamond (C(100) and C(111))^{2, 3, 4}. However, no studies have previously involved the co-adsorption of chlorine and atomic hydrogen on CVD diamond and used the reaction mechanism to propose methods to lower the growth temperature of diamond. The mobility of atomic hydrogen and chlorine is important in facilitating diamond growth at low temperatures. Therefore, to successfully investigate the role that chlorine plays in lowering the growth temperature of diamond, studies involving adsorption of chlorine on CVD diamond are required.

Alkyl surface chemistry has implications in the catalysis of alkyl groups in such reactions as the Fischer-Tropsch synthesis and Ziegler-Natta catalysed polymerisation. Much of the alkyl chemistry is well known on single crystal metal

surfaces with β -hydride elimination, hydrogen and alkyl reduction observed for numerous alkyl species. Possible further stages in the investigation of alkyl chemistry may include reactions on modified surfaces to emulate different catalysts or substitution of the α - or β -position. Substitution at the β -position provides information about the termination steps which in industrial catalysis usually occur at either the α - or β -position. Fluorine substitution at these positions is reported to affect the activation barrier of some products differently to unsubstituted alkyl species which can be used to further understand alkyl reactivity.⁵ The presence of different co-adsorbed species is also studied in relation to catalytic activity as the alkyl chemistry can be altered with poisoning occurring at high coverage. For example, sulphur poisoning is problematic in industry, reducing the activity of catalysts and lowering the lifetime of these catalysts. Hence, $\text{CF}_3\text{CH}_2\text{SH}$ and $\text{CF}_3\text{CH}_2\text{I}$ have been studied to further understand surface activated alkyl chemistry and the effect of the co-adsorbed species on this chemistry.

New plasma assisted CVD techniques mean lower growth temperatures are possible using TiCl_4 . Unfortunately chlorine incorporation is problematic. Few studies have been undertaken to elucidate how chlorine incorporation occurs during titanium deposition. This research is the initial step towards understanding the interaction of TiCl_4 on surfaces by studying the adsorption of TiCl_4 on $\text{Pt}(111)$.

1.3 Thesis Outline

This thesis is divided into seven chapters with Chapter 1 containing a brief introduction.

Chapters 2 and 3 provide the theory behind the spectroscopic techniques used in the elucidation of reaction mechanisms and instrumentation used to conduct such studies.

Chapters 4 to 6 are devoted to results and discussion. Chapter 4 explores the reaction of Cl_2 on CVD grown diamond surface and the implication that chlorine and in general halogens may play in the lowering of substrate temperatures during CVD deposition. Chapter 5 details the study of the reactions of trifluoroethyl species (CF_3CH_2^-) on GaAs(100). This alkyl group is derived from two different precursors, $\text{CF}_3\text{CH}_2\text{SH}$ and $\text{CF}_3\text{CH}_2\text{I}$. The research in essence provides the effect of co-adsorbed sulphur and iodine on the surface reactions of CF_3CH_2^- species. Chapter 6 investigates the decomposition of TiCl_4 on a Pt(111) surface.

There are three appendices which contain descriptions of the XPS analysis and spectra that were omitted from the main text.

1.4 References

1. B. E. Bent, *Chem. Rev.*, **96**, (1996), 1361
2. A. Freedman, *J. Appl. Phys.*, **75**, (1994), 3112
3. Hadenfeldt, S; Benndorf, C, *Surf. Sci.*, **404** (1998), 227
4. T. Ando, K. Yamamoto, S. Suehara, M. Kamo, Y. Sato, S. Shimosaki, M. Nishitani-Gamo, *J. Chin. Chem. Soc.*, **42**, 285
5. J. G. Forbes, A. J. Gellman, *J. Am. Chem. Soc.*, **115**, (1993), 6277

CHAPTER II

EXPERIMENTAL THEORY

This chapter provides a brief discussion of the theories underlying the surface science techniques used in this investigation. The techniques are: Temperature Programmed Desorption (TPD), X-ray Photoelectron Spectroscopy (XPS), Auger Electron Spectroscopy (AES), and Low Energy Electron Diffraction (LEED). Figure 2.1 shows the schematic of each technique, in particular the 'probe' and the analysed particle in each technique.

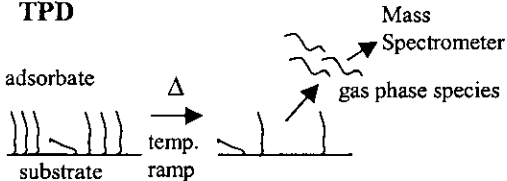
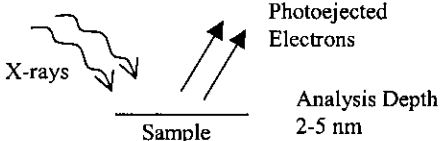
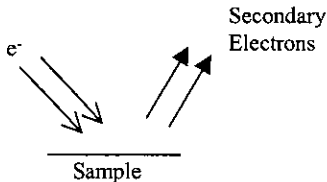
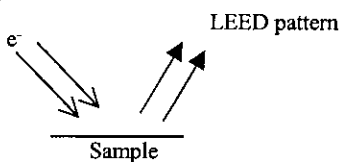
Information Provided	
TPD 	• Nature of binding states • Relative population of binding states • Activation energy • Reaction order
XPS 	• Semi-quantitative • Elemental identification • Chemical information (<i>i.e.</i> oxidation state, lattice sites, molecular environment, <i>etc.</i>) by use of chemical shifts in photoemission peaks
AES 	• Elemental information • Some chemical information • Used to monitor surface cleanliness
LEED 	• Surface structure • Used to monitor surface cleanliness

Figure 2.1 A schematic representation of the four techniques described in this chapter and a summary of the information provided by each technique.

2.1 Temperature Programmed Desorption (TPD)

Temperature Programmed Desorption is used to investigate the nature and population of the binding states of the adsorbed layers on a substrate and the activation energy and reaction order of the desorbing process.¹

Bonding of the adsorbate to the surface can be divided into two general classes:

- Physisorption – where the adsorbate is bonded to the surface by weak van der Waals forces of energy $< 40 \text{ kJ mol}^{-1}$ and
- Chemisorption – where the adsorbate is bonded more strongly ($> 40 \text{ kJ mol}^{-1}$) to the surface as a result of a chemical interaction.

If a temperature ramp is applied to the substrate then the surface adsorbates will desorb from the surface *via* an activated process. Whereas the adsorption process would have been a non-activated process. During desorption, the adsorbed species are lifted from the bottom of the physisorption or chemisorption potential energy wells.

The desorption rate of a species from the surface is given by the Polanyi-Wigner equation:

$$-dN/dT = \nu_n N^n \exp(-E_d/RT)$$

where:

n is the reaction order

N is the surface coverage of the species in question

ν is the pre-exponential factor

R is the gas constant

T is the temperature (K)

E_d is the activation energy of desorption of the species (kJ mol^{-1})

For $n = 1$, $E_d/RT_{\max}^2 = (\nu_1/\beta) \exp(-E_d/RT_{\max})$

For $n = 2$, $E_d/RT_{\max}^2 = (N_0\nu_2/\beta) \exp(-E_d/RT_{\max})$ where N_0 is the initial coverage, β is the heating rate (K s^{-1}) and $T_{\max}$ is the temperature at the peak maximum in a TPD spectrum plotted as intensity versus substrate temperature.

Based on these equations, the kinetic order can be determined by monitoring the TPD spectra as a function of increasing coverage of an adsorbate.¹ A first order reaction with a fixed activation energy is characterised by a peak-maximum that does not shift as a function of surface coverage. Alternatively, if the peak-maximum decreases with increasing exposure for a fixed activation energy then the reaction kinetics relating to the desorption process may be second order. This second scenario can also be related to repulsive interactions amongst adsorbed species.

It has been shown by Redhead¹ that the activation energy can be related to the temperature at the peak maximum by the following equation:

$$E_d/RT_{\max} = \ln(\nu_1 T_{\max} / \beta) - 3.64$$

where:

$T_{\max}$ is the temperature at which the desorption rate is a maximum

ν_1 is the pre-exponential factor, 10^{13} s^{-1} (the order of the atomic vibrational frequency of the crystal lattice)

β is the heating rate (K s^{-1})

This approximation only holds true if the pumping speed is much greater than the adsorbate desorption rate.² The activation energy is calculated using this equation to estimate the bond energy of an adsorbed layer with the substrate since adsorption is not an activated process. The activation energy obtained using TPD spectroscopy relates directly to the desorption energy. As a guide, an E_d value of 40 kJ mol⁻¹ or greater is indicative of chemisorbed species and anything below this value is generally assigned as physisorbed species.

Applying a temperature ramp induces reactions of the adsorbed species, either reactions of the adsorbate with the surface or within itself and for this reason the experimental process has sometimes been referred to as temperature programmed reaction spectroscopy. In our research we have used this heating and simultaneous monitoring of the reaction products by a mass spectrometer to study the surface chemistry of the molecule of interest. The technique fulfils the requirement that an activation energy be supplied before any reaction or dissociation can occur.

We have used TPD in combination with XPS to provide an accurate assessment of the behaviour of a molecule adsorbed onto a substrate.

2.2 Surface Spectroscopic Techniques and Surface Specificity

In this research two electron spectroscopic techniques were used to provide information on elemental compositions of adsorbed layers, the changing nature of these layers and the surface stoichiometry of GaAs(100) as the substrate was heated. These spectroscopies provide information about the nature of the adsorbed species on the surface because they only detect the first few layers on the surface. Hence, the effect of electron irradiation, temperature and

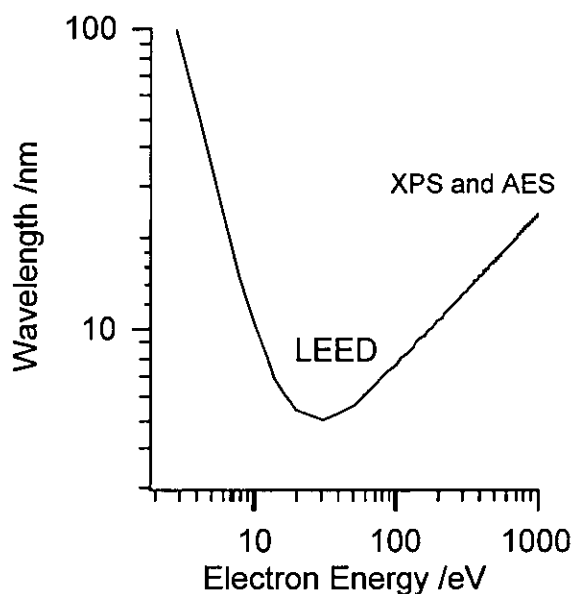


Figure 2.2 The “universal curve”: demonstrates the mean free paths for inelastic scattering of electrons in solids as a function of electron energy.⁴

coverage on the adsorbate and substrate states can be studied. The mean free path of electrons in a solid is important for electron spectroscopy as this property determines if an electron can escape from the surface and subsequently be detected. The mean free path is dependent on the kinetic energy of the emitted electrons from the surface. According to Figure 2.2, emerging electrons with KE in the 10

– 1000 eV range have a mean free path of a few atomic layers.³ Therefore, techniques such as X-ray Photoelectron Spectroscopy, Auger Electron Spectroscopy and Low Energy Electron Diffraction, which detect electrons in the 100 – 1000 eV KE range, can provide invaluable information on the chemistry in the surface layers.

2.2.1 X-ray Photoelectron Spectroscopy (XPS)

XPS is a surface analytical technique that is useful for the identification and quantification of surface states. The technique consists of analysing the energy of the emitted electrons generated by X-rays of fixed photon energy incident on a surface. The photoemissions arise following ionisation of electrons from the bound states in a solid as shown in Figure 2.3 (a). The kinetic energy of these electrons is given by the equation⁵:

$$KE = h\nu - BE - \phi_s$$

where: $h\nu$ is the energy of the incident X-ray photon

BE is the binding energy of the level from where the electron originated

ϕ_s is the work function of the spectrometer

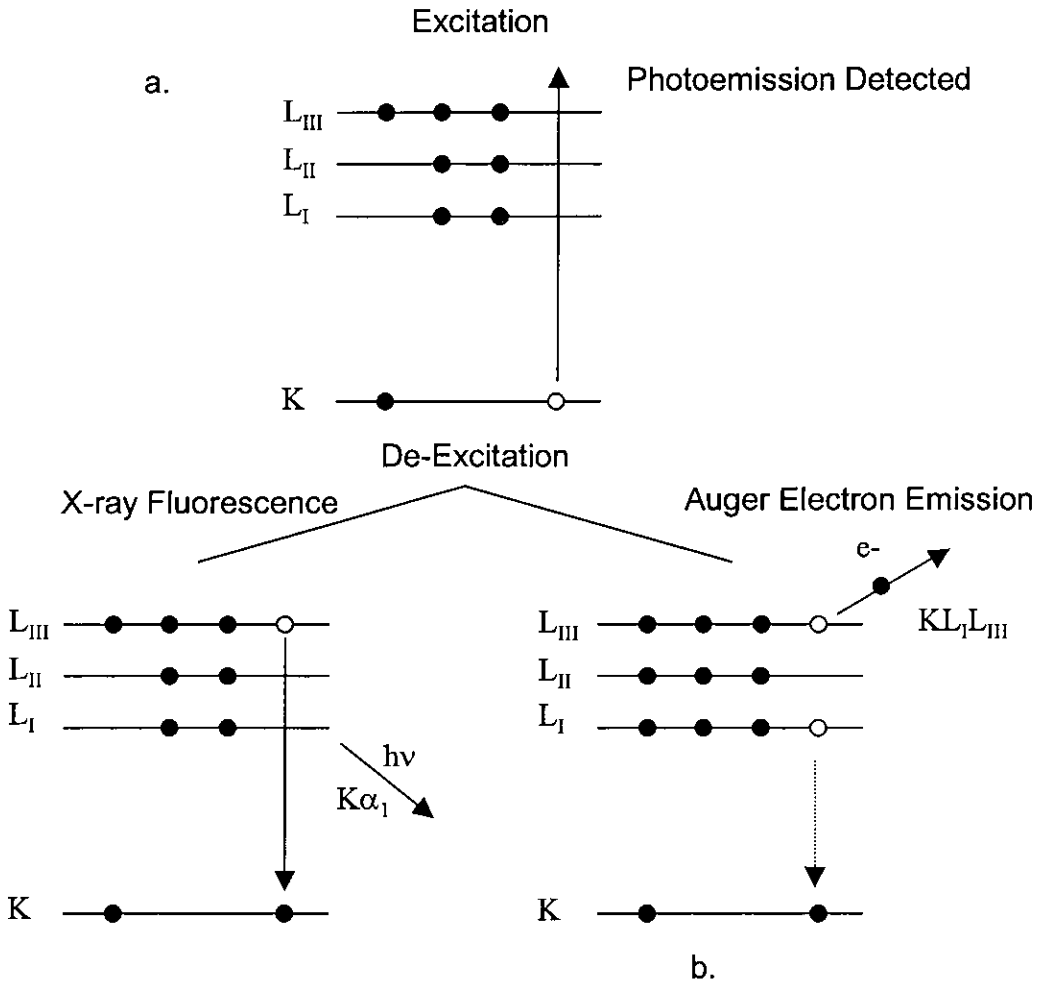


Figure 2.3 Energy level diagram for **a.** the XPS process and **b.** the emission of an Auger electron.⁶

Since the work function remains approximately constant, the equation can be simplified to:

$$KE = h\nu - BE$$

Note that the binding energy is the ionisation energy for the atom in the solid.

The source used to generate X-rays for XPS consists of a filament, anodes (normally solid metal targets, e.g. Al or Mg) and an aluminium window (to prevent stray electrons from passing into the UHV chamber). High-energy (10-15 keV) electrons are accelerated towards the anode causing ionisation in the core (K) levels. The anode emits a characteristic X-ray spectrum when electrons from a lower energy level fill core holes created by the high-energy electron beam as depicted in Figure 2.3 (a). The spectrum consists of characteristic emission lines that are specific to the particular metal anode used. The anodes most commonly used in XPS are either Mg $K_{\alpha 1,2}$ ($h\nu = 1253.6$ eV) or Al $K_{\alpha 1,2}$ ($h\nu = 1486.6$ eV).

An unresolved $K_{\alpha 1,2}$ doublet usually dominates the emission spectrum. This doublet is related to the decay process from $2p_{1/2} \rightarrow 1s$ and $2p_{3/2} \rightarrow 1s$.

Other emission lines are also present in the spectrum, e.g. $K_{\alpha 3,4}$, and can lead to the production of "satellite photoemission peaks" in the XPS spectrum because they are at a slightly different energy (~ 10 eV) to the dominant $K_{\alpha 1,2}$ emission. Hence, one needs to be careful in the assignment of photoemission peaks when using conventional non-monochromatic laboratory sources.

2.2.2 Chemical Information from XPS

One of the important features of XPS is that the analysis of the data can be semi-quantitative. The peak height or area can be measured for the photoemission feature and this value can be related directly to the amount of

that species present on the surface. By keeping all of the spectrometer conditions constant, the change in elemental populations can be investigated as a function of substrate temperature or exposure.

The positions of the photoemission peaks can be related directly to the energy of the electron being excited from a core level. Thus, changes in the chemical environment of an element results in changes in the peak position of that element in the XP spectrum. Shifts in binding energy can therefore be used to monitor surface decomposition reactions, chemical reactions involving adsorbed species and reactions between adsorbed species and reactive gases such as oxygen.

2.2.3 Auger Electron Spectroscopy (AES)

When an atom on a surface is ionised by the ejection of a core electron, it can return to the ground state by an alternative route to that observed in XPS (see section 2.2.2). In the AES process, an electron from a higher energy level fills the core vacancy with the available energy transmitted in a radiationless process to another electron, which is subsequently ejected from the atom with a characteristic kinetic energy. This ejection of the secondary electron is called the Auger process (Figure 2.3 (b)). Whilst this figure shows the creation of the core level by X-rays, most AES instrumentation uses an electron gun to ionise the core electrons.

The kinetic energy of the Auger electron is characteristic of the energy levels of the atom and is independent of the energy of the incident electrons or exciting radiation. The electronic transitions from these levels, K, L_I, L_{II} are shown in Figure 2.3 (b). However, the Auger process can also occur with both electrons

derived from the same level but from a different subshell, or either one or both of the valence levels. Therefore, to distinguish between these possibilities a nomenclature has been devised that designates the levels from which the three electrons originate. As an example Figure 2.3 (b) schematically shows a core electron being ejected from the 1s orbital (K level) and an electron decaying from the 2s orbital (L_1 level) to the 1s orbital. The Auger electron is ejected from the $2p_{3/2}$ orbital (L_3 level) and is described as a KL_1L_3 Auger electron. Its kinetic energy will be:

$$KE_{KL_1L_3} \sim E_K - E_{L_1} - E_{L_3}$$

2.2.4 Low Energy Electron Diffraction (LEED)

LEED is an electron diffraction technique, which can be used to determine the surface structure. This technique is used to measure the diffraction of electrons from the surface of a solid to produce a two dimensional structure of that surface.⁷ Electrons (20-200 eV) are diffracted from the surface following the principles of Bragg's law and electron diffraction generates spots on a luminescent screen. The LEED pattern is not a real space representation of the surface, as observed by Scanning Tunnelling Microscopy, but the reciprocal space image of the surface. Analysis of the LEED pattern in terms of the size of the unit mesh can provide information on the surface structure.

2.3 References

1. P. Redhead, *Vacuum*, **12**, (1962), 203
2. D. Woodruff, T. Delchar, *Modern Techniques of Surface Science – Second Edition*, Cambridge University Press, Cambridge, UK, (1994), 184
3. G. Ertl, J. Kupperts, *Low Energy Electrons and Surface Chemistry*, Deutsche Bibliothek Cataloging-in-Publication Data, Weinheim, Germany, (1984), 6
4. R. Park, *Methods of Experimental Physics* (R. Cellotta, J. Levine eds) **22**, Academic Press Inc., Orlando, USA, (1985), 198
5. G. Ertl, J. Kupperts, *Low Energy Electrons and Surface Chemistry*, Deutsche Bibliothek Cataloging-in-Publication Data, Weinheim, Germany, (1984), 68
6. G. Ertl, J. Kupperts, *Low Energy Electrons and Surface Chemistry*, Deutsche Bibliothek Cataloging-in-Publication Data, Weinheim, Germany, (1984), 29
7. H. S. Nalwa, *Advances in Surface Science*, **38**, Academic Press, Los Angeles, UK, 30-31

CHAPTER III

EXPERIMENTAL

This chapter presents a description of the two ultra-high vacuum (UHV) chambers used for the results presented in Chapters 5 and 6.

3.1 Ultra-High Vacuum (UHV) Chambers

3.1.1 The Temperature Programmed Desorption (TPD) Chamber

The TPD chamber was originally built by Dr. Neil Avery of CSIRO, Melbourne and is described in detail elsewhere¹; however a number of changes and additions have been made in recent years. The chamber is constructed of stainless steel with a mu-metal can on the inside that isolates the inner components from magnetic fields. The system is pumped by a triode ion pump with a pumping speed of 1550 L s^{-1} . Pressure measurements were made using a naked Bayard-Alpert ion gauge, with base pressures of less than 2×10^{-9} mbar routinely obtained. A schematic representation of the vacuum chamber is shown in Figure 3.1, highlighting the relative positions of each component in the chamber.

The essential features of the UHV spectrometer are:

- One LEG 24 Electron Gun, which can be operated with an energy range of 5-100 eV for Low Energy Electron Diffraction (LEED) and up to 3 kV for AES.
- A VG Microtech Rear-view LEED optics for LEED and AES studies, with the electron beam produced by a LEG 24 electron gun.

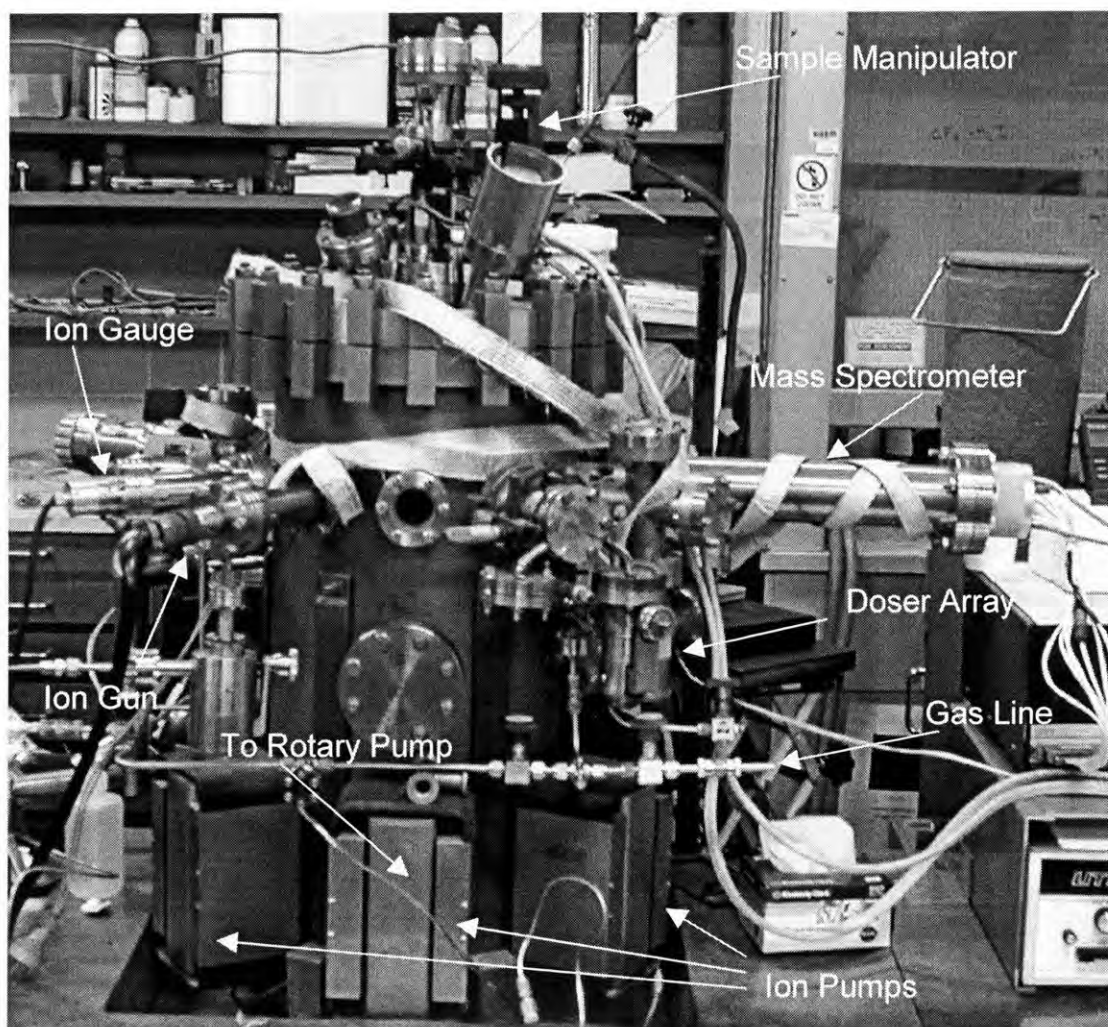
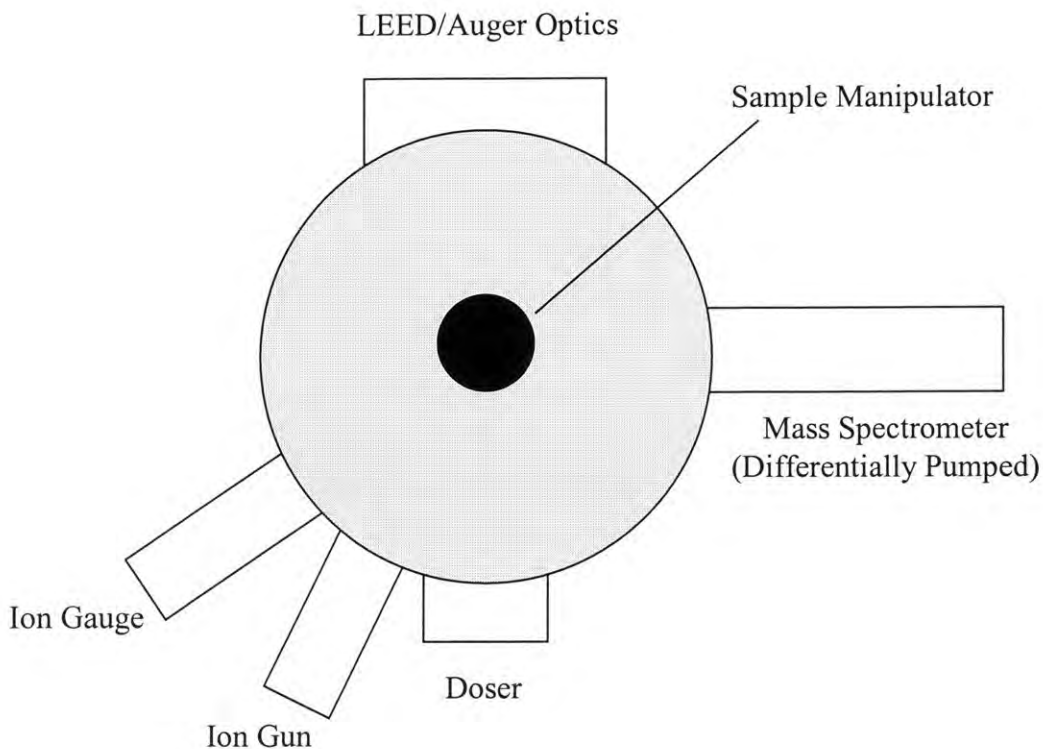


Figure 3.1 A schematic overview and photograph of the TPD chamber.

- A UTI Model 100C Precision Mass Analyzer is used for TPD experiments and to determine the purity of gases leaked into the system. The mass spectrometer is differentially pumped.
- A Varian 981-2043 argon ion gun which is filament operated and routinely used to clean the surfaces.
- A micro capillary array doser is used to leak in vapours on to the surface for analysis.
- A Varian 929-0023 titanium sublimation pump
- A Varian manipulator with x-, y-, z- translation and rotation of 360° about the normal.

Temperature programmed desorption studies are carried out with a UTI 100C quadrupole mass spectrometer. This mass spectrometer has a resolution of one atomic mass unit and can monitor masses in the range of 2 - 300 amu. The mass spectrometer is differentially pumped to increase the pumping speed of the desorbing species from the mass spectrometer cavity. A selective area probe, with a diameter of approximately 7 mm, also ensured that only species originating from the surface of the sample are monitored. The sample could be positioned within a few millimetres of the probe ensuring reproducible results in the TPD experiments.

3.1.2 Evacuation of the TPD chamber

The UHV pressures required for TPD experiments were obtainable in the following manner. The chamber was initially evacuated *via* a rotary pump which reduces the pressure in the chamber from atmospheric pressure to less than 10^{-2} mbar. The rotary pump was isolated from the chamber and then a sorption pump (filled with molecular sieve material (Type 4A, 2.5-5 mm) and cooled with liquid nitrogen) was used to further reduce the pressure to less than 10^{-4} mbar. The ion pump was then used in isolation and after several hours of pumping, the pressure in the chamber was reduced to less than 5×10^{-7} mbar. Subsequently, the chamber was baked for 24 hours with a final base pressure of less than 2×10^{-9} mbar being obtained when the system was cooled to room temperature. In addition, a Varian 929-0023 titanium sublimation pump was used to increase the pumping speed in the chamber. Once the pressure in the chamber was below 10^{-8} mbar, the system's components could be out-gassed and the chamber became operational.

3.1.3 The X-ray Photoelectron Spectroscopy (XPS) Chamber

The components of the XPS chamber were purchased from VG Microtech and assembled at UNSW by the Singh group with the invaluable help of the UNSW workshops. It is a two-chamber system constructed of stainless steel with a gate valve that separates the two chambers. A diode ion pump with a pumping speed of 1550 L s^{-1} evacuates the main chamber. The second chamber is smaller and is used for sample transfer and was evacuated by a turbo-molecular pump (300 L s^{-1}). The principal chamber can reach a base pressure of less than 5×10^{-10} mbar after bake-out. Figure 3.2 shows a photograph of the

vacuum chamber with the positions of each of the instruments used in this study labelled.

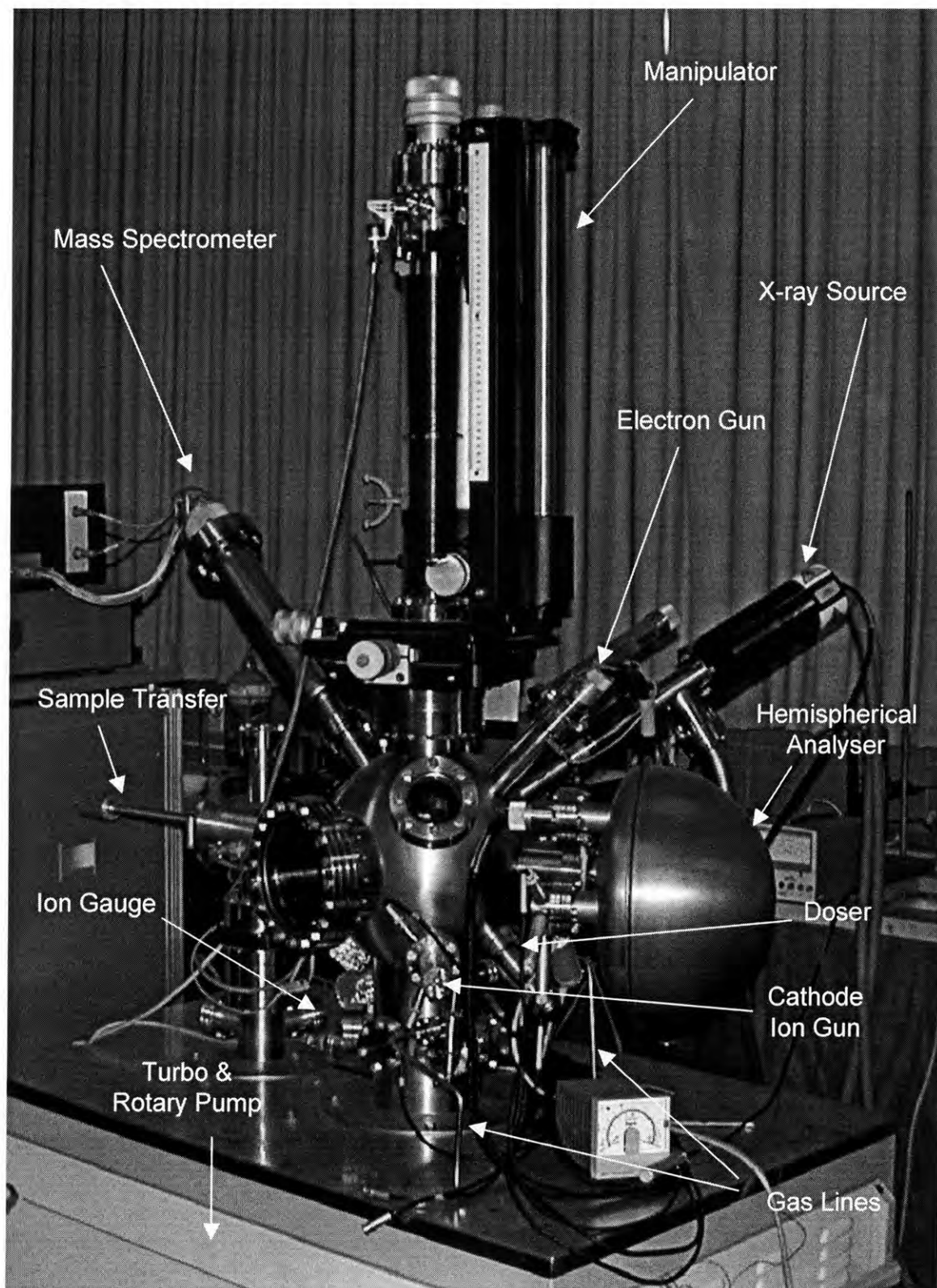


Figure 3.2 A photograph of the XPS chamber.

The characteristic features of the XPS chamber include:

- A PSP TX400/2 X-ray Source for XPS with two filament anodes, Mg and Al, with a filament potential of +10 to +15 kV.
- A LEG63 Electron gun for AES with a maximum electron energy of 5 keV
- A VG100AX Electron Energy Analyser to detect electrons from the sample during XPS and AES. Detection of electrons was with a secondary electron multiplier.
- An AG5000 Cold Cathode Ion gun for cleaning the sample with an energy range between 0.3 to 5 keV.
- A UTI 100C Precision Mass Analyzer to determine the purity of gases leaked into the system.
- Omniax MX manipulator capable of x-, y-, z-translation and rotation of 360° about the normal.

The X-ray source was operated at 200 W (20 mA x 10 kV) during the XPS measurements.

The VG100AX Electron Energy Analyser was used to record the XPS and AES measurements. Electrons emitted from the surface enter the analyser system and are transferred by two lenses that operate as coarse filters. Electrons with specific energy pass through the narrow band filter while electrons with greater and lower energy are adsorbed by the analyser walls. Detection of the electron signal was *via* a Channeltron. The 100 mm concentric hemispheric analyser operates in two different modes. Fixed analyser mode is used for XPS where

the pass energy is fixed regardless of the kinetic energy. This mode is more sensitive to high kinetic energies where XPS peaks are more likely to appear. Retard ratio mode is used for AES where the ratio between the pass energy and the kinetic energy is fixed. This mode is more sensitive at low kinetic energies which is more favourable for AES.

3.1.4 Pumping of the XPS Chamber

To attain UHV pressures in this system, a rotary pump (RV8, 10 L s^{-1}) initially evacuated the main chamber from atmosphere to less than 10^{-1} mbar. When the chamber reached this pressure, the Turbotronik NT 151/361 turbo-molecular pump (345 L s^{-1}) was engaged with the rotary pump used as the backing pump. After the pressure in the chamber was less than 5×10^{-4} mbar, the MidiVac diode ion pump was used to evacuate the chamber. The isolated ion pump evacuated the chamber further to less than 5×10^{-7} mbar. The system was subsequently baked for 24 hours. After cooling, the base pressure of the system was approximately 5×10^{-10} mbar. This pressure was sufficient to begin the out-gassing of the X-ray source, electron gun, mass spectrometer and sample.

3.2 Single Crystals and Chemicals Used

3.2.1 Surface Structure of GaAs(100) - (4x1) and Pt(111)

Two crystals, Pt(111) and GaAs(100), were used in the study. The GaAs(100) wafers are purchased from Spectra Physics and cut using a diamond scribe to the desired shape. The Pt(111) crystal was cut and polished at CSIRO and

used as received. In each case the crystal was attached to a manipulator for the TPD and XPS experiments.

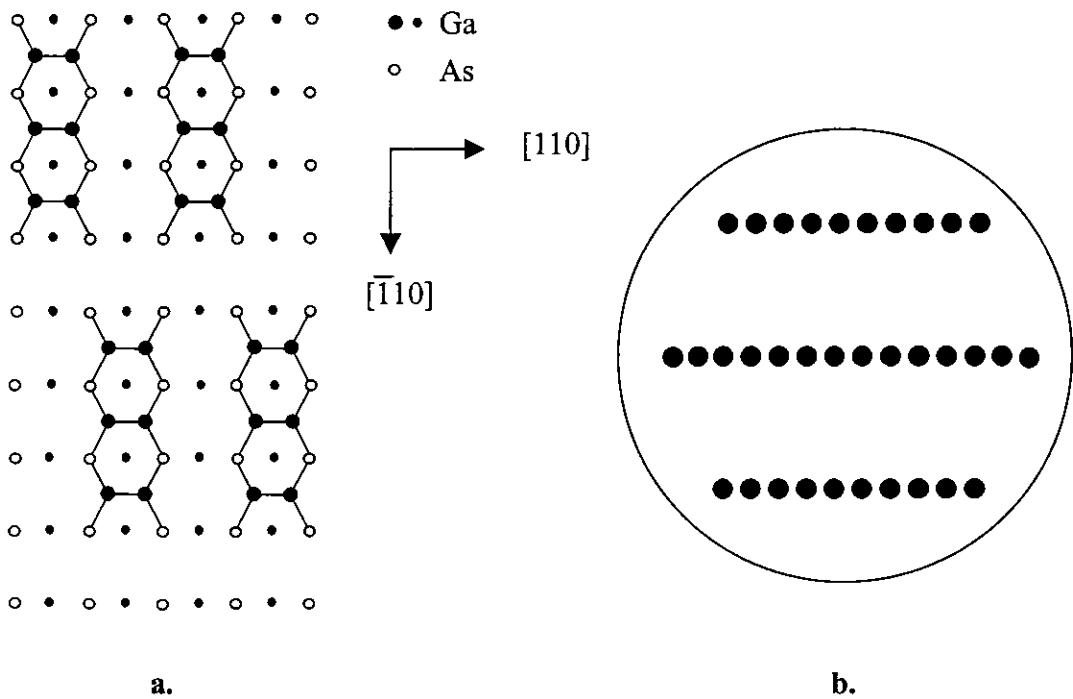


Figure 3.3 A schematic representation of **a.** the c(8x2) reconstructed GaAs(100) surface⁵ and **b.** the LEED pattern for the (4x1) reconstruction of the GaAs(100) surface.

For surface analysis, the surface structure is very important. In semi-conductors, such as GaAs, the surface atoms compensate for the loss of the nearest neighbours in vacuum by reordering the first few layers of the surface to satisfy valency and hence undergo reconstruction.² The GaAs(100) surface when heated to 820 K reconstructs to form a gallium rich c(8x2)/(4x2) structure. However, in our studies we observed a (4x1) structure.³ This structure is the result of disorder along [110] in the c(8x2) structure (see Figure 3.3 (a)).⁴ The c(8x2) surface consists of two (4x2)s offset by one unit cell in the [110] direction as seen in Figure 3.3 (a).⁵ As a result of this structure, the gallium dimers are bonded to a partially exposed second layer of arsenic atoms with the potential

for adsorption to also occur with this second layer. The surface exposed for (4x1) consists of 0.75 ML of Ga and 0.25 ML of As with three different reaction sites available; gallium sites that are isolated (two Ga atoms per unit cell), gallium sites that are adjacent to another gallium dimer (four Ga atoms per unit cell) and arsenic sites (four As atoms per unit cell).^{4, 6} A schematic of the (4x1) LEED pattern is reproduced in Figure 3.3 (b).

In vacuum, there is no reconstruction of the Pt(111) surface with the bulk body centred cubic structure transferred to the surface. Due to the two dimensional nature of the surface, a hexagonal array is the resulting structure as shown in Figure 3.4.

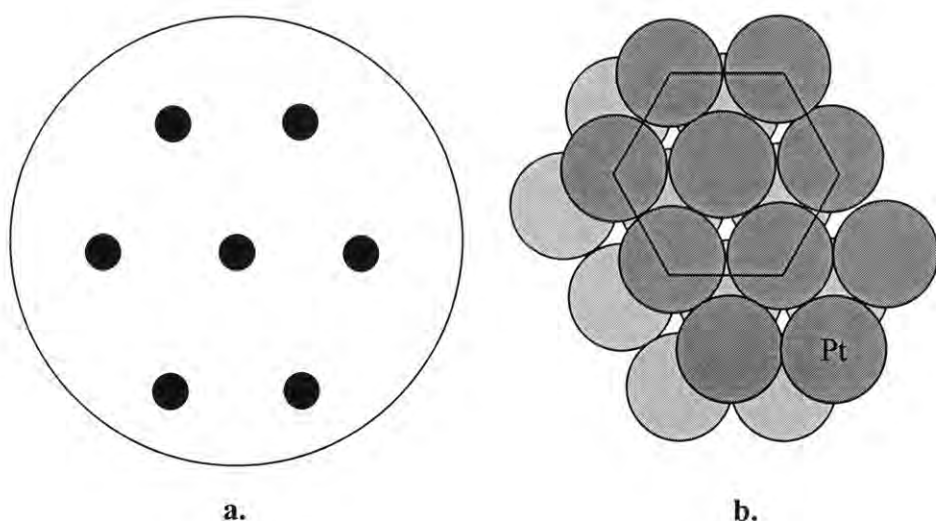


Figure 3.4 A model of **a.** the LEED pattern of Pt(111) and **b.** the Pt(111) surface structure.

3.2.2 TPD Chamber

The Pt(111) crystal was mounted onto the support rods of the manipulator, by spot welding 2 x 0.25 mm tantalum wires to the back of the crystal. These wires were screwed in to the support rods to make good thermal contact. The

platinum crystal was resistively heated by passing direct current through the crystal (Figure 3.5).

The GaAs(100) samples used in this study were mounted on a 0.25 mm thick tantalum backing sheet that was spot-welded to two stainless steel support rods. The rods were connected to two copper support strips through which current was passed. This design served to resistively heat the tantalum sheet, and then by thermal contact, heat the GaAs sample.

The Pt and GaAs crystals were cooled by thermal contact with a liquid nitrogen reservoir. Sapphire plates separate the sample from the reservoir. The reservoir was cooled by a flow system with liquid nitrogen entering one end and evacuated the other end by a rotary pump (see Figure 3.5). As the temperature of the reservoir dropped, the sapphire plates became conducting and cooled the sample. At higher temperatures, the sapphire plates became insulating thereby preventing heat transference from the sample to the reservoir and hence only the sample was heated.

An alumel/chromel thermocouple (Type K) was used for temperature measurements of the sample. For the Pt(111) sample, the thermocouple was spot-welded directly to the bottom of the crystal to a point furthest away from where the heater contact points were spot-welded. For GaAs(100), the thermocouple was spot-welded onto a thin piece of tantalum foil that was in thermal contact with the GaAs sample but thermally isolated from the tantalum backing plate by a thin sliver of mica.

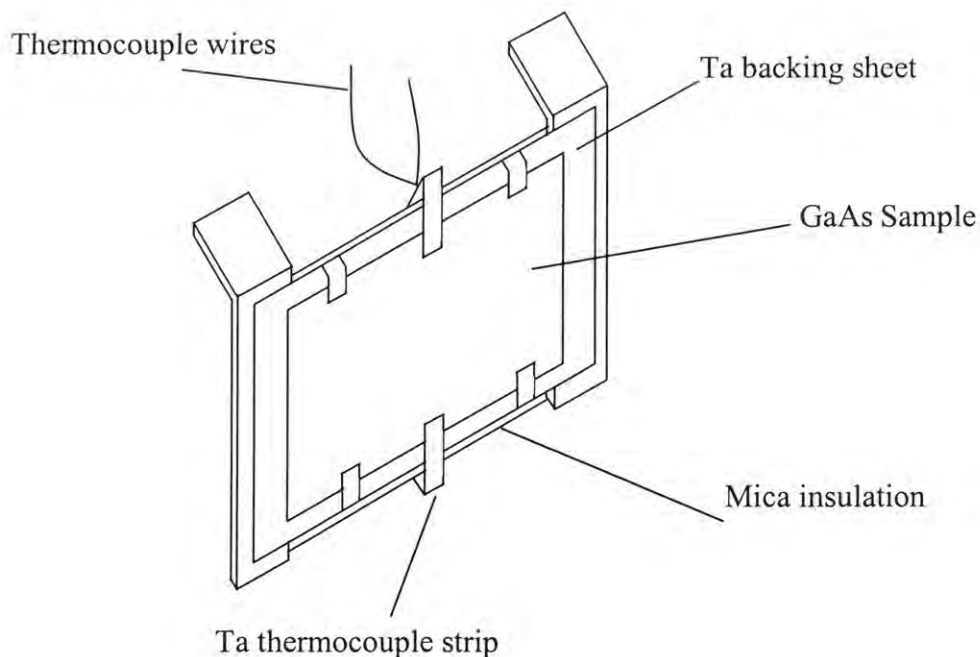
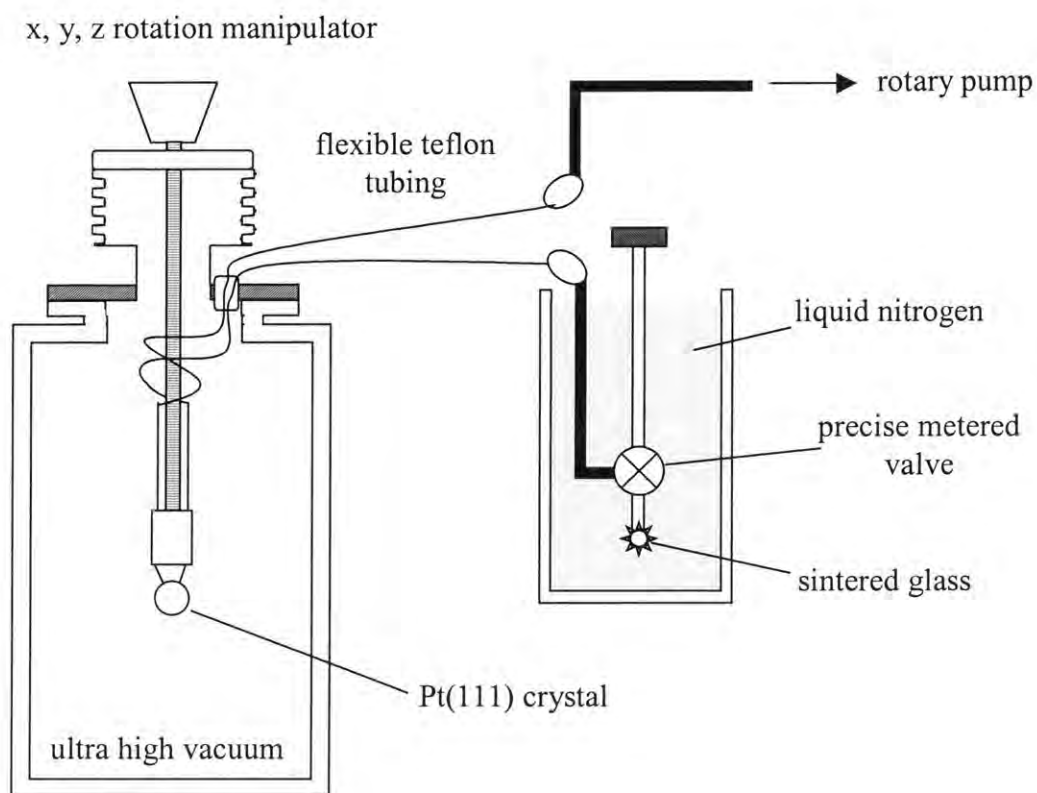


Figure 3.5 A diagram of the TPD chamber depicting the sample set-up in detail when the platinum crystal is attached and a detailed illustration of GaAs(100) sample mount.

Prior to insertion into the UHV chamber, the GaAs(100) and Pt(111) crystals were washed with acetone and iso-propanol to remove any organic surface

contaminants. No wet chemical etching for GaAs(100) was used. The cleaning of the surfaces was done in the UHV chamber by a combination of annealing and argon bombardment. The surface was annealed to 1070 K for Pt(111) and 770 K for GaAs(100). Argon bombardment involved leaking argon into the chamber at a pressure of $1 - 2 \times 10^{-5}$ mbar. The ion gun was operated at 15 mA and 2.0 V for cleaning Pt(111) and 25 mA and 0.5 V for GaAs(100). Drain currents of 3.0 μ A were typically recorded and this value could be maximised by focusing the argon ion beam or repositioning the sample. The crystals were heated to the annealing temperature after bombardment to restore the crystal surface structure which may have been destroyed during bombardment. This cycle of argon bombardment and annealing was repeated until the surface was clean as determined by LEED. A (4x1) structure indicated that the GaAs(100) surface was clean.

Due to the carbide impurities on the Pt(111) crystal, annealing and Argon ion bombarding were found to be inadequate and in this case heating the sample in an oxygen pressure was used. Oxygen was leaked into the chamber at 5×10^{-6} mbar while the Pt(111) crystal was heated to 870 K. After several minutes, the chamber was evacuated of oxygen and the crystal heated to restore the crystal surface structure. This process of oxygen cleaning and annealing was repeated until the surface was clean and the surface order was restored as determined by LEED and AES.

The gas and liquid vapours handled in this study are leaked into the chamber through microcapillary array dosers (see Figure 3.6). There are two arrays, each connected to a separate leak valve which allowed precise amounts of the adsorbate gases to be leaked into the chamber. The doser could be positioned

reproducibly within a few millimetres of the surface. Dosing in this manner allowed the sample to be dosed reproducibly and without increasing the background pressure to levels that would degrade the base pressure in the chamber.

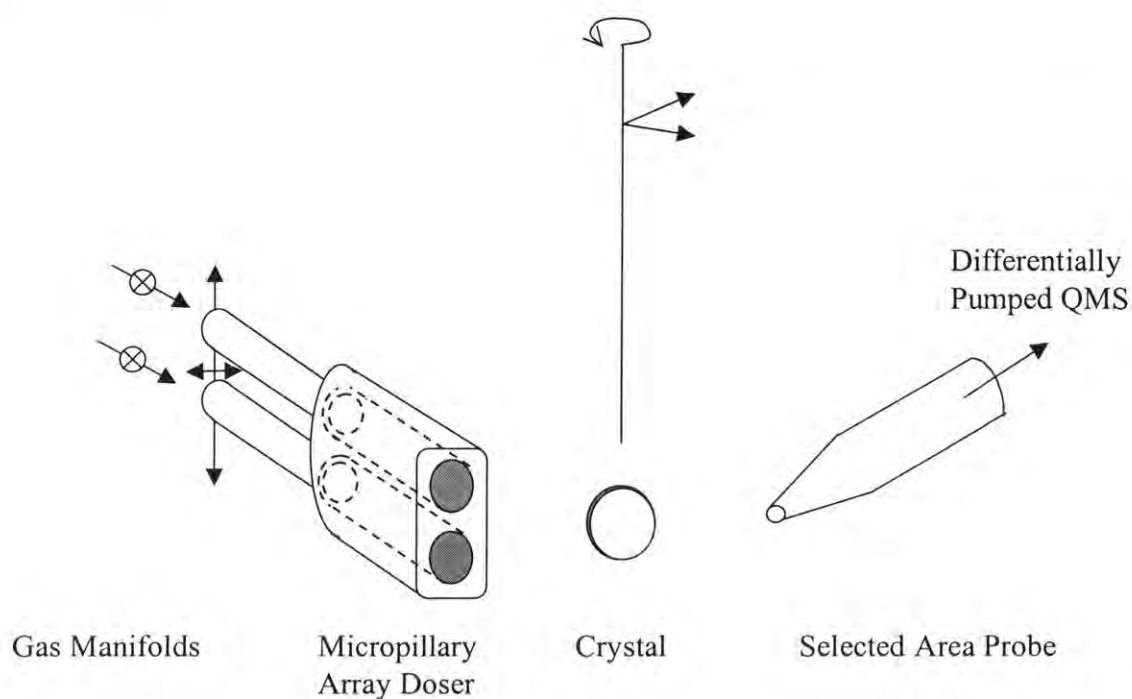


Figure 3.6 An illustration of the microcapillary array doser and mass spectrometer arrangement.

3.2.3 XPS Chamber

The Omniax MX manipulator in the XPS system has the same sample arrangement for both the Pt(111) and GaAs(100) crystals. Tantalum or molybdenum clips held the crystal in place against a molybdenum backing plate. The backing plate was electrically isolated from the heater *via* alumina bushes. A copper braid connects the copper reservoir and the backing plate which allows the sample to be cooled down to liquid nitrogen temperatures. A Type N thermocouple was spot welded to the backing plate. It is obscured under a tantalum clip to prevent the ceramic insulation of the thermocouple and

heater filament from being exposed and potentially charging the sample during AES or XPS data acquisition.

The sample was heated by conduction from a backing plate which in turn was heated by a ceramic insulated tantalum wire (outer diameter = 0.25 mm) filament.

The crystals were cleaned using the cold cathode ion gun. Unlike in the TPD chamber, the gun used in this chamber creates a plasma discharge. Higher pressures of argon ($4 - 5 \times 10^{-5}$ mbar) were required with a beam energy of 2.0 eV used for Pt(111) and 0.4 eV for GaAs(100).

3.2.4 Liquid and Gas Samples

2,2,2-Trifluoroethanethiol (TFET) (95 %), 1,1,1-trifluoroethyl iodide (TFEI) (99 %) and titanium tetrachloride (99.9 %), supplied by Aldrich Chemicals, were attached to the gas line and purified by several freeze-pumped-thaw cycles prior to leaking into the chambers. This process consists of freezing the compound with liquid nitrogen and then pumping over the frozen solid to remove any impurities. The compounds were then isolated from the pump and allowed to thaw. The purity of the vapours was determined by comparing the mass spectrum of the gas to the literature. Argon (Aldrich, +99.998 %) and Deuterium (Messer Grieshem, 99.7 %) were also used in this study as supplied.

The liquids used in this study all have reasonable vapour pressure at room temperature so that there is significant vapour pressure in the gas line compared to the background pressure of the gas lines. Furthermore, the gases and liquid vapours used in this study have to be of the highest purity to prevent contamination of the surface when the compounds were leaked into the

chamber. The gas manifolds in both chambers were pumped over using a rotary pump (Edwards RV5, 5 L min^{-1}) to less than 5×10^{-3} mbar before the liquids contained in Young's tap sample tubes were opened to the lines. The passivation of the gas line was done to ensure that the highest purity of gas enters the UHV chamber and to prevent memory effects from previous samples. Once sufficient passivation of the gas-lines had occurred, the reagent vapours could be leaked into the UHV chamber. A separate gas line had been constructed for argon, which ensures that the argon used for cleaning the crystals was of the highest purity. The argon line was pumped by the same procedures noted above.

3.3 Experimental Procedures

3.3.1 Dosing Experiments

The crystal face was positioned in front of the doser and the vapours were leaked into the chamber. Based on the relationship, $1 \text{ L} = 1.333 \times 10^{-6} \text{ mbar s}$, the vapours were leaked into the chamber at a certain pressure and period. For example, to leak in 1 L at 1.333×10^{-6} mbar for 1 s would be difficult, so a more reasonable value would be to leak 1 L at 2.2×10^{-8} mbar for 60 s.

3.3.2 TPD Experiments

In the TPD experiments, a differentially pumped mass spectrometer was used to monitor desorbing species while applying a heating ramp to the surface.

The crystal was dosed with the vapour for a known exposure. When the chamber had been pumped down to below 1×10^{-8} mbar, the mass spectrometer was tuned to the desired ion. For example, if we wish to study

$\text{CF}_2=\text{CH}_2$ ($m/z = 64$ amu), then the mass spectrometer would be tuned to 64 amu. The mass spectrometer were turned on and left for some time (approx. 5-10 minutes) to equilibrate with the background conditions. During this period, the sample was positioned away from and orthogonal to the mass spectrometer filament to minimise electron-induced dissociation of the adsorbate layers under the electron beam. As will be shown in Chapter 6, this was sufficient to prevent electron dissociation of the adsorbates on the surface from occurring.

A linear heating ramp was applied to the crystal and the species being thermally desorbed from the sample were monitored by the mass spectrometer as a function of temperature.

3.3.3 XPS and AES Experiments

XPS and AES are used in this investigation to monitor the adsorbed species on the surface. In the XPS experiments, the sample position was maximised for the count readings at the Ga $3d_{5/2}$ peak (~ 20 eV) for GaAs(100) and the Pt $3d_{5/2}$ peak (~ 71.0 eV) for Pt(111) of the clean surface. In XPS, the angle between the X-ray source, the sample and the detector was 54° . These positions were re-used throughout the day so that there was reproducibility between the experiments. Additionally, the signal intensity was maximised by adjusting the lens voltage (the voltage on the lenses as the electrons enter the analyser) and the magnetic trim (offsets the influences of any stray magnetic fields).

For AES analysis in the TPD chamber, the LEED optics was used as a retarding field analyser. In addition, a lock-in amplifier modulated and increased the intensity of the Auger signal. For the XPS system, the channeltron was used to detect AES electrons as described for XPS. For both chambers, an

electron beam of 2.5 – 3.0 keV was generated with a drain current typically of 3 μA .

Four XPS regions were scanned for $\text{CF}_3\text{CH}_2\text{SH}$ and $\text{CF}_3\text{CH}_2\text{I}$ adsorption on GaAs(100): the substrate region: Ga 3d and As 3d (10 – 62 eV); the adsorbate regions: C 1s (274 – 304 eV), F 1s (675 – 702 eV) and depending on the molecule, S 2p (153 – 173 eV) for $\text{CF}_3\text{CH}_2\text{SH}$ and I 3d (614 – 642 eV) for $\text{CF}_3\text{CH}_2\text{I}$. The results are presented in Chapter 5.

Three XPS regions were scanned for TiCl_4 adsorption on Pt(111), namely the substrate region: Pt 4f XPS region (65 – 78 eV) and the adsorbate regions: Ti 3p XPS region (452 – 467 eV) and the Cl 2p XPS region (192 – 203 eV). The results are presented in Chapter 6.

Due to the corrosive nature of all the chemicals used in this research, the XPS and AES experiments were commenced only after the residual gas from dosing had been pumped away and the base pressure was below 1×10^{-8} mbar.

Uptake plots to determine the saturation coverage of the different compounds were conducted. The appropriate XPS or AES regions were scanned prior to dosing the surface and after the surface had been cleaned. Subsequently, the surface was exposed to the compound for a known exposure. The appropriate XPS or AES regions were again scanned. This process of dosing and analysing was repeated until there is no further observed increase in the intensity of the XPS or AES peaks due to the compound being studied.

Thermal desorption studies using XPS and AES techniques were performed to monitor the different surface species as a function of substrate temperature.

Following adsorption at liquid nitrogen temperatures when multi-layers or condensed layers of the compound formed on the surface or at room temperature when only the chemisorbed layers are formed, the XPS or AES regions were scanned. The surface temperature was increased in small increments followed by cooling and monitoring of the surface using XPS or AES. This continued until there were no variation in the substrate and compound spectra or until the annealing temperature was reached, whichever was achieved first.

3.3.3 LEED Experiments

LEED was used in this study to investigate variations in surface structure following exposure to reactants and to observe any lasting effects of post-annealing of the substrate. LEED patterns were observed for electron energies between 50 – 200 eV.

3.4 References

1. N. R. Avery, *Surf. Sci.*, **125**, (1983), 771
2. G. A. Somorjai, *Introduction to Surface Science*, A Wiley-Interscience Publication, New York, USA, (1994), 48-51
3. D. K. Biegelsen, R. D. Bringman, J. E. Northrup, L. E. Swartz, *Phys. Rev. B*, **41**, (1990), 5701
4. D. J. Frankel, C. Yu, J. P. Harbison, H. H. Farrell, *J. Vac. Sci. Technol. B*, **5**, (1987), 1113
5. I. Kamiya, D. E. Aspne, L. T. Florez, J. P. Harbison, *Phys. Rev. B*, **46**, (1992), 15894
6. N. K. Singh, A. Bolzan, J. S. Foord, H. Wright, *Surf. Sci.*, **409**, (1998), 272

CHAPTER IV

THE EFFECT OF CHLORINE ON CVD DIAMOND GROWTH

In this chapter the adsorption mechanisms of chlorine on a polycrystalline diamond surface will be investigated. These adsorption studies were performed in the laboratory of Prof. J. S. Foord at the University of Oxford, UK.

4.1 Introduction

Since the first discovery of natural diamond, there has been an interest in acquiring or fabricating diamond and diamond-like materials due to their unique properties. The bulk diamond structure consists of sp^3 -hybridised carbon atoms covalently bonded with the carbon atoms separated by 1.545 Å bond length and position in space with tetrahedral symmetry.¹ The bulk-structure terminates at the surface with dangling bonds that, in air, are usually capped by hydrogen. In vacuum, the dangling bonds have no such hydrogen termination and the large surface free energy causes the first few layers to reconstruct. Both the C(100) and C(111) surfaces reconstruct to form π -bonds between the carbon atoms of the first layer to produce a (2x1) LEED pattern.² When hydrogenated, the hydrogen atoms break the π -bonds on both surface structures with the C(100) preserving the (2x1) structure and the C(111) surface relaxing to form a (1x1) structure.^{2, 3, 4}

The unique structure of diamond gives rise to its remarkable properties. Diamond is the hardest material known, has the lowest coefficient of thermal expansion, is chemically inert and resistant to wear, has a low friction coefficient, is electrically insulating and is optically transparent from the ultra violet to the infrared region of the electromagnetic spectrum.^{1, 5}

Over the years, the demand for natural diamond has increased while the supply has become stagnant. This trend has resulted in the development of alternative growth techniques such as the high-pressure and high-temperature (HPHT) method.¹ This method is problematic as poor crystallites are formed due to the inclusion of graphite, metals (from the catalyst) and/or metal carbides.¹ Also, the crystals grown are often too small for use on a technological scale.¹ To overcome these limitations, the coating of less exotic materials with diamond thin films grown by chemical vapour deposition (CVD) is becoming a viable alternative.

4.1.1 CVD Diamond Growth

In the last ten years, there has been an interest in the growth of diamond by CVD techniques. These films have comparable properties to natural diamond (e.g. mechanical, tribological, and electronic properties) and the CVD processes offer a more commercially viable alternative to HPHT methods. In addition, the potential to coat large surface areas opens up a wide range of applications of CVD diamond thin films.

For example, high-quality loudspeakers contain diamond coated tweeter diaphragms that produce high-quality sound reproduction.¹ CVD diamond electronic heat sinks are becoming more readily available. Traditionally, metals such as copper and silver have been used as heat sinks but these metals are being replaced by higher thermal conductive CVD diamond.^{1, 5} Diamond coating of instruments such as diode lasers results in high thermal conductivity and thus equal cooling of the laser.⁶ Other applications including the coating of IR windows, lenses and sunglasses are under development.^{1, 5}

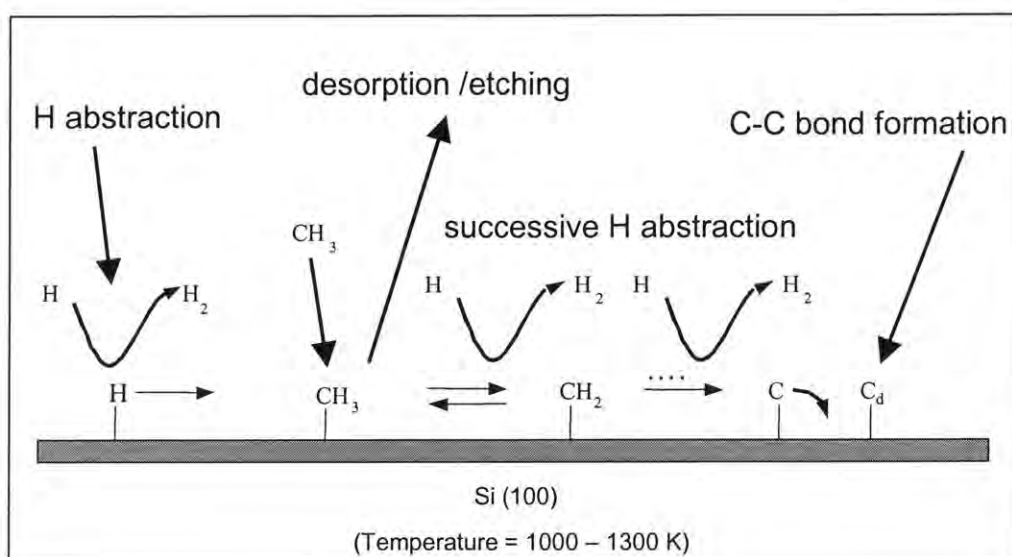


Figure 4.1 A schematic of the reactions during diamond thin film formation when using a CH_4/H_2 precursor mixture.

There are many techniques and gas mixtures used for the deposition of CVD diamond thin films. A popular growth method is the use of a mixture of hydrocarbons (e.g. methane or acetylene, 1 - 2 vol%) and hydrogen.^{7, 8} A hot filament or high frequency microwave pulse is used to generate the reactive dissociated hydrocarbon species that interact both in the gas phase and on the substrate surface to form diamond. Several researchers have established the diamond growth mechanisms that occur at the substrate.^{5, 9} A general outline of the reactions involved during thin film growth using a CH_4/H_2 mixture is summarised in Figure 4.1. Atomic hydrogen abstracts surface bound hydrogen to create a vacant site.^{5, 9} Adsorption of a methyl radical to this site can occur.^{5, 9} Additional atomic hydrogen can then abstract the hydrogen of the adsorbed methyl radical, whereupon carbon-carbon bond formation occurs and ultimately diamond growth.^{5, 9}

High quality homogeneous diamond thin films can be grown and depend strongly on reaction conditions including concentration of the gas mixtures of

methane and hydrogen and the growth temperature. Possible defects that arise on CVD diamond surfaces are twinning and shacking faults and these are formed due to deposition conditions.^{10, 11}

In order to grow high quality diamond films with reasonable growth rates, high deposition temperatures greater than 850 K are required. The high temperature of the substrate initiates several competing reaction pathways that inhibit diamond growth (see Figure 4.1) and include desorption and etching of the adsorbed methyl groups. High temperatures are necessary for abstraction of the surface bound hydrogen. This abstraction is an exogenic process and results in the creation of a site for diamond growth to occur.⁵ However, high substrate temperatures limit the deposition of diamond on materials such as high-speed drill bits (steel) as the structural hardness of steel is lost at these high temperatures. Therefore, it has become necessary to develop CVD techniques for the growth of diamond thin films at lower temperatures.

4.1.2 Low Temperature CVD Diamond Deposition

It has been reported that replacing hydrocarbons with halocarbons or adding halogens to the gas mixture can lower the surface temperature without compromising the film quality. Moreover, film quality can increase as a result of using halocarbons. Halocarbons which have been used in this way include carbon tetrafluoride,^{12, 13} trifluoro methane,^{6, 12, 14, 15, 16} dichloro difluoro methane,¹³ and ethyl chloride.^{6, 14, 17, 18} The addition of chlorine to a mixture of methane and hydrogen has also been investigated.^{17, 19} These gas mixtures have been shown to reduce the substrate temperature to as low as 640 K.⁶ The

lowering of the growth temperature widens the range of substrates on which diamond films can be deposited.

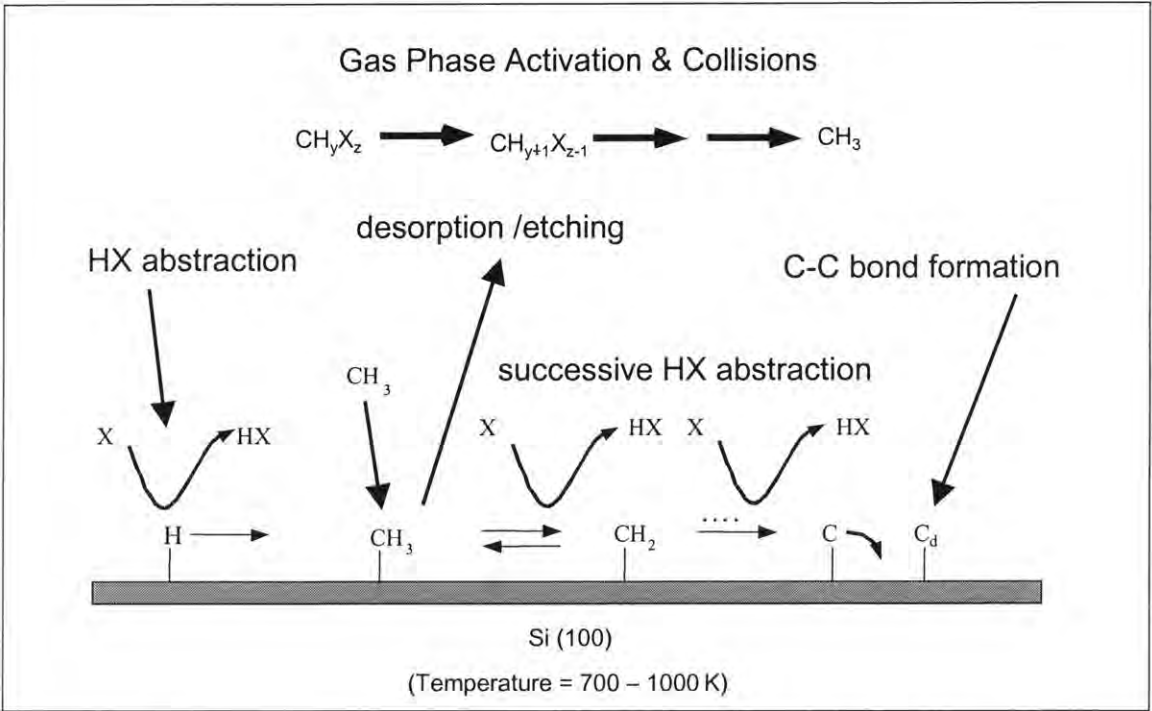
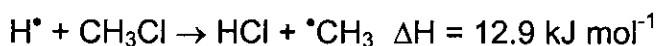
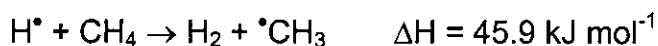


Figure 4.2 A schematic of CVD diamond growth mechanism using a $\text{CX}_y\text{H}_z/\text{H}_2$ mixture, where $\text{X} = \text{F}$ or Cl .

The initial step for diamond growth using halocarbons involves activation of the halocarbon in the gas phase (Figure 4.2). Either a hot filament or high frequency microwave pulse is used to form CX_y or CX_yH_z radicals. Due to the high reactivity of these species, the hydrogen atmosphere facilitates the displacement of halogen groups by atomic hydrogen. The carbon shell is stripped of the fluorine or chlorine atoms with a hydrocarbon radical remaining. This mechanism has been confirmed using mass spectrometry where the residual gases were established to contain only hydrocarbons (*i.e.* C_2H_2 and CH_4) and no halocarbons when using CF_4 or CCl_4 as part of the feed gas.^{13, 20} These transient species are the same species that are formed when hydrocarbon mixtures are used to deposit diamond.

This gas phase activation of the halocarbon precursor depends on dissociation of the C-X bond. The C-F bond (545 kJ mol^{-1} in CF_4)²¹ is stronger than the C-H bond (439 kJ mol^{-1} in CH_4)²¹. Thus based on bond strengths, the formation of CH_x radicals is more favourable for simple hydrocarbons than for fluorinated hydrocarbons. Nonetheless, the breaking of the C-F bond is overcome by the high exothermic formation of the reaction product, hydrogen fluoride ($\Delta H = -20 \text{ kJ mol}^{-1}$).^{15, 20} Conversely, the abstraction reaction to form molecular hydrogen is endothermic ($+68 \text{ kJ mol}^{-1}$), requiring higher temperatures for the process to occur.¹⁵ For fluorinated hydrocarbons like CF_3H , the presence of HF in the mass spectrometer during deposition confirms that the exothermic nature is sufficient for abstraction to occur and to facilitate diamond growth at lower temperatures.²²

On the contrary, the C-Cl bond (349 kJ mol^{-1} in CH_3Cl)²¹ is weaker than the C-H bond (439 kJ mol^{-1} in CH_4)²¹ and dissociates easily in the conditions usually present in a CVD chamber. In addition, the formation energy of methyl radicals is reduced by a factor of three for chloromethane compared to methane.¹⁵



The growth of diamond on the surface commences when a hydrocarbon radical or halogen radical in the gas phase abstracts hydrogen from the surface to create a vacant site. The growth cycle when using halocarbons (Figure 4.2) then proceeds using the same mechanism as described for a methane and hydrogen mixture. The major difference is that in addition to hydrogen-hydrogen abstraction, there is halogen abstraction of hydrogen atoms bound to the

carbon moiety to form HX. Continued abstraction of hydrogen by chlorine or fluorine from the adsorbed radical species results in carbon-carbon bond formation leading to the formation of deposited diamond films.

Additional research supports the theory that the same mechanism applies when halocarbons and hydrocarbons are used to grow CVD diamond. At 920 K, the {100} phase is predominantly deposited when using a CH₄/H₂ mixture while above 1120 K, the {111} facets are preferred.²⁰ When using halocarbons, the same trend in diamond morphology is observed.^{12, 20}

The importance of HX formation is paramount for low temperature growth to occur. The lowering of the growth temperature when using a halocarbon precursor is attributed to an increased rate of abstraction of HX compared to H₂. Atomic chlorine and fluorine react faster than atomic hydrogen, 60 times faster in the case of chlorine at 940 K.^{16, 23} These halogen radicals react with the adsorbed hydrogen to form hydrogen chloride or hydrogen fluoride, which then desorbs into the gas phase, leaving a site for diamond growth to occur. Atomic hydrogen in the gas phase is observed to react with HCl to form molecular hydrogen and atomic chlorine.⁶ Hence, atomic chlorine can repeat the process of hydrogen removal from the surface to create potential growth sites. Unfortunately, HF is stable ($E_b = 570 \text{ kJ mol}^{-1}$)²¹ with negligible atomic fluorine formed by collisions with atomic hydrogen (Equilibrium constant = 1×10^{-7} , 500 – 1200 K).¹⁶

In addition to increased reaction rates at low temperatures, the presence of halogens in the precursor increases the relative hydrogen concentration. When CF₄ is added to the precursor mixture, there is an 80 % increase in the relative

atomic hydrogen concentration compared when using a methane/hydrogen mixture.¹³ While a 200 % increase is observed when CF_2Cl_2 is used.¹³ It is believed that the halogenated mixtures promote a high radical concentration. Moreover, Schmidt *et al.* showed the importance of the radical chemistry in the gas-phase by altering the distance between the filament and the substrate.^{6, 14, 16} As the filament distance is decreased, more atomic species are formed including atomic fluorine and chlorine.^{6, 16} The more halogens incident on the surface, the greater the chance of activation of the hydrogen-terminated surface and hence improve the diamond film quality.¹⁶

However, CVD diamond quality is reduced when large amounts of chlorine are present as this can lead to chlorine incorporation into and poisoning of the film. Films deposited at 690 K from a mixture of $\text{H}_2/\text{C}_2\text{H}_5\text{Cl}$ show a chlorine concentration of 3000 ppm in the bulk of the film.⁶ This is a problem that occurs during the growth of a number of other films using chlorine as part of the starting material, such as TiN grown using TiCl_4/N_2 .²⁴ By increasing the substrate temperature, chlorine desorbs from the growth front. If the deposition temperature is increased to 870 K for the $\text{H}_2/\text{C}_2\text{H}_5\text{Cl}$ mixture, there is a reduction in the chlorine concentration in the bulk to 40 ppm.⁶ The presence of chlorine during growth is important in reducing the growth temperature, however, chlorine incorporation into the film is undesirable. Hence, an alternative deposition procedure, which reduces the substrate temperature whilst retaining the quality of the film, is being sought.

An alternative method proposed for low-temperature diamond growth is to use a mixture of methane and hydrogen activated by a hot filament in the presence of a halogenated substrate. There are a number of methods used to

halogenate a surface and will be discussed in § 4.1.3. Precursors such as Cl_2 and XeF_2 are preferred over alkyl halides as they readily dissociate whereas the alkyl halides such as CF_4 require large amounts of energy, e.g. by plasma discharge, to dissociate the C-F bond.

If the surface is pre-chlorinated prior to deposition then surface chlorine, during growth conditions, can be abstracted by atomic hydrogen from the precursor gas mixture to form vacant sites. These sites offer an opportunity for methyl radicals to adsorb. The resulting gas phase HCl can then collide with atomic hydrogen to form molecular hydrogen and atomic chlorine. The atomic chlorine can remove surface bound hydrogen to form HCl and in the process, create additional sites for growth to occur. Hydrogen chloride, leaving the surface, can react in the gas phase and continue the growth process. The addition of chlorine has been shown to remove absorbed hydrogen from the surface more readily at lower temperatures than atomic hydrogen, thus reducing the deposition temperature. With the lowering of the substrate temperature, competing processes such as desorption of methyl species can be reduced. Also having an initially chlorinated substrate with no chlorine component in the precursor gas mixture minimises the chlorine concentration in the system, thus reducing the possibility of chlorine poisoning and poor quality diamond film. Little research has been undertaken to determine if this is a better method for CVD diamond growth.

Hence, the aim of this research was to use X-ray Photoelectron Spectroscopy (XPS) to investigate the associated kinetics of adsorption, thermal desorption and hydrogen etching of gaseous chlorine on CVD diamond deposited on $\text{Si}(100)$.

4.1.3 Halogen Precursors

There have been several halogen studies on both single crystal and polycrystalline diamond surfaces. The majority of these investigations have used atomic chlorine,^{25, 26, 27} atomic fluorine,^{4, 25, 26, 27} irradiated perfluorinated alkyl iodides²⁸ and xenon difluoride.^{29, 30} Little or no research has investigated the higher halides and theoretical calculations show that bromine cannot break the C=C π -bond, which is necessary for adsorption to occur.³¹ When perfluorinated alkyl iodides are adsorbed on the surface, iodine is not very stable, desorbing by 300 K.²⁸ In this study, molecular chlorine is used as the source of surface chlorine.

All fluorine sources react readily with a diamond surface. It has been determined that xenon difluoride dissociates on the surface to yield fluorine atoms at lower temperatures than molecular fluorine. Passivating a diamond film with xenon difluoride, Hsu *et al.* observed an enhanced chemical inertness and possible reduction in the coefficient of friction of the film.²⁹ On both the C(100) and C(111) surface, XeF₂ adsorbs dissociatively.²⁶ Fluorine adsorbs strongly on C(111) with 50 % of this state remaining on the surface when heated to 900 K.²⁶ While fluorine adsorbed on a C(100) surface is not as strongly bound with 50 % desorbing by 800 K.^{4, 26} Foord *et al.* have studied XeF₂ adsorption on CVD diamond and their results show similar trends to the work presented in this chapter.³⁰

Chlorine has been previously studied on diamond surfaces.^{26, 32, 33, 34} Chlorine adsorbs on diamond surfaces to a maximum coverage of 0.5 ML.²⁶ The chlorine is weakly bound to the surface due to the large size of the chlorine

atom and the close packed structure of diamond. Using diamond powder, Ando *et al.* observed that chlorine abstracts hydrogen from the diamond surface at low temperatures.³⁴ Chlorine also chemisorbs and desorbs readily from the diamond surface with most of the chlorine desorbed by 570 K.²⁶ This is characteristic of a good intermediate for the chemical modification of and growth on the diamond surface. Although interactions of chlorine have been studied previously on diamond surfaces, none have investigated chlorine adsorption and desorption on CVD diamond using XPS.

4.1.4 Technique

The technique used to study chlorine adsorption on diamond was XPS. The theory of this technique has been discussed in § 2.2.1.

4.1.5 Aims

The primary aim of this work was to investigate the interaction of chlorine on CVD diamond at low temperatures and to determine the implications for growing diamond thin films using a hydrocarbon gas mixture. This study:

1. Monitored the adsorption characteristics of chlorine (using Cl_2 gas as the precursor) on clean and pre-hydrogenated diamond surfaces.
2. Studied the thermal stability of the adsorbed chlorine adlayer formed in (1).
3. Investigated the susceptibility of the adsorbed chlorine to hydrogen etching at different atomic hydrogen partial pressures.

4.2 Experimental

The experiments performed in this chapter were conducted at the University of Oxford under the supervision of Dr Nagindar Singh in the laboratory of Prof. John Foord.

4.2.1 Chamber Description

The UHV system used in this study consisted of two chambers linked by a gate valve. The primary chamber comprised XPS and TPD instrumentation. It also contained a filament which could be used to generate radical species (e.g. atomic hydrogen) by running a current through it. The secondary deposition chamber was also available but was not utilised in this study.

A HA100 Hemispherical Analyser System was used to record the XPS measurements. The 100 mm concentric hemispheric analyser was operated in fixed analyser transmission (FAT) mode, at a pass energy of 50 eV and 25 eV for survey and region scans, respectively. An Al K_{α} X-ray source was used for the acquisition spectra.

A VSW Mass Analyst was the mass spectrometer used for the detection of background species. The mass spectrometer lacked sensitivity at high mass and peaks greater than 20 amu were poorly resolved.

A tantalum filament was used to generate hydrogen radicals from the background hydrogen gas. It consisted of a thin tantalum wire (0.25 mm diameter, 30 mm length) which was coiled several times to maximise the surface area. The ends of the tantalum wire were spot welded to two stainless steel rods. These rods were attached to electrical feed-throughs mounted on a

CF 70 conflat flange. The conflat flange was mounted on a linear drive so that the filament could be positioned close to the front of the sample face. The filament was normally operated by passing a 2.8 A current through the tantalum wire with the filament glowing red to white hot. The sample to filament distance was maintained at 30 mm during atomic hydrogen dosing to ensure that the same atomic hydrogen flux was experienced by the sample. This distance was also used to prevent the surface temperature from exceeding 370 K, which would have occurred for shorter distances.

The chamber was initially pumped from atmosphere to $<10^{-2}$ mbar with a rotary pump. This was sufficient for the oil diffusion pump to commence pumping. The chamber was baked for 18 hours to remove hydrogen, water, carbon monoxide and carbon dioxide. After the chamber cooled down, the base pressure was 3×10^{-10} mbar, obtained using only the diffusion pumps. At this pressure, the X-ray source, the sample, the mass spectrometer and tantalum filament could be out-gassed.

4.2.2 Diamond CVD Sample and Gases

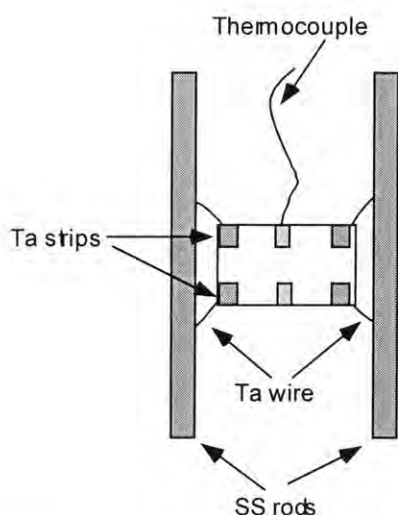


Figure 4.3 Schematic of the sample mount.

The diamond sample was mounted on two half looped tantalum wires each supporting a piece of Ta foil with the outer foil clipping over the sample to secure it in place (Figure 4.3). The ends of the tantalum wire were spot welded to two stainless steel rods. These stainless steel rods were connected to the feed-throughs which were used to

supply the heating current to the substrate. The feed-throughs were a part of the manipulator which was capable of movement in the x-, y-, z-directions, rotations of 360° along the normal and Acuport operations.

Temperature measurements were made using a Type K thermocouple. A single tantalum strip was clipped to the back of the substrate and the thermocouple wire was spot-welded to the back of this tantalum strip.

Dr R. B. Jackman at the University College, London, supplied the diamond substrate. It consisted of a CVD grown diamond film deposited on a Si(100) wafer by microwave-assisted CVD, to a thickness of ~20 µm. Experiments were performed on 10 x 20 mm pieces.

The diamond substrate was heated by conduction by passing a current through the Ta backing plate. Using this method, the sample could be heated to temperatures above 1470 K.

The diamond sample was cleaned by heating to 1270 K. The presence of the diamond plasmon loss feature (surface and bulk) in the 305 - 325 eV binding energy region in XPS confirmed the phase purity of the surface.^{8, 35, 36} Note the inset in Figure 4.7 shows the C 1s plasmon loss feature in more detail. Furthermore, the absence of a 6 eV loss peak characteristic of graphite clearly indicates that the film contains no graphite.

Chlorine gas with 99.50 % purity was purchased from Argo International Ltd. Hydrogen gas with 99.99 % purity was purchased from BOC. The chlorine and hydrogen reagent gases were used as supplied and no further purification was performed.

Gases used in this study were leaked into the chamber using a leak valve. The substrate surface was reproducibly positioned within 10 mm of the doser. A rotary pump evacuated the gas lines to less than 5×10^{-3} mbar before the reagent gases were allowed into the lines. A separate line attached to an alternative leak valve was constructed for the hydrogen gas which prevented the mixing of hydrogen and chlorine in the gas lines. Hydrogen entered the chamber in direct line-of-sight of the tantalum filament and sample, to prevent interference from hydrogen interacting with the walls.

The chlorine gas line was passivated thoroughly prior to any dosing experiments. Furthermore, the purity of the gases was confirmed using the quadrupole mass spectrometer prior to the XPS experiments.

4.2.3 XPS Experiments

During the XPS experiments, the sample was positioned, such that there was a maximum count reading at the C 1s region (~285 eV) for the clean surface. This position corresponded to an angle of 54° between the X-ray source, the sample and the detector. Once this position was determined, it was reused throughout the experiments that day to ensure consistency between the experiments.

The survey scan was recorded between 0 - 1287 eV using an FAT of 50 eV. The chlorine (Cl 2p) XPS region was measured between 201 - 217 eV using an FAT of 25 eV. The carbon (C 1s) XPS region was monitored between 287 - 347 eV using an FAT of 25 eV. This range included the C 1s peak and the plasmon loss region. The binding energies of the C 1s and Cl 2p XPS peaks were determined relative to that of the C 1s peak at 285.0 eV for a clean diamond

surface. Unshifted spectra and any spectra that may be absent in this chapter can be located in Appendix A.

XPS experiments would commence after the system had pumped any residual gas remaining from dosing and corresponded to a base pressure below 10^{-8} mbar. This method was utilised to prevent corrosion of the X-ray source and detector.

4.2.4 Saturation Experiments

Uptake plots to determine the saturation coverage of chlorine were acquired. Initial investigations commenced with dosing the surface with a known exposure of molecular chlorine. The Cl 2p region was scanned to determine and confirm the presence of chlorine on the surface. Exposing the surface continued by aliquot dosing until the intensity of the XPS peaks no longer increased.

4.2.5 Thermal Desorption Experiments by XPS

Thermal desorption studies using XPS to monitor the surface species were performed to determine the strength of the chlorine adlayer on the diamond surface. This information can be used to determine if the surface bound chlorine is stable at the high temperatures necessary for diamond growth. The procedure began with the surface dosed with chlorine to saturation level (23 L). The saturation level was ascertained from the experiments described in § 4.2.4. XPS of the saturated surface was recorded over the relevant regions, followed by heating of the surface in small increments, ranging from 20 to 75 K. The XPS spectra were recorded over the same energy ranges as described in

§ 4.2.4. This process was repeated until sufficient desorption (25 % total of the original chlorine concentration) of the surface bound species had occurred.

4.2.6 Reactions on Hydrogenated CVD Diamond

During the CVD process, a large amount of hydrogen both on the surface and in the gas phase is present. A set of experiments were undertaken to simulate these conditions. These experiments investigated the effect of the uptake of chlorine on a pre-hydrogenated surface and the thermal stability of the resulting chlorine adlayer. To pre-hydrogenate the diamond surface, hydrogen was leaked into the chamber to the desired pressure (10^{-4} mbar for 20 minutes). The sample was positioned in front of the tantalum filament and a current was applied to the filament to generate hydrogen atoms. These incident hydrogen atoms hydrogenated the surface. The uptake of chlorine on the pre-hydrogenated surface were similarly performed to that outlined in § 4.2.4. Thermal desorption experiments of the chlorine adlayer on the pre-hydrogenated surface were completed using the same methodology as in § 4.2.5.

4.2.7 Chlorinated CVD Diamond Reactions with Atomic Hydrogen

The chlorine saturation layer was also monitored as a function of hydrogen pressure and time. The initially clean surface was saturated with chlorine (23 L) as outlined in § 4.2.4. As in § 4.2.6, atomic hydrogen was generated when molecular hydrogen was leaked into the chamber to the desired pressure (in the range of $10^{-7} - 10^{-4}$ mbar) and for a certain period. The sample was then monitored using XPS and a decrease in chlorine concentration was observed. Experiments were continued with the hydrogen atom exposure time increasing

until sufficient chlorine was removed from the surface. This experiment was monitored for four different hydrogen pressures (10^{-7} , 10^{-6} , 10^{-5} , 10^{-4} mbar).

4.3 Results

4.3.1 XPS Survey Spectra

Survey scans (Binding Energy (BE) = 0 – 1287 eV) of the annealed diamond surface were acquired to determine the cleanliness of the substrate (Figure 4.4). The only peaks observed occur at 285 eV BE assigned to C 1s, 1222 eV assigned to the Auger transitions of carbon and 534 eV assigned to O 1s. Oxygen is often found in CVD diamond films and accounts for no more than 1 % on this surface. Peaks due to the underlying silicon substrate, as expected, were not present in the spectrum since the diamond film was greater than a few microns thick. No other impurities were observed by XPS. This surface is referred throughout this chapter as the clean or pre-annealed surface.

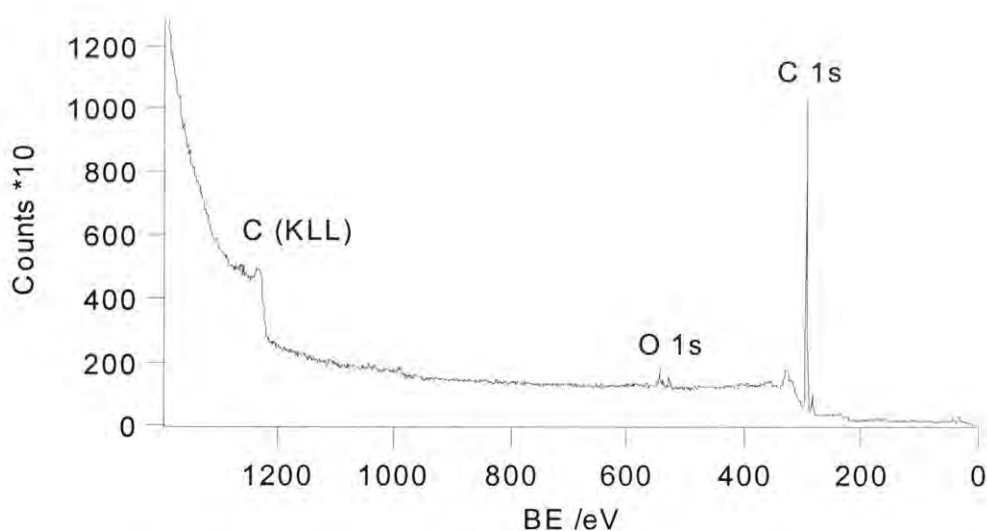


Figure 4.4 Survey scan of the CVD diamond film after heating to 1270 K.

4.3.2 Adsorption of Chlorine on Diamond Films

The adsorption characteristics of chlorine on a pre-annealed diamond surface were studied to understand the adsorption mechanisms involved. Figure 4.5 shows the XP spectra of the Cl 2p region (BE = 190 – 207 eV) as a function of

increasing exposure of chlorine on the initially clean diamond surface at 298 K. One broad photoemission feature was observed. Although not visually discernable due to the limited resolution of the spectrometer, this feature consists of two doublets (each doublet being due to spin-orbit split $2p_{1/2}$ and $2p_{3/2}$ peaks) due to two binding states of chlorine. This is shown in more detail when peak-fitting software is used for the exposures of 2 and 68 L of chlorine on the diamond surface (Figure 4.5).

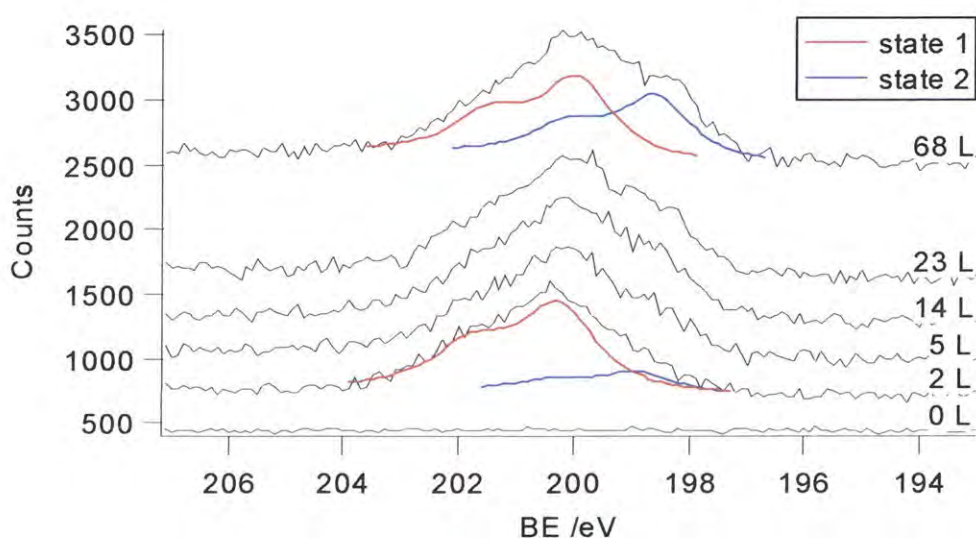


Figure 4.5 The XP spectra of Cl 2p region as a function of molecular chlorine exposure on CVD diamond at 298 K.

The peak at higher binding energy of 200.2 eV ($2p_{3/2}$) has been assigned state 1 while the lower binding energy peak at 198.7 eV ($2p_{3/2}$) has been assigned state 2. These definitions are used throughout the chapter. In each spectrum, the two doublets have a FWHM of 1.6 eV for each individual peak with a peak area ratio of 1:2 for $p_{1/2}$: $p_{3/2}$ doublet and a 1.5 eV separation between them. Peak synthesis of the Cl 2p spectra (1 L to 68 L) shows the following observations. The first doublet has peaks at 200.2 eV ($p_{3/2}$) and 201.7 eV ($p_{1/2}$) at 1 L. The second doublet has peaks at 198.7 eV ($p_{3/2}$) and 200.2 eV ($p_{1/2}$) at

1 L. For higher exposures, the binding energies for both states shift by ~ 0.5 eV. The chlorine states reach saturation following an exposure of 2 L of chlorine gas. The two states populate simultaneously at low coverage as indicated when the areas of the two peaks are plotted against the chlorine exposure (Figure 4.6). For higher chlorine coverage, the uptake rate is reduced with no change in the peak area observed for exposures greater than 15 L. Observe that state 1 has a 30 % greater population than state 2 at saturation coverage.

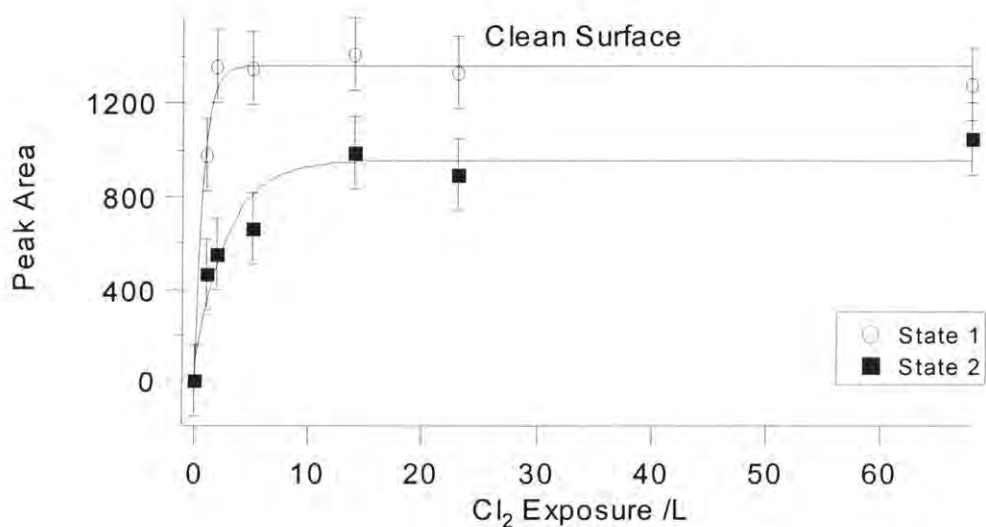


Figure 4.6 The peak area as a function of increasing chlorine exposure for the two different chemical states, state 1 (○) and state 2 (■).

The total coverage of the chlorine on the surface was determined to be 7.2 ± 0.8 % based on the total area of the Cl 2p (3465 counts) and C 1s peak (16443). This calculation takes into account the different number of scans and uses the XPS sensitivity factors for carbon (0.25) and chlorine (0.73).³⁷ The monolayer coverage of chlorine was determined using the covalent radii of carbon (0.077 nm) and chlorine (0.099 nm).³⁸ The calculated monolayer coverage of chlorine on CVD diamond was 0.09 ± 0.01 ML. There are significant errors associated with these calculations due to, for example,

surface roughness, crystallographic heterogeneity and errors in background subtraction.³⁰ Although these errors do affect the calculated monolayer coverage, this value provides an estimate of the chlorine concentration on the surface.

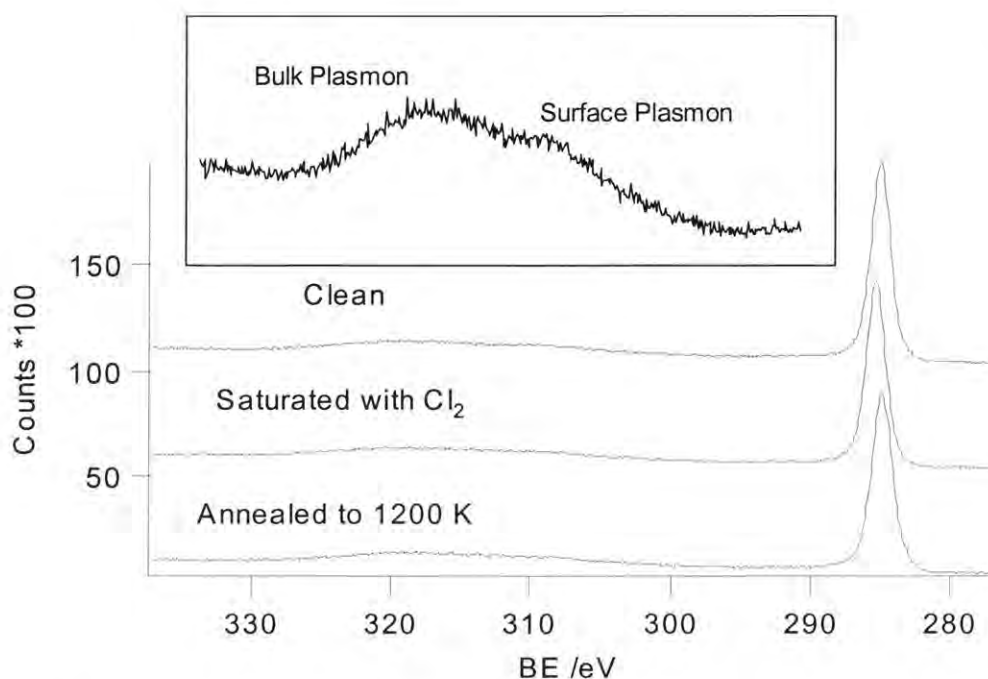


Figure 4.7 The C 1s Region at 3 different periods during the experiment. 1. Clean surface, 2. diamond surface saturated with chlorine and 3. after annealing the surface to 1200 K. The insert shows the plasmon loss spectra of C 1s expanded.

The C 1s region was also monitored at different stages in the experiment. Figure 4.7 shows the C 1s region monitoring the clean diamond film, the effect of a saturated chlorine coverage on the C 1s binding energy position and following desorption of that chlorine layer. Each spectrum has a prominent peak due to the C 1s peak and the plasmon loss region at 310-340 eV (see subset in Figure 4.7). The plasmon loss region is a characteristic feature of diamond thin films and this feature can be used to identify the different carbon phases. The absence of a loss feature 6 eV below the C 1s peak, due to graphite, confirms that the carbon phase of the sample is only diamond.^{8, 35, 36} During the

experiments, the plasmon loss feature retained the diamond characteristics, indicating that the film remained chemically intact and no degradation of the film occurred from etching by chlorine or hydrogen. There were no new features in the C 1s region when saturating the diamond thin film with chlorine although there was a shift to higher binding energy of the C 1s peak of +0.4 eV and a reduction in the peak area by 8 %. The peak shifts back to the clean surface value following annealing of the surface to 1200 K. It should be noted that the chemically shifted carbon peaks, expected on the higher binding energy side of the substrate C 1s peak, due to adsorbed chlorine was not present at all.

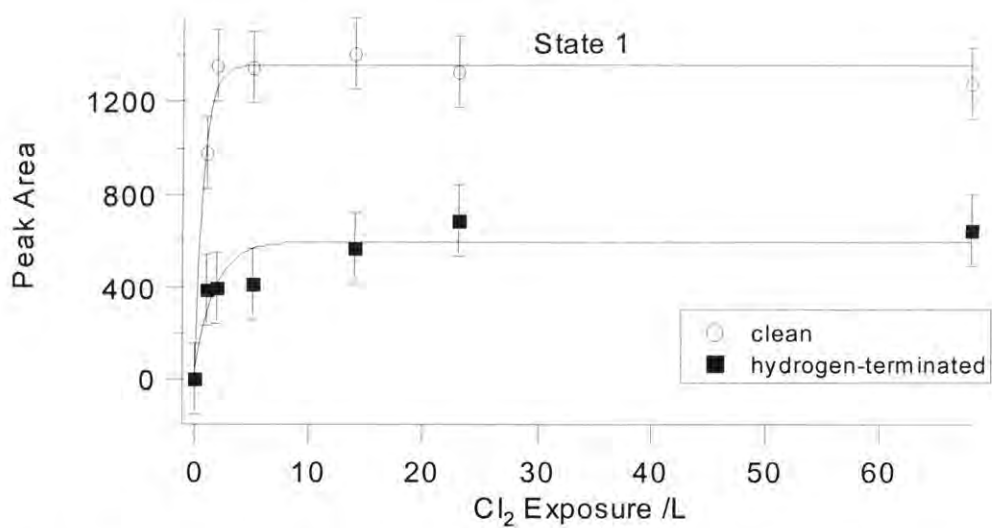


Figure 4.8 A comparison of the uptake of chlorine on a pre-annealed surface (O) and a hydrogen-terminated surface (■) for state 1.

Chlorine adsorption was also studied on a surface that was pre-adsorbed or terminated with hydrogen atoms. The preparation of the hydrogenated or hydrogen-modified surface is described in § 4.2.6. Two peaks are observed for chlorine adsorption on the hydrogen-modified surface with the $p_{3/2}$ component occurring at 200.3 and 199.0 eV, for state 1 and 2, respectively. Examination of the binding energy positions of both states as the chlorine exposure (not

shown) increases does not reveal an apparent shift. The spectra for the adsorption of chlorine on hydrogen-terminated surface are not shown as they are similar in shape to the clean surface spectra (see Appendix A, Figure A2).

Figures 4.8 and 4.9 show the peak areas of the two chlorine states as a function of increasing exposure of chlorine. Figure 4.8 shows the plot of the area of state 1 on a pre-hydrogenated and an initially clean diamond surface at 298 K. Figure 4.9 shows the trend observed for state 2. The raw data for these uptake plots are derived from spectra presented in Figure 4.5 and Figure A2.

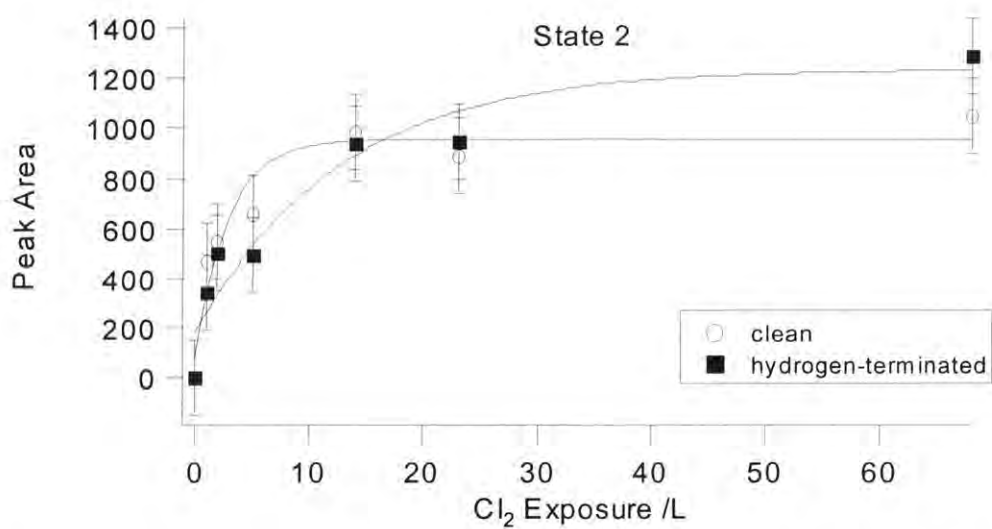


Figure 4.9 A comparison of the uptake of chlorine on an initially clean surface (O) and a hydrogenated surface (■) for state 2.

Both uptake curves for state 1 in Figure 4.8 follow the same characteristic fast uptake followed by levelling out at saturation, with saturation occurring at a lower chlorine concentration as expected on the pre-hydrogenated surface than on the initially clean surface. The maximum concentration of chlorine on the hydrogen-modified surface is 54 % of the clean surface. In contrast, adsorption of chlorine in state 2 on the pre-hydrogenated surface has an initially slower uptake rate than on the clean surface. After 15 L, the rate of chlorine uptake on

the hydrogen modified surface increases for state 2, exceeding chlorine adsorption on the clean surface. At saturation, chlorine adsorbs 30 % more for state 2 on the hydrogen-terminated surface than on the initially clean surface. The uptake for state 2 seems to be activated by the presence of pre-adsorbed hydrogen while surface hydrogen poisoning reduces the coverage for state 1.

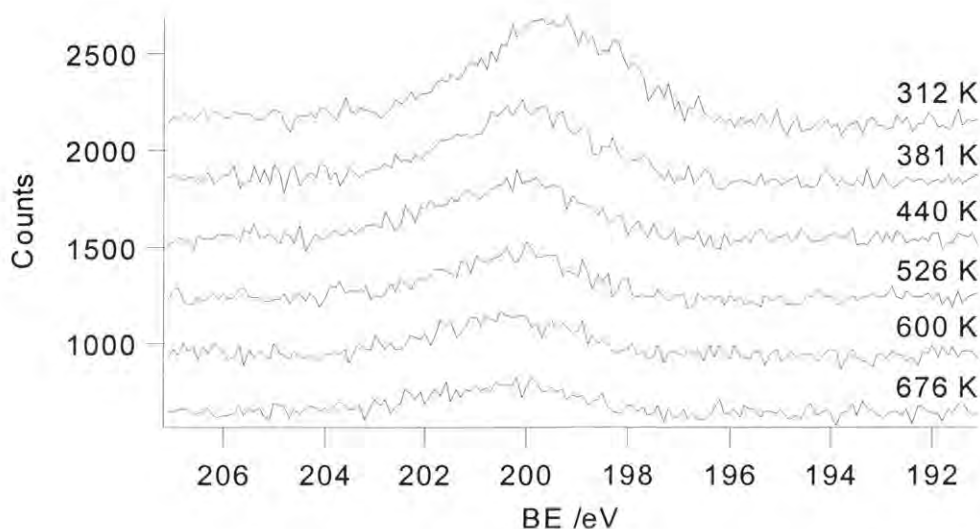


Figure 4.10 The thermal stability of the chlorine layer (Cl_2 exposure is 23 L at 298 K) on a pre-annealed diamond surface observed using the Cl 2p XPS region.

4.3.3 Thermal Desorption of Chlorine on CVD Diamond

Thermal stability of the chlorine adlayer was determined following adsorption on both the clean and hydrogenated diamond surface. This entailed forming a Cl saturated surface, heating, followed by monitoring the remaining chlorine on the surface. The XP spectra of the Cl 2p region following chlorine adsorption on an initially clean surface are plotted as a function of substrate temperature (Figure 4.10). As expected, as the temperature is increased, the peak intensity decreases. This trend is observed when the residual chlorine concentration in terms of area under the Cl 2p peaks is plotted against the substrate temperature (Figure 4.11). In each case, the residual chlorine concentration

was determined for the clean surface by setting the intensity of the saturated chlorine coverage as 1.0 and the intensities of the data points at different temperatures have been normalised to this value. Thermal desorption analysis of the residual chlorine concentration following adsorption on a hydrogen-terminated surface was studied in a similar manner. Peak fitting of this data produces the characteristic two states. Recall that chlorine surface coverage at saturation on a hydrogen-terminated surface reaches a value that is 0.54 of the clean surface value.

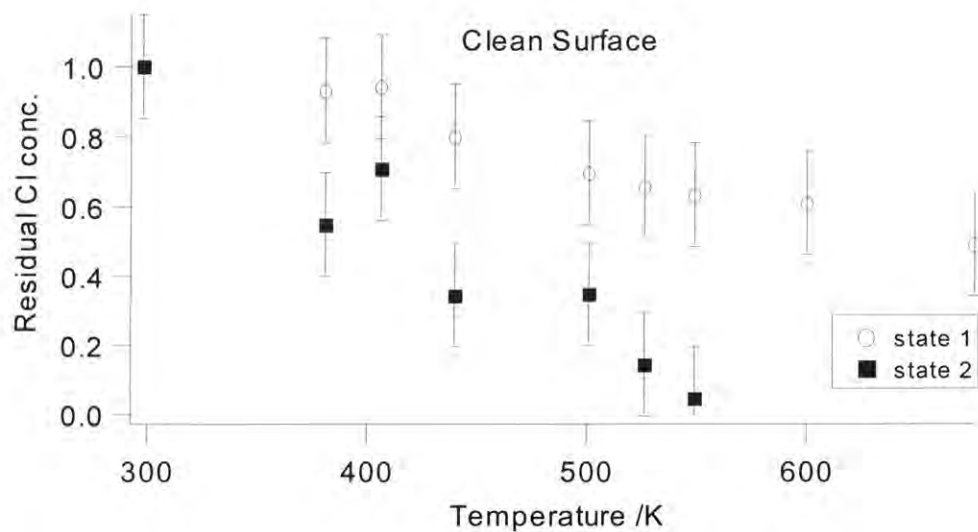


Figure 4.11 The Cl 2p peak area as a function of increasing temperature for the state 1 (○) and state 2 (■) on a pre-annealed diamond surface.

The residual chlorine concentrations in states 1 and 2 are plotted as a function of temperature for the two different surfaces, *i.e.* a clean (Figure 4.11) and hydrogen-terminated surface (Figure 4.12). As expected, for both cases the chlorine concentration decreases as the substrate temperature increases. However, a number of differences between the two surfaces exist. In the case of the clean surface, the chlorine concentration decreases gradually in both state 1 and 2. Chlorine in state 1 is reduced to half its original value only after

heating to ~680 K. Chlorine in state 2 decreases more rapidly and is reduced by 50 % at ~ 420 K, and continues to decrease until state 2 is undetected at ~ 600 K.

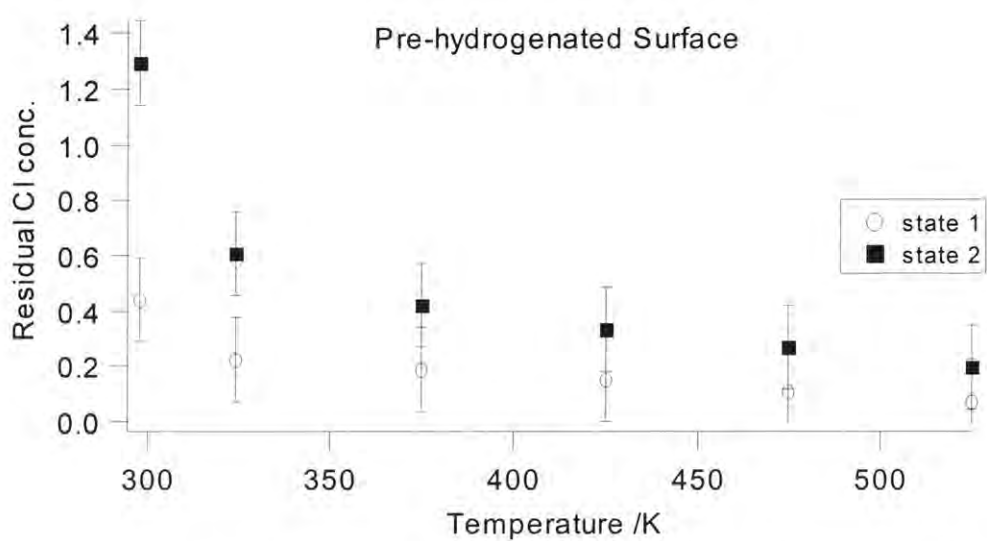


Figure 4.12 The Cl 2p peak area as a function of increasing temperature for the state 1 (○) and state 2 (■) on a hydrogen-terminated diamond surface.

For the pre-hydrogenated case, (Figure 4.12) the initial decreases in chlorine concentration are very rapid for both states. State 1 reduces to 50 % of the original value by ~375 K while for state 2 this occurs at ~320 K. Interestingly, state 2 is more stable for the pre-hydrogenated surface while it is state 1 which is the more stable phase for adsorption on the initially clean surface.

It should be noted that the desorption behaviour of state 2 from both the clean and hydrogen-terminated surface are similar and this is readily observed when the two profiles are plotted on the same graph (Figure 4.13). Conversely, the behaviour of state 1 is clearly different for the two surfaces (Figure 4.14). Chlorine desorbs from state 1 more readily from the hydrogen-terminated surface compared to the pre-annealed surface.

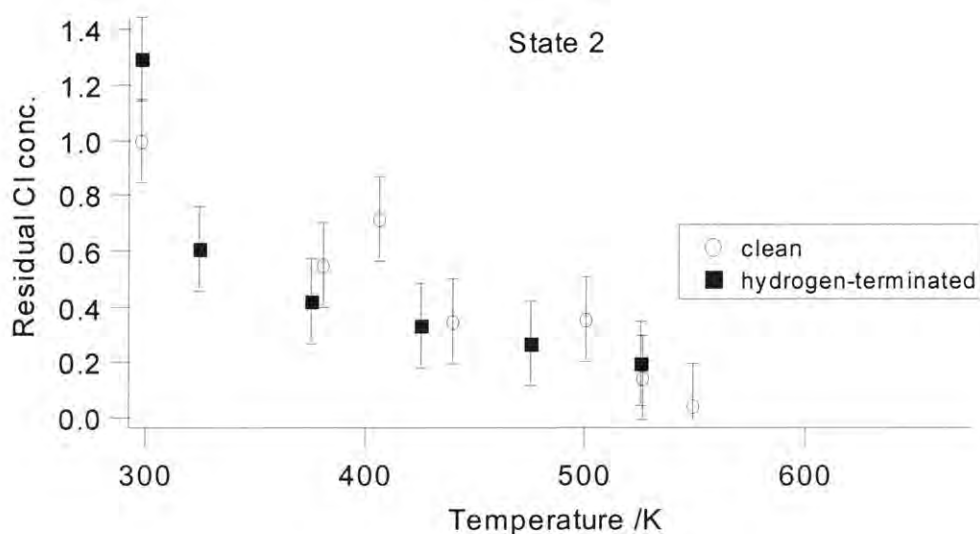


Figure 4.13 The Cl 2p peak area as a function of increasing temperature for the analysis of the thermal stability of surface chlorine (23 L at 298 K) on the pre-annealed (○) and hydrogenated (■) diamond surface for state 2.

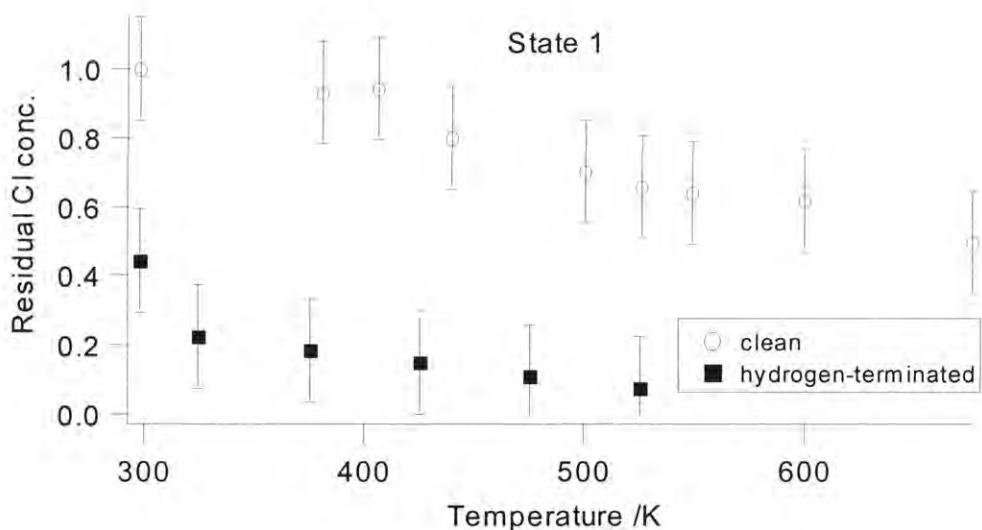


Figure 4.14 The thermal stability of the chlorine layer (23 L at 298 K) on the pre-annealed (○) and hydrogenated (■) diamond surface for state 1, studied using the Cl 2p XPS region.

4.3.4 Hydrogen Etching of the Chlorinated Diamond Film

For these experiments, the clean diamond surface was initially saturated with chlorine followed by etching by atomic hydrogen. Molecular hydrogen was leaked into the chamber at a set pressure (*i.e.* 1×10^{-7} , 1×10^{-6} , 1×10^{-5} or 1×10^{-4}

mbar) to generate hydrogen radicals at these pressures, as described in § 4.2.6. Figure 4.15 and 4.16 show the exposure times of hydrogen graphed against the residual chlorine concentration for state 1 and state 2, respectively.

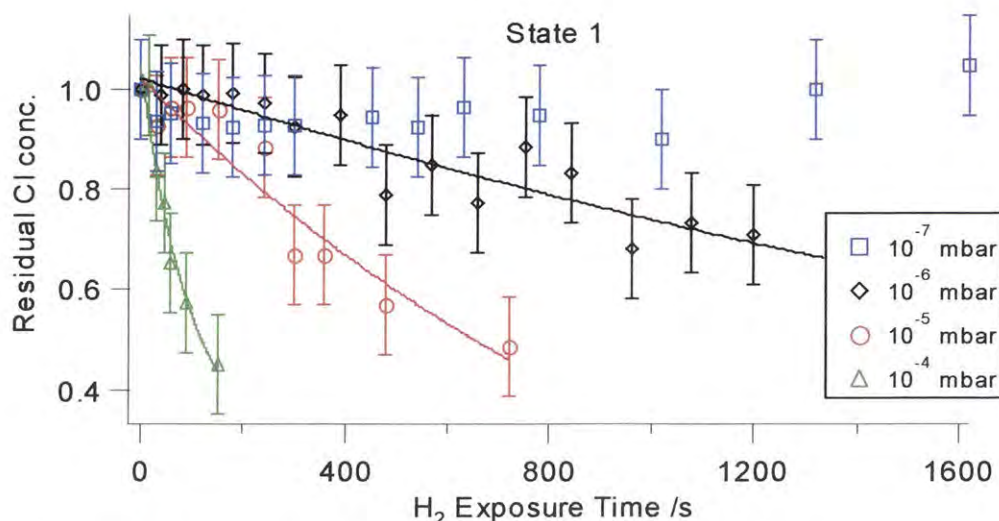


Figure 4.15 The plot of the Cl 2p peak area as a function of hydrogen exposure time at four different pressures for state 1: $P_{H_2} = 10^{-7}$ mbar ($\square$), 10^{-6} mbar ($\diamond$), 10^{-5} mbar ($\circ$) and 10^{-4} mbar ($\triangle$).

For state 1, there is negligible etching of the chlorine for a pressure of 10^{-7} mbar (within experimental error). As the hydrogen pressures increases from 10^{-6} to 10^{-4} mbar, the etching rate steadily increases.

In addition to the decreasing surface chlorine concentration, as the etching proceeds, the chlorine spectra show a shift in the binding energy position for state 1. The binding energy of the saturation coverage is 200.0 eV and this value shifts to +0.8 eV as the surface is exposed to atomic hydrogen. With a 10^{-4} mbar hydrogen pressure, this shift of +0.8 eV was reached within 30 s of the start of the etching while longer times were observed for lower pressures.

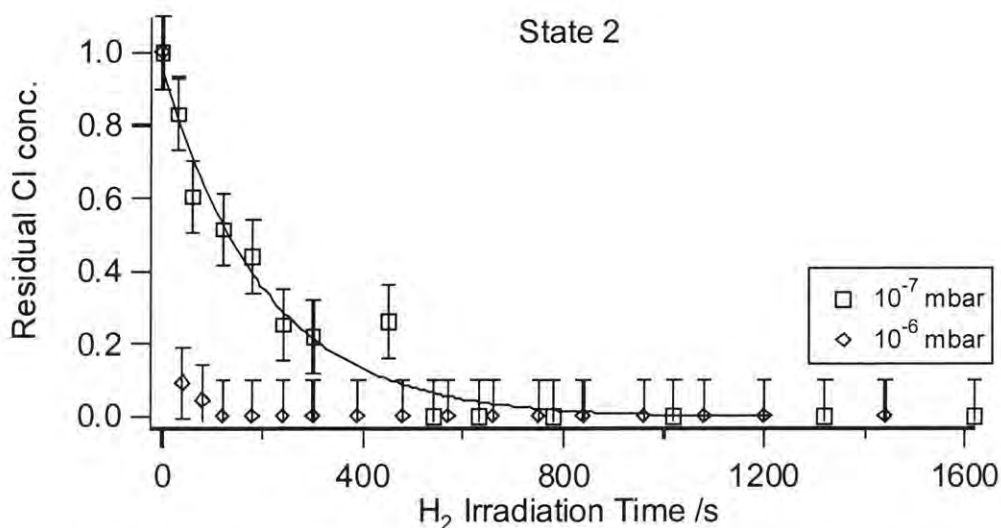


Figure 4.16 The plot of the Cl 2p peak area as a function of hydrogen exposure time at two different pressures for state 2: $P_{H_2} = 10^{-7}$ mbar ($\square$) and 10^{-6} mbar ($\diamond$).

For state 2, chlorine is etched readily at all pressures. In the case of 10^{-4} and 10^{-5} mbar hydrogen pressure there is no chlorine in this state after the first exposure time (15 s) of hydrogen atoms and therefore the results are not included in Figure 4.16. When using a hydrogen pressure of 10^{-6} mbar, the surface chlorine is completely removed after an etching time of 1 minute. A slower etch rate is observed at a hydrogen pressure of 10^{-7} mbar but even so, the chlorine is removed in the relatively short period of 800 s.

An observed shift in the binding energy of chlorine when exposed to hydrogen was also observed for state 2. This shift of +1.3 eV was greater for state 2 and occurred incrementally between 0 – 300 s at 10^{-7} mbar hydrogen pressure while immediately detected after 40 s at 10^{-6} mbar.

4.4 Discussion

The results presented in this chapter give significant understanding of the adsorption, desorption and etching kinetics of chlorine on CVD grown diamond film.

Structurally, CVD diamond surfaces contain a mixture of {100} and {111} textures and defect sites.³⁹ The results presented in § 4.3 indicate that chlorine adsorbs dissociatively onto the surface and binds to at least two different states. It is not uncommon for two or more chlorine states to be observed on diamond surfaces. TPD data of chlorine desorption from diamond powder by Ando *et al.*³⁴ show three distinct chlorine states. Similarly, XPS data for chlorine adsorption on C(100) show two peaks at 198.4 and 200.0 eV.^{34, 40} Limited research has been conducted on the exact nature of these different states.⁴⁰

Similarly, two fluorine states have been observed using the technique of time differential perturbed angular distribution at 60 and 27 MHz for fluorine adsorbed on C(111).^{41, 42} It has been reported that fluorine binds to the C(111) through the p_z orbitals of the carbon to form the covalent C-F bond.⁴³ In that study it was found that fluorine was able to penetrate into the lattice to the depth of the first two layers.⁴³ The fluorine adsorbed between the first two layers is defined as "semi-ionic". "Semi-ionic" fluorine has also been observed in fluorine linked "in-plane" sp^2 C of the graphene layers of carbon black,⁴⁴ the fluorine-graphite intercalation compounds,^{45, 46} fluorine-intercalated carbon fibres,⁴⁷ and fluorinated fullerenes⁴⁸. The term "semi-ionic" represents a bonding configuration that is intermediate between ionic (197 eV for Cl 2p) and covalent (200 eV for Cl 2p) and this is deduced from the XPS binding energies

lying somewhere in between the two values. The exact nature of the “semi-ionic” bond can differ, ranging from the fluorine atom bonded between the top and second layer to a fluorine bridge bond between two carbon atoms. In some cases, such as in the xenon difluoride adsorption on CVD diamond thin films, the exact nature of the “semi-ionic” species is still unknown.³⁰

For fluorine, a “semi-ionic” bond is identifiable by the carbon atom having a low electronic charge while the fluorine has a high electronic charge.^{44, 45} A similar analysis can be conducted on chlorine and the “semi-ionic” bonding state can be identified by calculating the difference between the C 1s and Cl 2p binding energies. The higher of the two differences is the bonding state of the “semi-ionic” species (since Cl 2p peak occurs at lower BE than C 1s, the reverse of F 1s). For the saturation coverage of chlorine on an initially clean surface, with values of 199.8 (state 1) and 198.4 eV (state 2) for Cl 2p_{3/2} and 285.4 eV for C 1s peak, then state 2 with the higher value of 87.0 eV is the “semi-ionic” bound state and state 1 with the lower value of 85.6 eV is the covalent state. Furthermore, compounds with similar BE values to state 1 contain carbon-chlorine covalent bonds. For example, polyvinyl chloride or chlorobenzene have a p_{3/2} peak occurring at ~200 eV, similar to the value for state 1.⁴⁹ Whereas Woedtke *et al.* reported a lower BE value 198.6 eV for chlorine aggregation on C₆₀ which is believed to be a non-covalent interaction as observed for state 2.⁵⁰ The results presented in section 4.3 agree with this assignment and the following discussion will provide clear evidence of this.

The coverage of chlorine (0.09 ML) is quite low and is consistent with Chaney *et al.*³⁹ who observed that the maximum uptake of chlorine on polycrystalline diamond is reduced compared to natural C(100). Theoretical calculations of Cl-

terminated diamond clusters have found that there is appreciable electronic repulsion between neighbouring chlorine atoms, leading to overcrowding.^{31, 51, 52}

There is a 0.1 Å overlap between chlorine atoms on adjacent dimer rows which would prevent adsorption of chlorine atoms on adjacent carbon atoms.⁵² This overlap may inhibit adsorption of chlorine on adjacent carbon atoms and suggest the reason for the low concentration of chlorine, even on natural diamond.

When the surface is saturated with chlorine, the XPS C 1s data shows no additional chemically shifted peaks, indicating that C-Cl is not observed. A similar result is reported for HREELS data of chlorine on C(100) and CVD diamond thin films by Chaney *et al.*³⁹ with no C-Cl stretch peak observed. It has been hypothesised that the chlorine possibly attaches to the C(100) surface as a bridge-bonded species.³⁹ This is not entirely unexpected as has been demonstrated for chlorine adsorption on Si(100).⁵⁸ Such a state would be weakly bound and may explain the weak intensity of the C-Cl peak in the C 1s data. Furthermore, LEED patterns of fluorine adsorbed on C(111) show the surface structure is only perturbed with the (2x1) pattern retained.⁴³ The presence of chlorine on CVD diamond is best described as perturbing the surface carbon and hence the C 1s peak.

This shift in the C 1s spectrum of +0.4 eV when chlorine is adsorbed on the surface and the subsequent shift back upon heating to remove the chlorine layer can be attributed to several phenomena, including surface charging⁵³ and band bending^{30, 47, 53, 54}. A similar shift is observed for fluorine intercalated carbon fibres,⁴⁷ atomic deuterium⁵³ and trifluoromethyl iodide adsorbed on C(100)⁵⁴, and xenon difluorine³⁰ adsorption on CVD diamond films. The exact

nature of the shift observed in this study is difficult to ascertain with the possibility of surface charging and band-bending both contributing to the overall shift. However, the absence of a chemically shifted C-Cl peak in the C 1s spectrum indicates a small coverage and hence unlikely to be due to band bending. Furthermore the low coverage of 0.09 ML based on the Cl 2p/C 1s peak ratios also indicates that surface charging is the most likely reason for the shift.

Hamza *et al.* found that diamond deposition temperatures below 1100 K resulted in the surface bonds being tied up with hydrogen and thus making epitaxial diamond growth slow.³ The uptake of chlorine on a hydrogen-terminated surface indicates that the presence of chlorine in the feedstock could lower the deposition temperature and increase the rate of diamond growth. Unlike atomic hydrogen, which is ineffective at temperatures below 1100 K of abstracting surface bound hydrogen, chlorine reacts with the surface hydrogen to generate new sites. This is observed with the uptake of chlorine on the hydrogen-terminated surface as the chlorine displaces the surface bound hydrogen. These new sites could lead to the deposition of diamond.



Chlorine uptake on the hydrogen-modified surface showed two interesting results for the two different states of the bound chlorine atoms. Both states initially have a reduced uptake rate of chlorine onto the hydrogen terminated surface compared to a clean surface. A surface reaction such as (1) depletes the surface hydrogen.²⁵ If half of every chlorine molecule that arrives at the surface is removed by reacting with hydrogen then this will reduce the initial

uptake of chlorine on the hydrogen-modified surface by half compared to the clean surface. For state 2, there is a subsequent increase in the uptake rate of chlorine after ~15 L. The hydrogenation of the surface activates more sites for chlorine adsorption in state 2. Conversely, the presence of hydrogen poisons the surface for chlorine adsorption in state 1.

Furthermore, the hydrogenation of the surface could result in adsorption of hydrogen at the defect sites. This would allow the impinging chlorine to eliminate/substitute the surface hydrogen and thus adsorb at the defect sites. There is no evidence of a third peak in the Cl 2p XPS region and as suggested in previous work by Chaney *et al.*³⁹ the hydrogen on defect sites is not substituted by chlorine.

The thermal stability of the chlorine layer shows that the covalent state 1 is more stable than the "semi-ionic" state 2 when desorbing from an initially clean diamond surface. This is consistent with the reported studies that found that the covalent C-F layer is more thermally stable than the "semi-ionic" form.^{30, 46} A similar relationship between "semi-ionic" and covalent chlorine is observed in this study.

The thermal desorption profile of state 2 is similar to the desorption profile of chlorine desorption from C(100) with 50 % of the chlorine layer desorbed by 400 K with complete desorption occurring by 600 K.^{26, 27} Freedman *et al.* observed a chlorine peak at 198.6 eV, consistent with the binding energy of state 2.²⁶ It has been hypothesised that chlorine forms a bridge-bond on the dimer of the C(100) surface. Using SIMS, Chaney *et al.* observed predominantly Cl-C₂ fragments when studying chlorine adsorption on C(100)

providing additional support for a bridge-bonding species.³⁹ Furthermore, adsorption of chlorine on a hydrogen terminated C(100) results in an increased population of chlorine.²⁵ The same increase for chlorine adsorption in state 2 on a hydrogen-terminated surface is observed in this study, although not to the same extent as observed for Hadenfelt *et al.*²⁵ Such bridge-bonding is not uncommon for chlorine and reported for a number of systems including metal complexes⁵⁵ and when chlorine adsorbs on Si(100)⁵⁸. The data presented here indicates that the same or similar “semi-ionic” bonding occurs for chlorine adsorption on state 2 in CVD diamond as reported for the C(100) surface and is likely to be a bridge-bonded species.

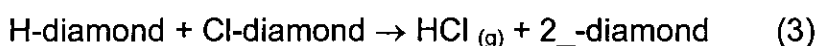
Schmidt *et al.* found that increasing the growth temperature from 690 K to 870 K, reduces the chlorine concentration in the film from 3000 ppm to only 40 ppm when using ethyl chloride to grow diamond thin films.⁶ The chlorine atoms degrade the film quality at low temperatures.^{17, 19} It is hypothesised that the chlorine is incorporated into the diamond films as it cannot desorb completely at lower temperatures.^{6, 17} These temperature ranges indicate that state 2 is not problematic during the growth of CVD diamond thin film as it is weakly bound, completely desorbing by 550 K. Rather, it is state 1 which remains on the surface, bound at > 676 K for the pre-annealed surface and > 525 K for the hydrogen-terminated surface. These results suggest that chlorine incorporation into diamond thin films is due to the covalently bonded state 1.

The etching results in this chapter show that even at 298 K, chlorine can be abstracted by atomic hydrogen. Thus, the presence of chlorine on the surface can increase the number of growth site vacancies at lower temperatures. The weakness of the C-Cl bond enhances the growth of CVD diamond at low

growth temperatures. The removal of chlorine by hydrogen accelerates the generation of active surface sites, which is hypothesised to be a limiting rate step for low temperature diamond growth.¹⁷

The “semi-ionic” state 2 is etched very quickly by atomic hydrogen indicating that the surface state is weakly bound. These results provide additional evidence that state 2 is not present during low temperature diamond growth as the chlorine in this state is either desorbed or etched by atomic hydrogen during CVD conditions.

The covalent chlorine remains on the surface even when etched at 10^{-4} mbar. Although, this does not take into account the more severe conditions in a CVD reactor, characterised by higher temperatures and hydrogen pressures. A similar result was obtained for xenon difluoride adsorption on CVD diamond, with the “semi-ionic” fluorine etched completely, while the covalent fluorine remained on the surface.³⁰ Foord *et al.* hypothesise that the failure to etch the covalent fluorine is due to kinetic rather than thermodynamic factors since the formation of HF is significantly exothermic.³⁰ Since the same thermodynamic forces can be applied to the formation of HCl, the failure to etch the remaining chlorine may be similarly linked to kinetic factors. Covalent chlorine is an important active species during low temperature diamond growth and kinetic analysis of the reaction of atomic hydrogen and surface chlorine will increase the understanding of the creation of active sites for diamond growth at low temperatures.



where _diamond represents a vacant surface site.

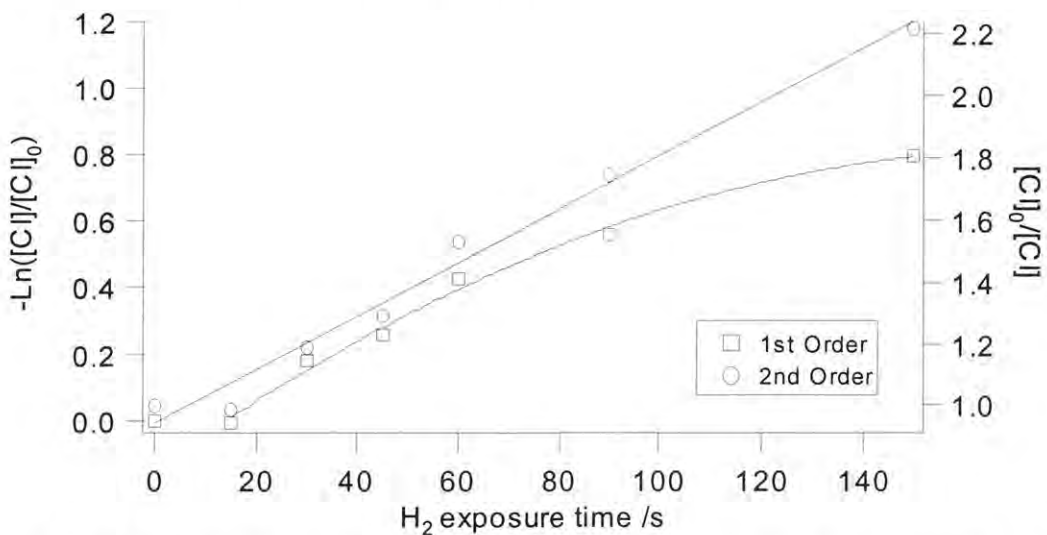


Figure 4.17 The kinetic analysis of chlorine etched by atomic hydrogen ($P_{H_2} = 10^{-4}$ mbar) for both first and second order analysis. First order analysis (left axis) shows the plot of the log of the chlorine concentration $[Cl]$ divided by the saturated coverage, $[Cl]_0$ as a function of hydrogen exposure time ($\square$). Second order analysis (right axis) shows the plot of the saturated coverage, $[Cl]_0$ divided by the chlorine concentrate, $[Cl]$ as a function of hydrogen exposure time ($\circ$).

$$\ln([Cl]/[Cl]_0) = -k(t - t_0) \qquad 1^{st} \text{ order}$$

$$[Cl]_0/[Cl] = k(t - t_0) \qquad 2^{nd} \text{ order}$$

where: $[Cl]_0$ is the original chlorine concentration at t_0

$[Cl]$ is the chlorine concentration at the H_2 exposure time, t

k is the rate constant

In order to determine the kinetics of the etching process, kinetic analysis was performed on the etching data. Initially, the log of the residual chlorine concentration for state 1 was plotted as a function of time to determine if the process was first order. This analysis produced a curve and hence a first order rate was eliminated. Further analysis of state 1 was performed at each

hydrogen pressure, plotting the inverse of the residual chlorine concentration against the etching time (Figure 4.17). This was done to determine if the process was second order. All three plots show a straight line indicating the reaction was second order with respect to chlorine (Figure 4.18).

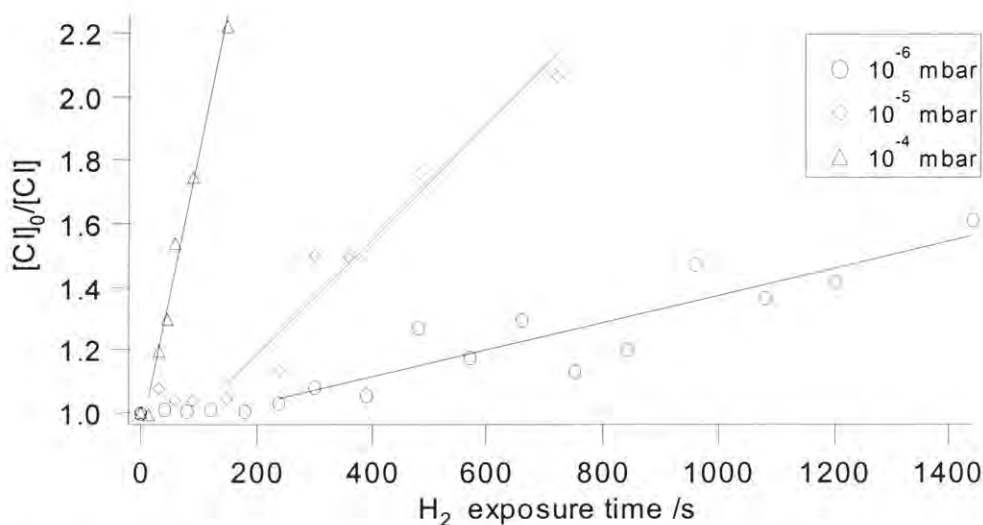


Figure 4.18 The second order kinetic analysis of chlorine etched by atomic hydrogen at a H₂ pressure of 10⁻⁴ mbar [Δ], 10⁻⁵ mbar [$\diamond$] and 10⁻⁶ mbar [$\circ$]. Second order analysis was determined by plotting the saturated coverage, [Cl]₀ divided by the chlorine concentrate, [Cl] as a function of hydrogen exposure time.

Kinetic analysis could not be performed with great accuracy for state 2 due to the limited data available at pressures other than 10⁻⁷ mbar. However, etching of state 2 at 10⁻⁷ mbar may suggest first order with respect to chlorine. Moreover, additional experiments are needed to conclusively ascertain the mechanism including experiments such as molecular beam time-of-flight.

Since the chlorine is adsorbed on the surface, the hydrogen abstraction reaction is a heterogeneous surface mechanism. There are two well-defined mechanisms in the literature, the Eley-Rideal mechanism where a gas phase molecule collides with a surface species to form a new product (2) and the

Langmuir-Hinshelwood mechanism where the reaction between the two surface species takes place on the surface (3).^{56, 57}

The increase of hydrogen pressure from 10^{-7} to 10^{-4} mbar increases the rate at which chlorine is abstracted from the surface by hydrogen for both state 1 and 2. As previously observed with the adsorption of chlorine on the diamond surface, adsorbed hydrogen can also affect the band structure of the diamond surface.⁵³ The hydrogen on the surface causes the additional shifts that are observed in the Cl 2p XPS region. In the case of a hydrogen pressure of 10^{-7} mbar, the charging of the surface occurs simultaneously to the abstraction of chlorine in state 2. Therefore, the abstraction of chlorine in state 2 is independent of the occupations of the surface states by hydrogen. This indicates that reaction (3) is unlikely and alternatively Eley-Rideal gas-surface collisions may occur. Furthermore, the same mechanism has been observed for hydrogen abstraction of bridge-bonded chlorine on Si(100).⁵⁸

The abstraction reaction for state 1 is difficult to confirm based on these results. The brief period of zero etching for 10^{-5} and 10^{-6} mbar of H_2 and zero etching completely for 10^{-7} mbar of H_2 indicates that for the abstraction reaction to occur, there needs to be a build up of hydrogen on the surface. As observed for state 2, there is a shift for state 1 to higher binding energy as atomic hydrogen adsorbs on the surface. This shift is believed to be hydrogen absorption affecting the band structure of the surface. For state 1, a shift of +0.8 eV is immediate in the case of 10^{-4} mbar of H_2 but takes 450 s for 10^{-7} mbar of H_2 . For all four pressures, this +0.8 eV shift occurs before abstraction of state 1 commences. This indicates that sufficient hydrogen has to be adsorbed on the surface, resulting in a change in the band structure of the surface. Moreover, in

the case of a hydrogen pressure of 10^{-7} mbar the shift does occur but no etching of the chlorine layer results. Therefore, there may still be insufficient hydrogen on the surface at this pressure. Nevertheless, the results indicate that the hydrogen abstraction of chlorine in state 1 does proceed through a hydrogen surface activation process (possibly reaction (3)).

The kinetic analysis in this study does not provide sufficient evidence to conclude which mechanism is occurring and additional experiments are necessary in order to determine the mechanism. Charles *et al.* have studied the same reaction on Au(111) using molecular beam time-of-flight (TOF) techniques.⁵⁷ Such an experiment is not feasible with the current instrumentation at the Foord group at Oxford, UK where this study was conducted or at the Singh group at UNSW, Australia. Future collaborations or the acquisition of such an instrument would be worthwhile to determine the exact nature of the chlorine abstraction by hydrogen on CVD diamond surfaces.

4.5 Conclusions and Future Work

The work presented shows chlorine adsorbs onto a CVD diamond surface at two different states. The higher binding energy state has been assigned as state 1 while the lower binding energy state has been defined as state 2.

The first state, at 199.8 eV, is a covalent C-Cl bond that is the stronger of the two and is most likely responsible for chlorine surface reactions during CVD diamond growth. The chlorine has been found to remain on the surface above 676 K on a hydrogen-free surface and above 575 K on a hydrogen-terminated surface. These temperatures are within the range of the lower limits of low temperature diamond deposition and explain chlorine incorporation into the films. The chlorine in state 1 is also found to be more resistant to etching by hydrogen; although CVD conditions require higher hydrogen pressures and this might not be a significant problem.

The second state, at 198.4 eV, involves a "semi-ionic" bond which is probably a bridge-bond between chlorine and two carbon atoms. This bridge-bonded species is weakly bound, desorbing by 400 K from both the pre-annealed and hydrogenated diamond surfaces. In addition, the "semi-ionic" chloride is easily etched by atomic hydrogen, even at 10^{-7} mbar. The ease of desorption of this state and the mild hydrogen pressures at which chlorine can be etched indicates that this state does not participate in low temperature diamond growth when chlorine is a component of the precursor mixture.

There is uncertainty in the abstraction mechanism of surface chlorine by hydrogen for state 1 and 2. It is obvious that the rate of the process for both states is proportional to the chlorine concentration, the hydrogen pressure with

state 1 also involving a surface hydrogen process. A more conclusive analysis is required and the use of molecular beam time-of-flight experiments would be a suitable method.

This work in the future should expand on the themes explored in this chapter in determining the processes for diamond growth, in particular for low temperature diamond deposition. Foord *et al.*³⁰ has already studied the reactions of fluorine (XeF_2) on CVD diamond. Other relevant mechanisms are required to be studied. These include adsorption of methyl radicals onto the CVD diamond and subsequent etching of the hydrogens attached to the methyl radical by fluorine and/or chlorine. The use of methane and the tantalum filament may produce an assortment of radicals, complicating the interpretation of the experimental data. Instead, pyrolysed azomethane is a good candidate to provide information about methyl adsorption on the surface. Similar experiments entailing adsorption of azomethane on a hydrogen- and halogen-modified surface should be investigated. TPD and deuterium labelled experiments would provide additional information on the mechanisms of diamond growth.

This work has provided invaluable information about the various states of chlorine on CVD diamond and the reactions of chlorine and hydrogen on the surface. These reactions in this chapter provide insight into the mechanisms for diamond grown in the presence of halocarbons at low temperatures. Furthermore, the results lay the foundations for exploring the reasons why diamond growth below 410 K is limited when using halocarbons.

4.6 References

1. P. K. Bachmann, R. Messier, *Chem. & Eng. News*, **May 15**, (1989), 24
2. D. D. Koleske, S. M. Gates, B. D. Thorns, J. N. Russell, J. E. Butler, *J. Chem. Phys.*, **102**, (1995), 992
3. A. V. Hamza, G. D. Kubiak, R. H. Stulen, *Surf. Sci.*, **206**, (1988), L833
4. A. Freedman, C. D. Stinespring, *Appl. Phys. Lett.*, **57**, (1990), 1194
5. M. N. R. Ashfold, P. W. May, C. A. Rego, *Chem. Soc. Rev.*, (1994), 21
6. I. Schmidt, C. Benndorf, *Diamond & Rel. Mater.*, **8**, (1999), 231
7. J. S. Foord, K. P. Loh, N. K. Singh, R. B. Jackman, G. J. Davies, *J. Cryst. Growth*, **164**, (1996), 208
8. K. P. Loh, J. S. Foord, R. B. Jackman, N. K. Singh, *Diamond Relat. Mater.*, **5**, (1996), 231
9. R. Joe, T. A. Badgwell, R. H. Hauge, *Diamond & Rel. Mater.*, **7**, (1998), 1364
10. H. Watanabe, S-G. Ri, S. Yamanaka, D. Takeuchi, H. Okushi, *New Diamond and Frontier Carbon Technology*, **12**, (2003), 369
11. A. Badzian, T. Badzian, *Cerm. Inter.*, **22**, (1996), 223
12. H. Maeda, M. Irie, T. Hino, K. Kusakabe, S. Morooka, *Diamond & Rel. Mater.*, **3**, (1994), 1072
13. N. G. Ferreira, E. J. Corat, V. J. Trava-Airoldi, N. F. Leite, *Diamond & Rel. Mater.*, **7**, (1998), 272
14. I. Schmidt, F. Hentschel, C. Benndorf, *Solid State Ionics*, **101-103**, (1997), 97
15. I. Schmidt, F. Hentschel, C. Benndorf, *Diamond & Rel. Mater.*, **5**, (1996), 1318
16. I. Schmidt, C. Benndorf, *Diamond & Rel. Mater.*, **6**, (1997), 964
17. I. Schmidt, C. Benndorf, *Diamond & Rel. Mater.*, **7**, (1998), 266
18. I. Schmidt, C. Benndorf, *Diamond & Rel. Mater.*, **10**, (2001), 347
19. J-J Wu, F. C-N. Hong, *J. Appl. Phys.*, **81**, (1997), 3647
20. M. Asmann, J. Heberlein, E. Pfender, *Diamond & Rel. Mater.*, **8**, (1999), 1
21. D. R. Lide (ED), in: *CRC Handbook of Chemistry and Physics*, 75th edition, CRC Press, Ann Arbor, MI, 1995

22. F. Hentschel, I. Schmidt, C. Benndorf, *Thin Solid Films*, **290-291**, (1996), 196
23. N. J. Komplin, B. J. Bai, C. Chu, L. Maragrove, R. Hauge, *Proc. 183rd Meeting Electrochem. Soc.*, (1993), 385
24. R. M. Fix, R. G. Gordan, D. M. Hoffman, *Mat. Res. Symp. Proc.*, **168**, (1990), 357
25. S. Hadenfeldt, C. Benndorf, *Surf. Sci.*, **402-404**, (1998), 227
26. A. Freedman, *J. Appl. Phys.*, **75**, (1994), 3112
27. A. Freedman, C. D. Stinespring, *Mater. Res. Soc. Sym. Proc.*, **204**, (), 571
28. V. S. Smentkowski, J. T. Yates Jr. *Science*, **271**, (1996), 193
29. D. S. Y. Hsu, N. H. Turner, *4th SDIO/IST Diamond Tech. Initiative Symp. Crsytal City, VA*, (1989)
30. J. S. Foord, N. K. Singh, R. B. Jackman, A. Guiterrez-Sosa, S. Proffitt, K. B. Holt, *Surf. Sci.*, **488**, (2001), 335
31. K. Larsson, S. Lunell, *J. Phys. Chem. A*, **101**, (1997), 76
32. N. Paris, N. Singh, *Proceedings - Australian Conference on Nuclear Techniques of Analysis*, **11**, (1999) 51
33. S. Proffitt, C. H. B. Thompson, A. Gutierrez-Sosa, N. Paris, N. K. Singh, R. B. Jackman, J. S. Foord, *Diamond and Related Materials* **9**, (2000), 246
34. T. Ando, M. Nishitani-Gamo, R. E. Rawles, K. Yamamoto, M. Kamo, Y. Sato, *Diamond & Rel. Mater.*, **5**, (1996), 1136
35. B. R. Stoner, G-H. M. Ma, S. D. Woelter, J. T. Glass, *Phys. Rev. B*, **45**, (1992), 11067
36. D. N. Belton, S. J. Schmieg, *J. Vac. Technol. A*, **8**, (1990), 2353
37. G. Ertl, J. Kupperts, *Low Energy Electrons and Surface Chemistry*, Deutsche Bibliothek Cataloging-in-Publication Data, Weinheim, Germany, (1984), 354-357
38. T. Moellar, *Inorganic Chemistry: A Modern Introduction*, New York, Wiley, (1982), 70 ff., 141 ff.
39. J. A. Chaney, C. S. Feigerle, *Surf. Sci.*, **425**, (1999), 245
40. T. Ando, K. Yamamoto, S. Suehara, M. Kamo, Y. Sato, S. Shimosaki, M. Nishitani-Gamo, *J. Chin. Chem. Soc.*, **42**, 285

41. S. Connell, K. Bharuth-Ram, J. P. F. Sellschop, M. C. Stemmet, H. Appel, J. E. Lowther, *Nuc. Instr. & Meth. Phys. Res.*, **B35**, (1988), 423
42. W. S. Verwoerd, *Nuc. Instr. & Meth. Phys. Res.*, **B35**, (1988), 509
43. T. Yamada, T. J. Chuang, H. Seki, Y. Mitsuda, *Mol. Phys.*, **76**, (1991), 887
44. G. Nanse, E. Papirer, P. Fioux, F. Moguet, A. Tressaud, *Carbon*, **35**, (1997), 371
45. I. Palchan, M. Crespín, H. Estrade-Szwarckopf, B. Rousseau, *Chem. Phys. Lett.*, **157**, (1989), 321
46. M. Koh, H. Yumoto, H. Higashi, T. Nakajima, *J. Fluorine Chem.*, **97**, (1999), 239
47. A. Tressaud, C. Guimon, V. Gupta, F. Moguet, *Mater. Sci. & Eng. B*, **30**, (1995), 61
48. Y. Matsuo, T. Nakajima, S. Kasamatsu, *J. Fluorine Chem.*, **78**, (1996), 7
49. C. Wagner, W. Riggs, L. Davis, J. Moulder, *Handbook of X-ray Photoelectron Spectroscopy*, edited by G. Muilenberg (Perkin Elmer, Eden Prairie, Minnesota, 1979)
50. S. Woedtke, A. Meeder, R. Adelung, R. Schwedhelm, L. Kipp, M. Skibowski, *Phys. Rev. B*, **63**, (2001), 155401
51. M. G. Wensell, Z. Zang, J. Bernholc, *Phys. Rev. Lett.*, **74**, (1995), 4875
52. T. I. Hukka, T. A. Pakkanen, M. P. D'Evelyn, *J. Phys. Chem.*, **99**, (1995), 4710
53. V. S. Smentkowski, H. Jansch, M. A. Henderson, J. T. Yates, Jr., *Surf. Sci.*, **330**, (1995), 207
54. V. S. Smentkowski, J. T. Yates, Jr, X. Chen, W. A. Goddard, III, *Surf. Sci.*, **370**, (1997), 209
55. F. A. Cotton, G. W. Wilkinso, *Advanced Inorganic Chemistry*, John Wiley, New York, 1988
56. B. Jackson, M. Persson, B. D. Kay, *J. Chem. Phys.*, **100**, (1994), 7687
57. Rettner, *J. Chem. Phys.*, **101**, (1994), 1529
58. C.C. Cheng, S. R. Lucas, H. Gutleben, W. J. Choyke, J. T. Yates, Jr., *J. Am. Chem. Soc.*, **114**, (1992), 1249

CHAPTER V

REACTIONS OF $\text{CF}_3\text{CH}_2\text{SH}$ AND $\text{CF}_3\text{CH}_2\text{I}$ ON GaAs(100)

In this chapter, the results for the surface studies of the adsorption and decomposition reactions of $\text{CF}_3\text{CH}_2\text{I}$ (TFEI) and $\text{CF}_3\text{CH}_2\text{SH}$ (TFET) on GaAs(100) will be presented. These two molecules adsorb on GaAs(100) dissociatively at room temperature. In the case of TFEI adsorption leads to the formation of the CF_3CH_2^- and atomic I species while $\text{CF}_3\text{CH}_2\text{S}^-$ and chemisorbed H species for TFET. Additional reactions can occur, including β -fluoride elimination, hydrogen reduction and coupling reactions. The reaction pathway taken by the CF_2CH_2^- species is dependent on the precursor from which it was derived and the identity of the co-adsorbed species, S and H in the case of $\text{CF}_3\text{CH}_2\text{SH}$ adsorption and I for $\text{CF}_3\text{CH}_2\text{I}$ adsorption.

5.1 Introduction

Alkyl reactions are important in understanding the catalytic processes that are widely used in industry. Examples of industrial processes include the Fischer-Tropsch reduction of CO to form longer chain hydrocarbons and the Ziegler-Natta catalysed polymerisation. Until recently, the study of alkyl reactions on semiconductors has been limited and the alkyl reaction mechanisms on these surfaces are not completely understood. Furthermore, few studies have been conducted on GaAs even though GaAs has been reported to be catalytically active.¹ The work presented in this chapter aims to broaden the knowledge of alkyl reaction mechanisms on GaAs by studying the adsorption of $\text{CF}_3\text{CH}_2\text{SH}$ and $\text{CF}_3\text{CH}_2\text{I}$ on GaAs(100). The substitution of the β -carbon with fluorine

provides an additional dimension to this study, as it will enable comparisons of reactivity of these compounds with investigations of ethyl iodide and ethanethiol previously conducted in our research group.

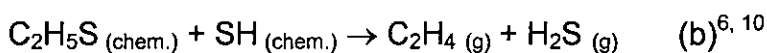
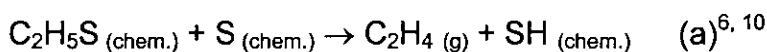
5.1.1. The Effect of the Co-Adsorbed Species on Alkyl Chemistry

The chemistry of the alkyl group can be affected by the co-adsorbed species. One major difference between chlorine, iodine and sulphur, that can affect the chemistry, is that the C-I and C-S bonds thermally dissociate, whereas the C-Cl bond desorbs intact.^{2, 3, 4} Electron irradiation of alkyl chlorides leads to dissociation of the C-Cl bond and the formation of a distribution of hydrocarbon fragments.^{2, 4} When ethyl chloride is irradiated on Ag(111), the fragments combine to give a mixture of ethene, ethane, butene and butane.⁴ Conversely, ethyl iodide and ethanethiol dissociate on Ag(111) and Ag(110), respectively, without electron irradiation.^{3, 5, 6} The sole product of ethyl iodide^{3, 5} adsorption on Ag(111) is butane while ethene, ethane and hydrogen are observed for ethanethiol⁶ adsorption on Ag(110).

The co-adsorbed species can have a profound effect on the rate of formation of the different species on the surface. On Cu(100) and Cu(110) surfaces, the conversion of ethyl groups into ethene is inhibited at high coverage due to large quantities of co-adsorbed iodine.⁷ The iodine atoms forms a "cage" around the alkyl groups, preventing the β -hydrogen from transferring to the surface. At elevated temperatures iodine is partially removed, resulting in the "cage" dissipating and allowing β -hydride elimination to occur. The same "cage" effect can prevent an alkyl group and a hydrogen atom combining on the surface. Furthermore, pre-adsorbed iodine on silver surfaces inhibits C-I bond cleavage

of CF_3I .^{8, 9} This effect reduces the amount of CF_3 species directly bound to the surface. If there is sufficient build-up of iodine on the surface, then only molecular adsorption is observed.⁸

Although the presence of large amounts of iodine on Cu and Ag surfaces can inhibit some reactions, adsorption on sulphided GaAs¹⁰ and Au⁶ surfaces leads to new desorption products. When ethanethiol adsorbs on a pre-annealed GaAs(100) surface, the only desorption products are ethene, ethane, hydrogen and butene.¹⁰ As the surface becomes sulphided, the formation of hydrogen sulphide and two coupling products, butane and diethyl sulphide are detected.¹⁰ These additional products are not observed when studying ethyl iodide on GaAs(100).^{10, 11} Ethanethiol adsorbs on an initially clean Au(100) surface to produce ethene, ethane and hydrogen.⁶ A sulphided Au(100) surface evolves hydrogen sulphide and diethyl sulphide upon ethanethiol adsorption.⁶ On both surfaces, as there is a build up of sulphur on the surface then ethene, ethanethiol and hydrogen sulphide are favoured.^{6, 10} It is postulated that at a high sulphur coverage, there is direct transfer of the hydrogen to surface species without the involvement of the substrate, as shown in reactions (a) and (b) below:^{6, 10}



5.1.2 Alkyl Reactions on Industrial Catalytic and Single Crystal Surfaces

The study of alkyl species on characterised surfaces is an important area of research. This knowledge widens the understanding of the elementary steps in

the catalytic process, e.g. dehydrogenation of paraffins or chain termination in polymerisation reactions. Elementary steps are difficult to determine during catalytic activity because there is usually a distribution of products, and secondary analytical tools for observation during the catalytic process are not available. Single crystal surfaces are excellent models for catalytic activity to study elemental steps and mechanisms using a wide array of surface science techniques.¹² Ziegler-Natta catalysis or Fischer-Tropsch synthesis are examples of catalytic processes where alkyl species are prominent in the mechanism, and surface studies have been used to postulate reaction mechanisms such as shown below:

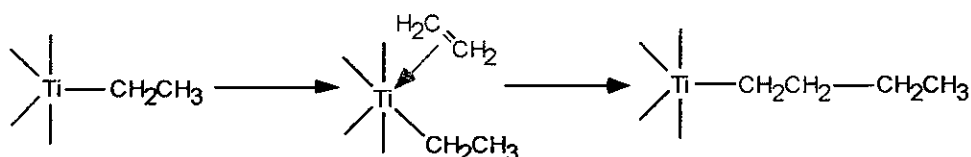


Figure 5.1 The olefin insertion reaction observed in the Ziegler-Natta catalyst.

The Ziegler-Natta catalysis or Fischer-Tropsch synthesis are discussed briefly below as they have relevance to the research results presented in this chapter.

5.1.3 Ziegler-Natta Catalysis and Olefin Insertion

The Ziegler-Natta catalysis generates polymers by olefin insertion into an alkyl species. The reaction site consists of a transition metal salt such as titanium tetrachloride and a metal alkyl, typically triethylaluminium. The first step in the catalytic process involves the migration of one of the ethyl groups from the aluminium centre to the titanium atom. Ethene, introduced into the system, π -bonds to the titanium atom. Subsequently, the π -bonded ethene is inserted between the ethyl group and the metal to produce an *n*-butyl group attached to the titanium atom (Figure 5.1). This olefin insertion process can theoretically

continue infinitely. The ethene site can be re-used after it is vacated for additional ethene to π -bond at the titanium atom and hence continue to increase the hydrocarbon chain length of the *n*-alkyl group. Titanium is not the only element that allows olefin insertion into alkyl groups. It has been widely reported that aluminium also undergoes such reactions.¹³ This catalytic process is least studied for elements in the same group as aluminium in the periodic table. This study hopes to broaden the knowledge of olefin insertion into alkyl species using gallium in the form of a Ga rich GaAs(100) surface.

This olefin insertion process has been proposed for the formation of butene on GaAs(100) by using the precursors $\text{CH}_3\text{CH}_2\text{I}$ and $\text{CH}_3\text{CH}_2\text{SH}$.¹⁰ In order for olefin insertion to take place, there must be a source of both alkyl and alkene groups on the surface at the same time. TPD data indicates that this occurs when CH_3CH_2 - groups adsorb on GaAs(100).¹⁰ Singh *et al.* dismissed other mechanisms such as direct coupling of ethyl groups followed by dehydrogenation since neither butane¹⁰ nor ethene¹⁴ on GaAs(100) are converted to butene. Uncertainty in the mechanism is due largely to the lack of conclusive spectroscopy data. Additional studies are required to further understand olefin insertion in order to improve Ziegler-Natta catalysis.

5.1.4 Fischer-Tropsh Synthesis, Methylene Insertion and Alkyl Termination

The Fischer-Tropsh synthesis is the polymerisation of methylene monomers ($\text{CH}_2=$) generated from the initial dissociation of carbon monoxide on a surface followed by hydrogenation.¹² This synthesis has been established as a means to grow longer chain hydrocarbons. There are numerous mechanisms hypothesised for the Fischer-Tropsh process with each model having its own

merits.^{12, 15} One such mechanism involves the initial formation of a vinyl species ($-\text{CH}=\text{CH}_2$) from a methylene species ($=\text{CH}_2$) and a methyne group ($\equiv\text{CH}$).¹² The carbon chain is increased by methylene insertion into the vinyl species.¹² The polymer terminates by hydrogen reduction to form an alkene.¹² Another possible mechanism proposed is that the methylene species initially react with hydrogen to form a methyl species.¹² Further reactions occur, with methylene species inserted into methyl groups.¹² Termination of the alkyl group results in an alkene or alkane by either β -hydride elimination or hydrogen reduction, respectively.¹²

Methylene insertion is an important process in the Fischer-Tropsch synthesis for carbon skeleton growth. This process has been studied on well-characterised surfaces, especially silver. When CF_3I and CD_2I_2 are co-adsorbed on $\text{Ag}(111)$, CF_3CD_2^- species are formed from CD_2 insertion into adsorbed CF_3 .¹⁶ Additional CD_2 insertion takes place to form $\text{CF}_3\text{CD}_2\text{CD}_2^-$ species. CF_2 groups have also been shown to insert into alkyl groups. When CF_3I is electron irradiated on $\text{Ag}(111)$, CF_2 groups are formed.¹⁷ Subsequently, CF_2 inserts into CF_3 groups to form CF_3CF_2^- on the surface.¹⁷ The three alkyl groups terminate differently with β -fluoride elimination of CF_3CD_2^- occurring to evolve $\text{CF}_2=\text{CD}_2$ while $\text{CF}_3\text{CD}_2\text{CD}_2^-$ combines with surface iodine to produce $\text{CF}_3\text{CD}_2\text{CD}_2\text{I}$, whereas CF_3CF_2^- desorbs directly as a radical.¹⁷

The termination of alkyl groups, especially by β -elimination (Figure 5.2) and hydrogen reduction (Figure 5.3), is a significant step in the Fischer-Tropsch synthesis. Both reactions are observed when alkyl groups are adsorbed on a single crystal surface. Since termination mechanisms usually involve either the

α - or β -carbon then the fluorine substitution at the β -position in the alkanethiol and alkyl iodide may provide valuable information about the chain termination, thus providing information on the reaction pathways of the Fischer-Tropsch synthesis.

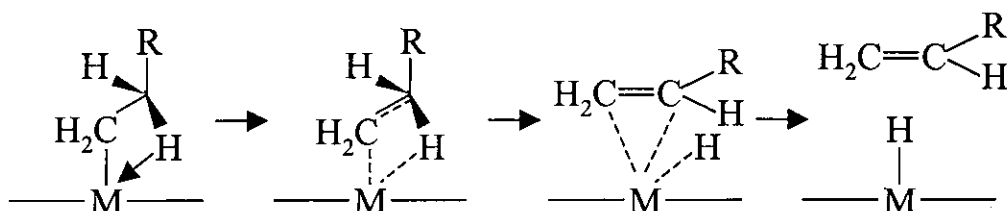


Figure 5.2 β -Hydride elimination of an alkyl group to generate an alkene - a proposed termination mechanism in the Fischer-Tropsch process.¹²

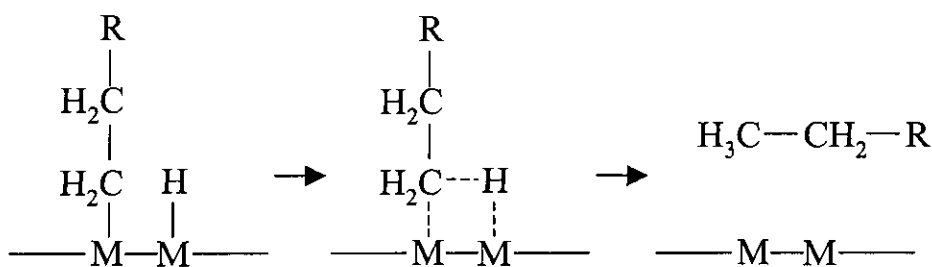


Figure 5.3 Hydrogen reduction of an alkyl group to form an alkane – a proposed termination mechanism in the Fischer-Tropsch process.¹²

Forbes and Gellman have extensively studied the mechanism of alkene formation from alkyl species on copper surfaces.¹⁸ The loss of hydrogen from the alkyl species can proceed through three different intermediates in order for the alkene to form (Figure 5.4). Intermediate (a) and (c) are the result of charge-separated states. Intermediate (a) has the highest energy due to the association of the negative charge with the hydrogen. Whereas intermediate (c) is the most stable as a result of the positively charged hydrogen atom and carboanion formed. Finally, state (b) has intermediary energy due to radical separation. For

propyl groups on Cu(111), the intermediate for propene formation is through the highest energy state (*i.e.* $C^{\delta+} \cdots H^{\delta-}$).¹⁸

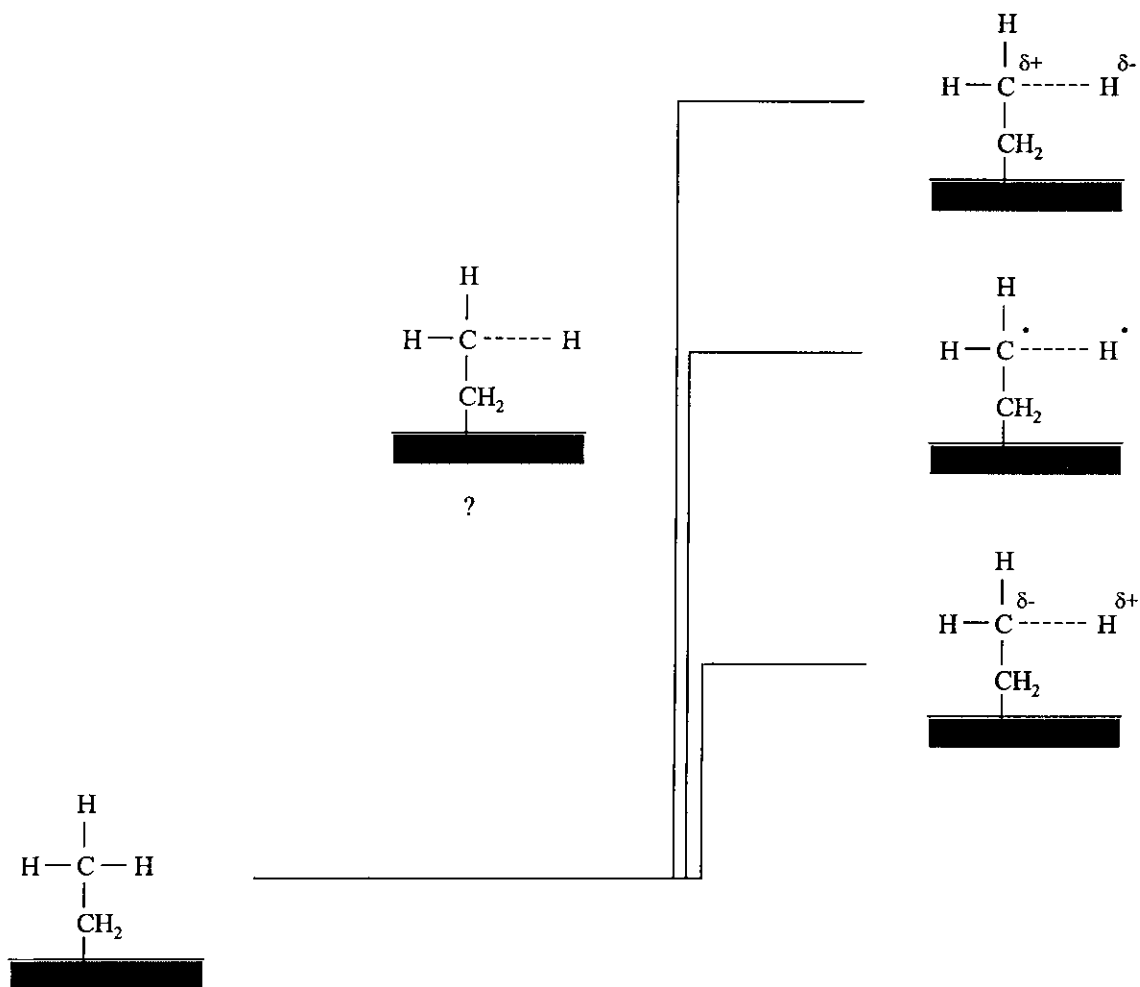


Figure 5.4 The three possible transition states for the formation of ethene from ethyl species on an undefined surface.¹⁸

β -Fluoride elimination has been previously reported for CF_3CH_2I and $CF_3CF_2CH_2I$ adsorption on Ag(111).¹⁹ The activation energy barrier for β -fluoride elimination transition state increases as a result of increase electron withdrawing group at the β -position.¹⁹ Hence the barrier is reduced when one of the fluorine atoms in CF_3CH_2I is replaced with CF_3 as in $CF_3CF_2CH_2I$.¹⁹ This decrease in the reaction barrier indicates a charge transferred state in the form $C^{\delta+} \cdots F^{\delta-}$. Of the three transition states noted above for hydrogen, the formation

of $F^{\delta-}$ would probably have the lowest energy due to the contrast in electronegativity between hydrogen and fluorine.

Once formed, the olefin can remain bonded to the surface and even participate in further chemical reactions as shown in § 5.1.3. The reactions of alkenes on different surfaces provide additional information about the alkene bonding. Fitzgerald *et al.* studied the reactions of ethene on a GaAs(100) surface and found that the molecule adsorbs non-dissociatively on the surface.¹⁴ The adsorption results in a π -bond between ethene and the surface with the C=C bond diminished.¹⁴ Ethene remains intact on the surface between 150 and 650 K with 40 % of the molecules decomposing upon further heating to generate CH_2 and CH groups.¹⁴ The adsorption of $CF_2=CF_2$ on Si(100) is the only fluoro-alkene reported to adsorb on a semiconductor surface.²⁰ The olefin adsorbs intact onto the surface but is unstable at high temperatures, desorbing below 150 K.²⁰ This low temperature desorption is due to the highly electronegative fluorine atoms that withdraw the electron density from the π -bond, effectively creating a single bond between the two carbon atoms.²⁰ Therefore, there is only a weak interaction between the surface and $CF_2=CF_2$.

Hydrogen reduction is also an important termination mechanism on surfaces. The alkane is formed from the reaction of an alkyl group and a hydrogen atom that has migrated to the surface site adjacent to the alkyl group (Figure 5.3). Alkane formation is dependent on the migration of hydrogen to a site adjacent to the alkyl group and the overall reduction is governed by the hydrogen concentration and the presence of an available adjacent site on the surface. At high temperatures, hydrogen is removed from the surface as H_2 desorption and

this competing process reduces hydrogen reduction of alkyl groups.²¹ Therefore, at higher temperatures proportionately more alkyl groups are converted to the alkene than the alkane resulting in alkane desorption at lower temperatures than the alkene. For example, when 1-ethanethiol adsorbs on Mo(110), ethane desorbs at 300 K while ethene at 340 K.²²

5.1.5 The Effect of Fluorine Substitution on the Alkyl Chemistry

Prior to this study of $\text{CF}_3\text{CH}_2\text{SH}$ on GaAs(100), the surface reactions of only two other fluorinated thiols had been studied, $\text{CF}_3\text{CH}_2\text{SH}$ ²³ and $\text{CF}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{SH}$,²¹ both on Mo(110). These two thiols adsorb dissociatively on the surface, breaking the S-H bond to form adsorbed thiolate and surface hydrogen. Napier *et al.*²³ observed four reaction pathways for $\text{CF}_3\text{CH}_2\text{S-}$ species on Mo(110). Initially, dissociation of the C-S bond produces $\text{CF}_3\text{CH}_2\text{-}$ species. β -Fluoride elimination and hydrogen reduction of the $\text{CF}_3\text{CH}_2\text{-}$ species generates $\text{CF}_2=\text{CH}_2$ and CF_3CH_3 , respectively. Direct desorption of the $\text{CF}_3\text{CH}_2\cdot$ radical is also observed. Finally, irreversible decomposition of $\text{CF}_3\text{CH}_2\text{SH}$ produces gaseous H_2 and HF and chemisorbed carbon, fluorine and sulphur.

Increasing the chain length of the fluorinated thiol changes the chemistry as reported for $\text{CF}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{SH}$ on Mo(110).²¹ After the initial cleavage of the S-H bond, the $\text{CF}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{S-}$ species formed further dissociates, with the breaking of the C-S bond. The hydrogen reduction of the alkyl group ($\text{CF}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{-}$) generates $\text{CF}_3\text{CH}_2\text{CH}_2\text{CH}_3$. With hydrogen atoms at the β -position, β -hydride elimination occurs to form $\text{CF}_3\text{CH}_2\text{CH}=\text{CH}_2$. As observed for $\text{CF}_3\text{CH}_2\text{SH}$, there is irreversible decomposition of $\text{CF}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{SH}$ to form the gases HF and H_2 and the adsorbed C, S, F species on the surface. Unlike

$\text{CF}_3\text{CH}_2\text{SH}$, $\text{CF}_3\text{CH}_2\text{CH}_2\text{CH}_2^\bullet$ radicals do not desorb from the surface. Instead, decomposition occurs where a δ -fluorine is eliminated followed by C-C bond scission to form $\text{CF}_2=\text{CH}_2$ and trace amounts of ethene ($\text{CH}_2=\text{CH}_2$).

A comparison of ethanethiol and $\text{CF}_3\text{CH}_2\text{SH}$ adsorption on Mo(110) shows analogous products. Ethanethiol reacts on Mo(110) to yield the elimination and hydrogen reduction products, $\text{CH}_2=\text{CH}_2$, CH_3CH_3 and H_2 . Ethanethiol also reversibly decomposes on Mo(110) to form chemisorbed carbon and sulphur. It is obvious that there are many similarities and differences between the adsorption of ethanethiol and 1,1,1-trifluoroethanethiol on Mo(110). It will be interesting to compare the behaviour of $\text{CF}_3\text{CH}_2\text{SH}$ in this work and $\text{CH}_3\text{CH}_2\text{SH}$ on GaAs(100)¹⁰.

There are significantly more studies of fluoro-alkyl iodides (in particular CF_3I) on metal surfaces than the corresponding thiols.

Usually when an alkyl iodide adsorbs on silver, the predominant mechanism is direct coupling of the alkyl species to form a longer chain alkane with no other carbon containing products formed.⁵ Elimination reactions do not occur on silver due to the inability of the silver surface to hydrogenate.³ However, this selectivity for coupling is not observed when CF_3I is adsorbed on Ag(111). Instead, the only desorption products are CF_3I , CF_3 and I at a low coverage.^{8, 9, 16, 17, 24} A kinetic barrier prevents the formation of hexafluoroethane with lateral repulsion between the CF_3 groups a possible reason.^{8, 9, 16} The desorption of CF_3 radicals, another reaction pathway, is thermodynamically more favourable than CF_3CF_3 formation.⁸ It has already been mentioned that a high coverage of

CF₃I results in electronic and site-blocking effects with only molecular thermal desorption observed.⁸

As previously noted, the electron irradiation of CF₃I adsorbed on Ag(111) produces additional and more interesting chemistry.¹⁷ Dissociation of the C-F results, forming CF₂ groups on the surface.¹⁷ Reactions of CF₃, CF₂ and I produce the CF₃CF₂[•] radical, C₂F₃I and CF₂I₂, none of which involve coupling *via* alkyl reduction.¹⁷ Decafluorobutane is not formed from the direct coupling of a CF₃CF₂- group and probably does not form for the same reasons outlined for hexafluoroethane formation from CF₃ groups. Clearly the alkyl fluoride species on Ag(111) surface do not directly couple to form the corresponding longer chain alkanes. This behaviour is different to that of hydro-alkyl iodides, where as noted above the only product is alkyl reduction to form higher alkanes.

Increasing the carbon length to CF₃CH₂I and CF₃CH₂CH₂I on Ag(111) does not produce alkyl reductive coupling either.¹⁹ Paul *et al.* observed that increased fluorine substitution of the alkyl group leads to a decreased rate of coupling.^{19, 25} The electronegative fluorine atoms either destabilise the transition state or stabilise the electron rich initial state.²⁵ The co-adsorption of fluorine substituted and unsubstituted alkyl species on the Ag(111) surface does lead to direct cross-coupling products but only in small concentrations.²⁵

Adsorption of CF₃I has also been observed on other surfaces including Ni(100),²⁶ Cu(111),²⁷ Pt(111)²⁸ and Ru(001)²⁸. On Ni(100), CF₃I behaves in a similar fashion to Ag(111) with only CF₃ and I radicals desorbing from the surface.²⁶

On Cu, Pt and Ru surfaces, CF_3I adsorption results in the breaking of the C-I and C-F bonds.^{27, 28} C-I and C-F bond cleavage on Cu(111) results in complete conversion to CF_2 with $\text{CF}_2=\text{CF}_2$ desorption only observed.^{27, 28} This methylene coupling is similar to when CH_2I_2 adsorbs onto Cu(111) with the desorption of $\text{CH}_2=\text{CH}_2$ reported.^{27, 29} When CD_2I_2 and CF_3I are co-adsorbed on Cu(111), cross-coupling occurs to produce $\text{CF}_2=\text{CD}_2$.²⁷ On the Pt(111) surface, only partial dissociation of the CF_3 groups occurs to form CF_2 .²⁸ No coupling occurs on the Pt(111) surface with most of the species leaving the surface as radicals (*i.e.* CF_2 , CF_3 and CF_3I).²⁸ On Ru(001) similar desorption products are observed as reported for Pt(111) with the only exception being the addition of CF_4 evolution by the combination of CF_3 and atomic F.³⁰

Si(100) is the only semiconductor surface where reactions of fluoro-alkyl iodides have previously been studied.²⁰ It was observed that trifluoromethyl iodide dissociates to form SiF_2 , SiF_4 , atomic I and a mixture of C_2F_x species.²⁰ The C_2F_x species are formed from dissociation of the C-I and C-F bonds.²⁰ When the carbon chain is increased to 2,2,2-trifluoroethyl iodide, there are no coupling products observed with $\text{CF}_2=\text{CH}_2$, SiF , atomic I, HI and H_2 the only desorption products formed.²⁰ The hydrogen from HI and H_2 is derived from α -hydride elimination with the electron withdrawing nature of the CF_3 group resulting in a partial negative charge on the α -carbon that allows the C-H scission to occur more readily.

Alkyl iodides have been studied on a number of surfaces but the more relevant reports are the analyses of alkyl iodides on GaAs(100) and in particular $\text{CH}_3\text{CH}_2\text{I}$. Singh *et al.* reported that ethyl iodide dissociates on the surface to form ethyl species and atomic iodide.¹¹ The ethyl groups undergo several

reactions including the desorption of ethene, ethane and butene. The presence of iodide atoms also produces etch products including As_2 , As_4 , GaI and AsI . Other iodide-containing molecules such as CH_2I_2 and CH_3I have been investigated on $\text{GaAs}(100)$ and shown to be effective at etching GaAs .³¹

These results indicate that substitution of the alkyl group with fluorine creates new and interesting chemistry which in most cases differs from unsubstituted alkyl iodide adsorption.

5.1.5 Aims

The aim of this work is to investigate the reaction products formed and thus to elucidate the reaction mechanisms of $\text{CF}_3\text{CH}_2\text{SH}$ and $\text{CF}_3\text{CH}_2\text{I}$ on $\text{GaAs}(100)$.

This aim is achieved by:

1. Studying the bonding and structural characteristics of the adsorption of $\text{CF}_3\text{CH}_2\text{SH}$ and $\text{CF}_3\text{CH}_2\text{I}$ using XPS, AES and LEED techniques.
2. Identifying desorption products formed by surface reactions of $\text{CF}_3\text{CH}_2\text{SH}$ and $\text{CF}_3\text{CH}_2\text{I}$ by mass spectrometry TPD scans.
3. Elucidating the reaction mechanisms of $\text{CF}_3\text{CH}_2\text{SH}$ and $\text{CF}_3\text{CH}_2\text{I}$, in particular, the β -fluoride elimination, hydrogen reduction and coupling reactions on $\text{GaAs}(100)$.
4. Comparing the influence of the co-adsorbed sulphur and iodine on the $\text{CF}_3\text{CH}_2\text{SH}$ and $\text{CF}_3\text{CH}_2\text{I}$ reactions.

SECTION B

SURFACE REACTIONS OF 2,2,2-TRIFLUOROETHANETHIOL ON GaAs(100)

5.2 Results

5.2.1 TPD Studies of 2,2,2-Trifluoroethanethiol

The initial set of experiments involved exposing the clean GaAs (100)-(4x1) surface to 2,2,2-trifluoroethanethiol (TFET) and subsequent analysis of the desorbing species using a quadrupole MS in a temperature programmed desorption (TPD) scan. During these experiments, three fluorocarbon products were detected, 1,1,1-trifluoroethane (CF_3CH_3), 1,1-difluoroethene (CF_2CH_2) and 1,1-difluoro-4,4,4-trifluorobutene ($\text{CF}_2=\text{CHCH}_2\text{CF}_3$). Apart from the aforementioned, desorption of hydrogen and As_2 were also observed. Each species' identity was confirmed by studying fragmentation patterns based on literature mass spectrometry data (see Appendix B, B1 for the literature spectra).

In Figure 5.5, the parent ion $\text{CF}_3\text{CH}_2\text{SH}$ ($m/z = 116$ amu) is shown as a function of TFET exposure at an initial substrate temperature of 300 K (Figure 5.6). Two desorption peaks are observed, that populate simultaneously. The low-temperature peak (State I) initially evolves at 438 K for a low surface coverage (10 L) shifting to 410 K at saturation coverage (100 L). This shift to lower temperatures as the coverage increases is indicative of second order kinetics, suggesting that the desorption of $\text{CF}_3\text{CH}_2\text{SH}$ occurs *via* recombination of surface $\text{CF}_3\text{CH}_2\text{S}$ - and atomic hydrogen. State II consists of a peak maximum at 530 K for 10 L that shifts to higher temperature as the coverage increases.

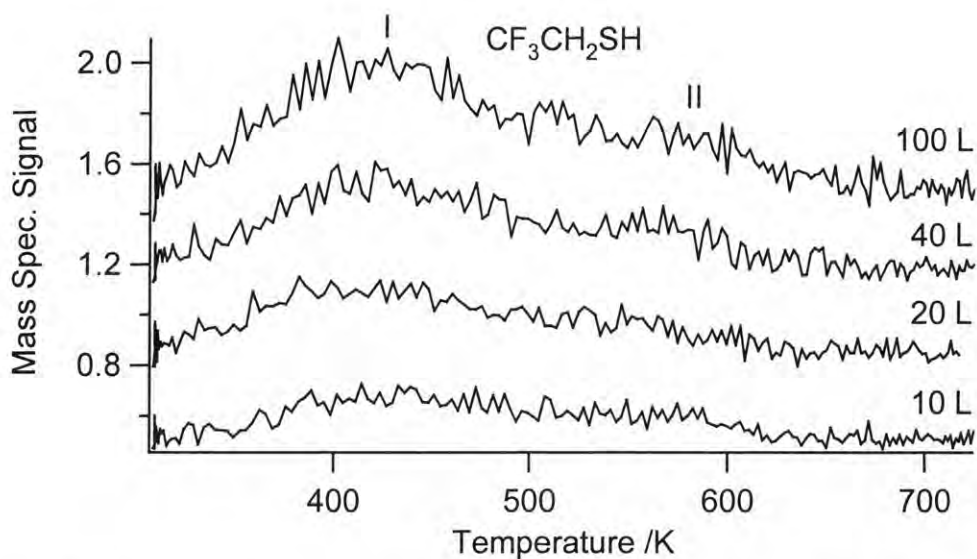


Figure 5.5 The temperature programmed desorption (TPD) spectra of the uptake of TFET on $\text{GaAs (100) - (4x1)}$ monitoring $m/z = 116$ amu ($\text{CF}_3\text{CH}_2\text{SH}$) at 300 K. The temperature ramp is 10 K s^{-1} .

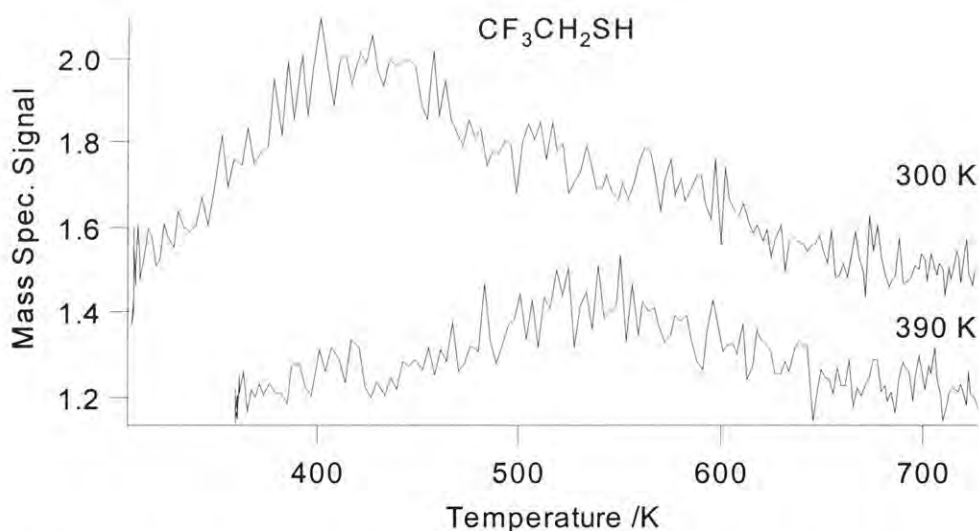


Figure 5.6 The temperature programmed desorption (TPD) spectra monitoring the desorption of TFET ($m/z = 116$ amu) from $\text{GaAs (100) - (4x1)}$ at 300 K and at a higher temperature of 390 K where the first state does not populate. The temperature ramp is 10 K s^{-1} .

The high-temperature state of $\text{CF}_3\text{CH}_2\text{SH}$ was studied further by exposing the surface with TFET (100 L) at room temperature and then at 390 K (when the low-temperature state is not expected to be stable on the surface) followed by a

TPD scan (Figure 5.6). The room temperature adsorption profile shows the two peaks previously observed in Figure 5.5. However, the TPD profile following adsorption at 390 K displays only one peak at 530 K with no contribution from the low-temperature state. Therefore, state (II) forms independently of state (I). A fragment of $\text{CF}_3\text{CH}_2\text{SH}$, the HSCH_2^+ ($m/z = 47$ amu) species was monitored to confirm (see Appendix B, §B1 for spectra) that the desorption traces in Figure 5.5 and 5.6 were indeed due to the desorbing $\text{CF}_3\text{CH}_2\text{SH}$ species. The TPD scan monitoring HSCH_2^+ for an exposure of 100 L showed a profile that resembled the $\text{CF}_3\text{CH}_2\text{SH}$ profiles presented in Figure 5.5 and 5.6.

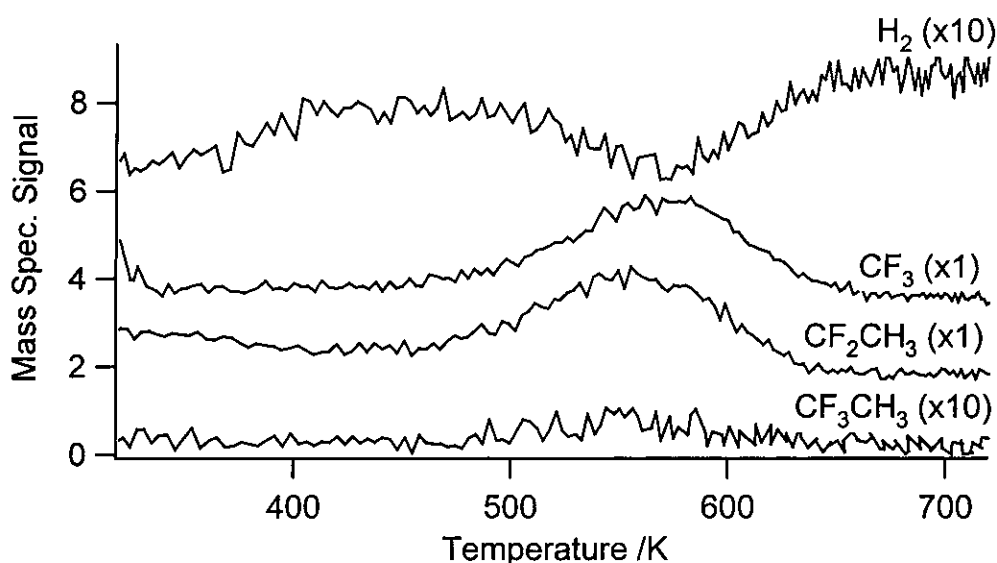


Figure 5.7 The temperature programmed desorption (TPD) spectra of H_2 ($m/z = 2$ amu), CF_3 (69 amu) CF_3CH_3 ($m/z = 84$ amu) and CF_2CH_3 ($m/z = 65$ amu) monitored after adsorption of TFET on GaAs (100) - (4x1) at 300 K. The temperature ramp is 10 K s^{-1} .

The evolution of H_2 ($m/z=2$), 1,1,1-trifluoroethane ($m/z = 84$), CF_3 ($m/z = 69$) and CF_2CH_3 ($m/z = 65$) (fragments of 1,1,1-trifluoroethane) were also monitored and the TPD traces are presented in Figure 5.7.

The hydrogen TPD spectrum consists of two peaks. The low-temperature peak is broad, stretching between 400 and 580 K and is due to combination of

surface hydrogen. This temperature range is consistent with previous investigations of the adsorption of atomic hydrogen from Ga-rich GaAs(100) surface sites where a temperature range of 380 to 580 K was observed.³² The second peak is centred at 650 K. This peak maxima is consistent with hydrogen desorption from As-rich GaAs(100) surface sites.³² Also note that the hydrogen spectrum has a rising background. This problem is the result of contributions of hydrogen in the background.

CF₃CH₃ and its cracking fragments, CF₃ and CF₂CH₃ show desorption at 555 K (Figure 5.7). Application of the Redhead equation to the CF₃CH₃ peak, using a pre-exponential factor of 10¹³ s⁻¹ and a heating rate of 10 K s⁻¹, gives an activation energy of desorption of CF₃CH₃ to be 138 kJ mol⁻¹. It should be noted that the CF₃ peak contains a shoulder on the higher temperature side which is due to the coupling product CF₂=CHCH₂CF₃ which will be discussed below.

In order to elucidate the mechanism by which CF₃CH₃ forms, isotope scrambling experiments were performed using deuterium. The clean surface was first dosed with deuterium (600 L) to a sub-monolayer coverage under an electron beam, the latter being produced by the AES gun. Following this process, the surface was dosed with TFET (100 L). It is known that CF₃CH₃ dissociates readily in the mass spectrometer such that only approximately 1 % of the parent ion current is detected.³³ Therefore, a more intense ion fragment of CF₃CH₃ that contains no contributions from any other source was used. The fragments ⁺CF₂CH₃ (m/z = 65) and CF₂CH₂D (m/z = 66) were monitored (Figure 5.8) since ⁺CF₂CH₃ is only a fragment of CF₃CH₃ and the CH₃ group is still intact allowing deuterium scrambling experiments to be observed. Both the CF₂CH₂D and CF₂CH₃ desorption traces show a peak at ~ 550 K. Therefore,

this observation indicates that CF_3CH_3 is formed from the combination of surface CF_3CH_2 - and surface hydrogen.

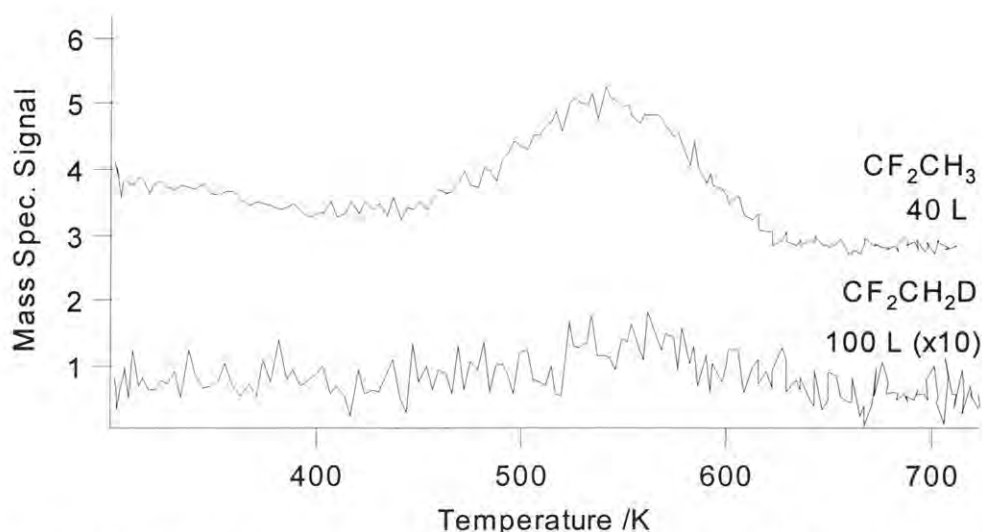


Figure 5.8 The temperature programmed desorption (TPD) spectra monitoring desorption of CF_2CH_3 ($m/z = 65$ amu) and $\text{CF}_2\text{CH}_2\text{D}$ ($m/z = 66$ amu), the most intense fragments of CF_3CH_3 and $\text{CF}_3\text{CH}_2\text{D}$, respectively. These spectra were observed after adsorption of 40 L of TFET on a clean (*i.e.* CF_2CH_3) surface and 100 L of TFET on a partially deuterated (*i.e.* $\text{CF}_2\text{CH}_2\text{D}$) surface at 300 K. The temperature rate is 10 K s^{-1} .

The $\text{CF}_2=\text{CH}_2$ desorption profile consists of prominent feature at 500 K (Figure 5.9). Application of the Redhead equation, using a pre-exponential factor of 10^{13} s^{-1} and a heating rate of 10 K s^{-1} , gives activation energy of 125 kJ mol^{-1} . The mass spectrometer fragments of $\text{CF}_2=\text{CH}_2$ ($m/z = 45$ amu CFCH_2^+ , 31 amu CF^+)³³ were used to confirm the identity of this product. Both ion fragments' TPD traces (see Appendix B, §B1 for the spectra) contain a peak at 500 K in agreement with Figure 5.9. It should be noted that these species do not form part of fragmentation patterns of any other desorbing species and are representative of the desorbing $\text{CF}_2=\text{CH}_2$ species.

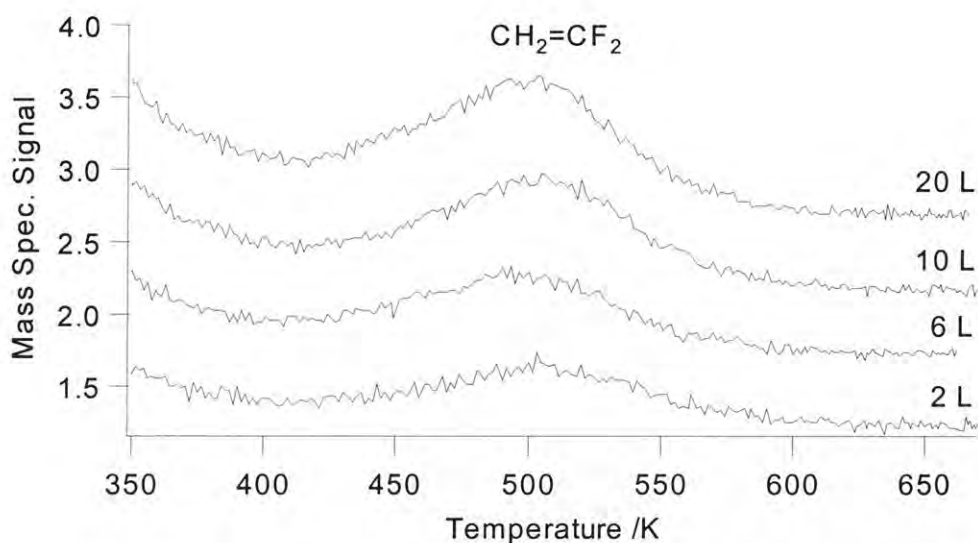


Figure 5.9 The TPD spectra of the uptake of TFET on GaAs (100) - (4x1) monitoring the desorption of $\text{CF}_2=\text{CH}_2$ ($m/z = 64$ amu) from GaAs (100) - (4x1) at 300 K. The temperature ramp is 10 K s^{-1} .

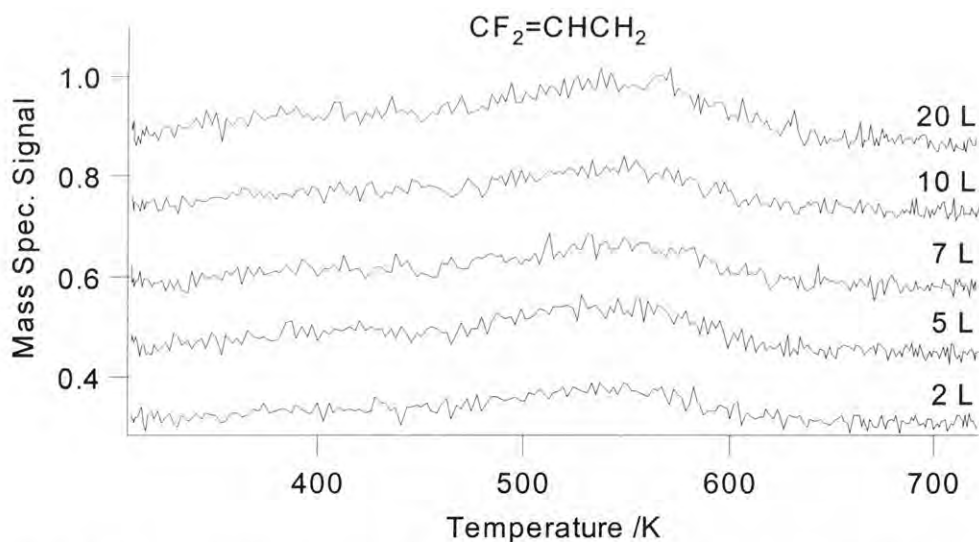


Figure 5.10 The TPD spectra of the uptake of TFET on GaAs (100) - (4x1) monitoring the fragment ($m/z = 77$ amu) at 300 K. The temperature ramp is 10 K s^{-1} .

In addition to hydrogen reduction and β -fluoride elimination, coupling products were investigated. Desorption profiles of some of the possible coupling products, e.g. $\text{CF}_3\text{CH}_2\text{CH}_2\text{CF}_3$ and $\text{CF}_2=\text{CHCH}_2\text{CF}_3$, were monitored. Neither showed any desorption features. However, the fragment ion $\text{CF}_2\text{CH}=\text{CH}_2^+$

($m/z=77$) was detected with a peak centred at 538 K (Figure 5.10) which corresponds to a desorption energy of 135 kJ mol^{-1} . The parent ion, $\text{CF}_3\text{CH}_2\text{CH}=\text{CF}_2$ ($m/z = 146$), was not detected and possibly due to low sensitivity, however, a shoulder in the CF_3 peak (see Figure 5.7) at the high temperature side provides further evidence that indeed $\text{CF}_3\text{CH}_2\text{CH}=\text{CF}_2$ is formed. The 77 amu ion is highly likely to be the mass spectrometer ion source fragmentation of this species. It has been reported that the CF_3 group (in the C1 position) weakens the bond between C1 and C2 in a C4 system.²¹ This is likely to occur for $\text{CF}_2=\text{CHCH}_2\text{CF}_3$, and the fragmentation produces $^+\text{CH}_2\text{CH}=\text{CF}_2$ ($m/z = 77$) ions which is detected in the mass spectrometer. This species is a resonance-stabilised allylic carbocation and hence is expected to be very stable in the mass spectrometer. Furthermore, as observed for CF_3CH_3 , dissociation of fluorine-containing species can result in the parent ion dissociating almost completely in the mass spectrometer.

Etching products of the surface were also investigated. Only As_2 ($m/z = 150$) was found with no evidence of GaF ($m/z = 88$), AsF ($m/z = 94$), GaS ($m/z = 101$) or AsS ($m/z = 107$). As_2 desorbs from the surface at 710 K for a clean surface due to incongruent melting of the GaAs and this is observed in the 0 L spectra of Figure 5.11 with a shoulder occurring at 710 K.^{11, 34} The surface was then heated to 700 K, below the anneal temperature to prevent re-ordering of the surface. This was followed by exposing the surface to TFET, then monitoring As_2 via a TPD scan, followed by heating to 700 K, etc.. As the TFET exposure was increased, the onset of desorption of As_2 is different and this temperature shifts to lower temperatures for successive TPD scans. This indicates that a build up of As_2 has occurred on the surface, the result of

etchants diffusing into the bulk and disrupting the Ga-As bonds. In the case of TFET, fluorine is the etchant, resulting from the β -fluoride elimination. The fluorine migrates in the bulk to form GaF with As₂ deposited onto the surface. The GaF desorbs spontaneously and is not detected.

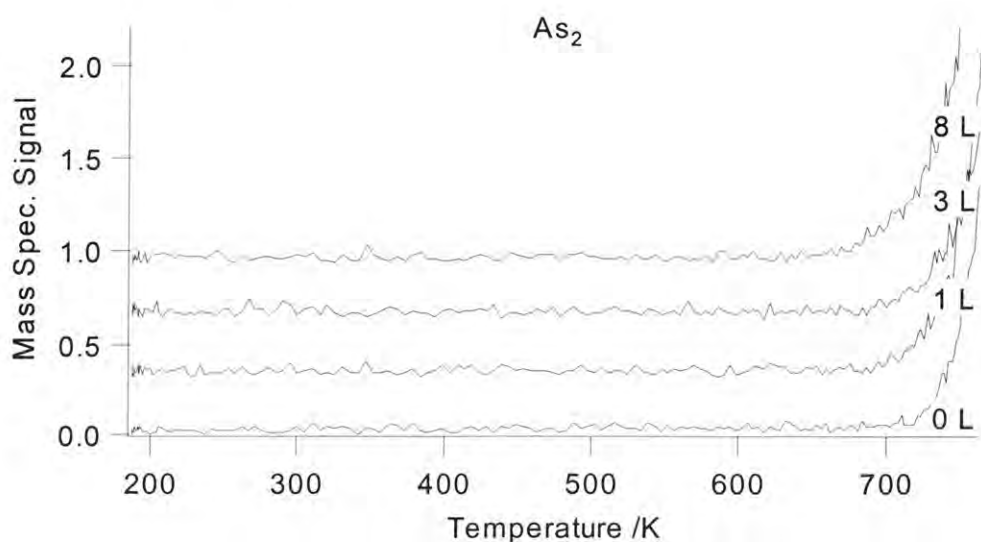


Figure 5.11 The TPD spectra of the uptake of TFET on GaAs (100) - (4x1) monitoring $m/z = 150$ amu (As₂) at 300 K. Between each experiments, the surface was heated to 710 K, instead of the usual annealing temperature of 770 K to prevent the reordering of the surface. The exposure values represent the overall exposure of TFET on the surface. The temperature ramp is 10 K s^{-1} .

It should also be noted that the following species were monitored but not detected. These included the direct alkyl coupling product, $\text{CF}_3\text{CH}_2\text{CH}_2\text{CF}_3$ ($m/z = 166$ amu), the fluorine reduction of CF_3CH_2^- to produce $\text{CF}_3\text{CH}_2\text{F}$ ($m/z = 102$ amu), hydrogen sulphide ($m/z = 32$ amu) and hydrogen fluoride ($m/z = 20$).

5.2.2 LEED and AES Studies

A (4x1) reconstruction pattern as shown in Figure 5.12 is obtained for the clean GaAs(100) surface which is lifted after TFET adsorption occurs. Heating the substrate to 770 K does not restore the surface to the ordered (4x1) structure.

Only by repeated argon bombardment cycles at elevated temperatures (570 K) does the surface return to the original (4x1) reconstruction.

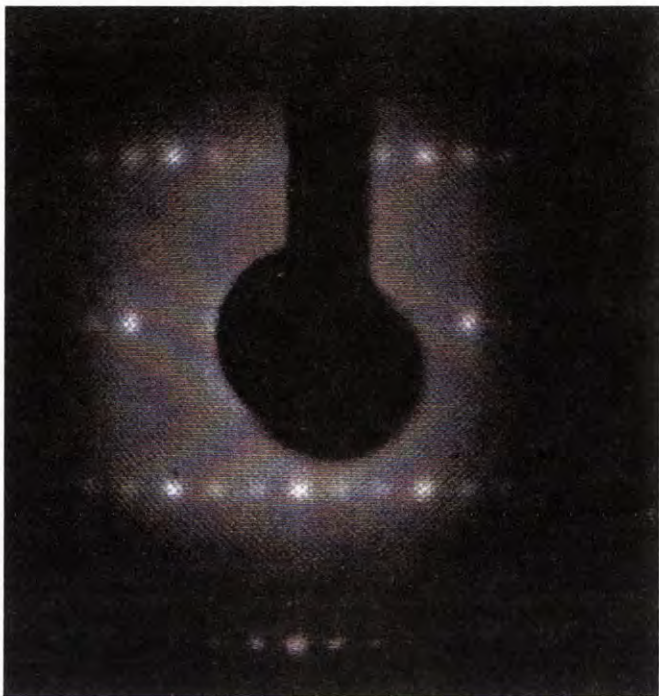
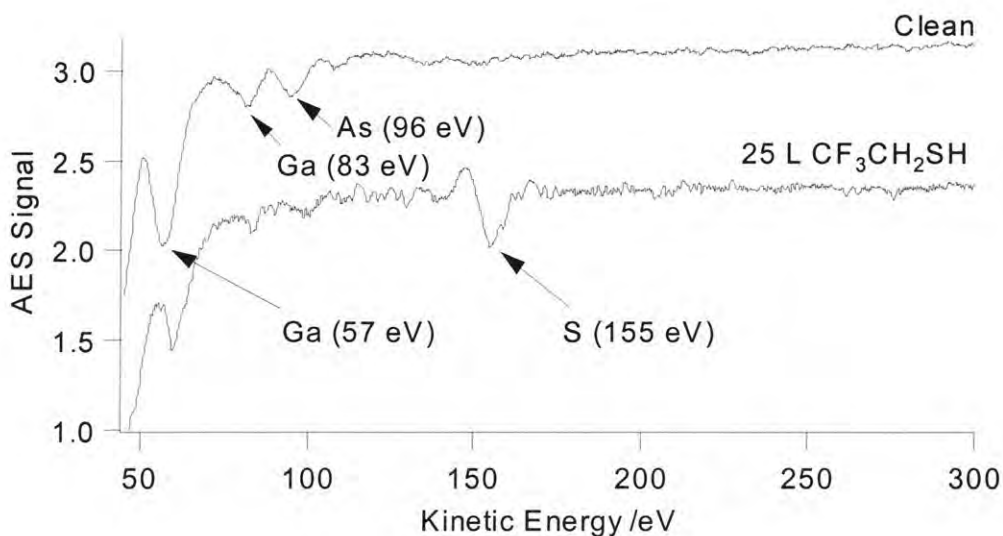
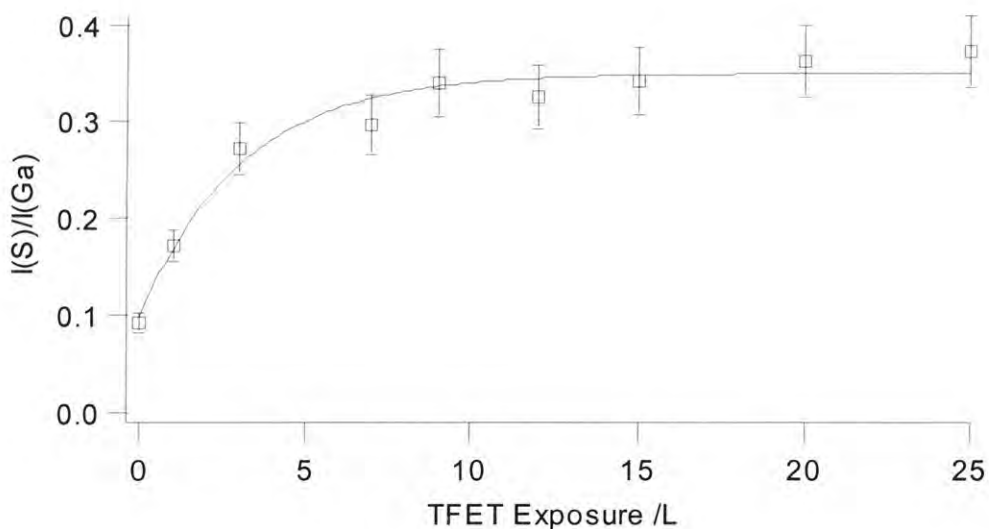


Figure 5.12 The LEED pattern of the clean GaAs(100)-(4x1) surface.

The clean GaAs(100) surface shows strong Auger peaks of Ga (KVV at 57 eV, 83 eV) and As (KVV 96 eV) (Figure 5.13 (a)). When the surface was aliquot dosed with TFET, a peak due to sulphur KVV transition at 165 eV was detected and increased with increasing exposure of TFET until saturation. Figure 5.13 (b) shows the intensity of the S peak divided by that of the 57 eV Ga peak and plotted against the TFET exposure. For exposures greater than ~ 15 L the peak intensity increases only slowly as the surface approaches saturation.



a.



b.

Figure 5.13 (a) The AES spectra before and after adsorption of TFET (25 L) onto GaAs(100) – (4x1) and (b) the AES peak area of S (165 eV) divided by the peak area of Ga (57 eV) and plotted as a function of TFET exposure.

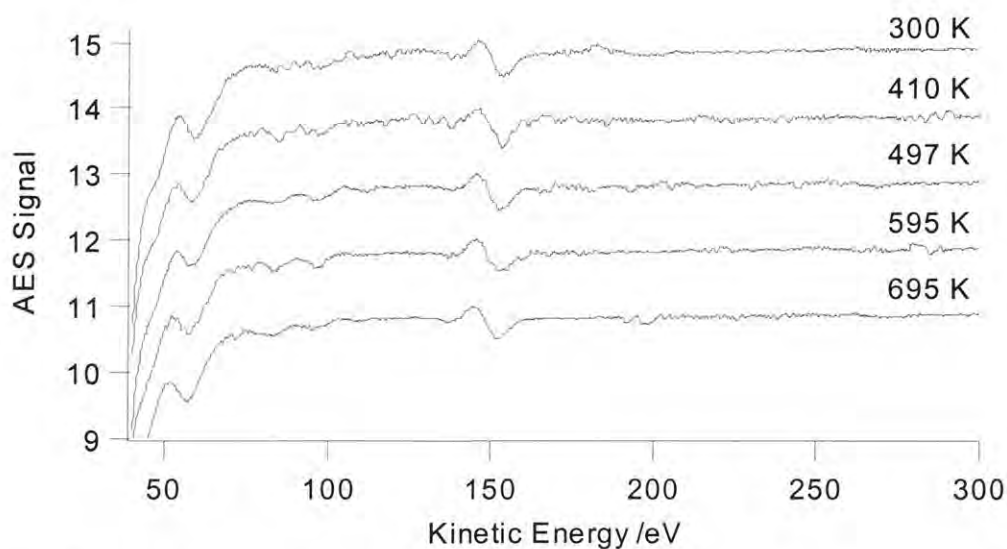


Figure 5.14 The thermal stability of TFET (20 L at 300 K) on GaAs(100) – (4x1) monitored using AES.

If the surface is heated, the sulphur concentration diminishes but significant amounts remain, even at 710 K as shown in Figure 5.14. This layer of sulphur may explain the lifting of the LEED pattern when the surface is exposed to TFET even after heating.

Although the carbon and fluorine regions were monitored by AES no peaks were observed. The reason for lack of carbon peaks is because of low sensitivity due to low surface coverage of the adsorbed species. In the case of fluorine, the lack of a peak at 647 eV was because fluorine diffuses into the bulk and hence not so easy to detect by AES which is very surface sensitive.

5.2.3 Uptake of TFET Observed Using XPS

The XPS uptake experiments were conducted at liquid nitrogen temperatures so that sub-monolayer, saturation and multi-layer coverages of TFET could be studied. XPS was used to monitor the surface reactions and in particular the changing chemical environments of the adsorbed species as a function of

temperature in order to elucidate the decomposition mechanisms. All three expected XPS regions of TFET were monitored (*i.e.* C 1s, F 1s & S 2p) as a function of TFET coverage. It should be noted that the data is poor for sub-monolayer coverages and this coupled with the low photo ionisation cross-section of C and S at low photon energies and interference effects of the As Auger and Ga 3s, respectively, resulted in poor signal to noise in the C 1s and S 2p region. Optimisation of the surface geometry was done prior any data acquisition using the counts on the C1s peak in order to minimise this. However, it must be noted that only limited conclusions can be drawn from this data because of the quality.

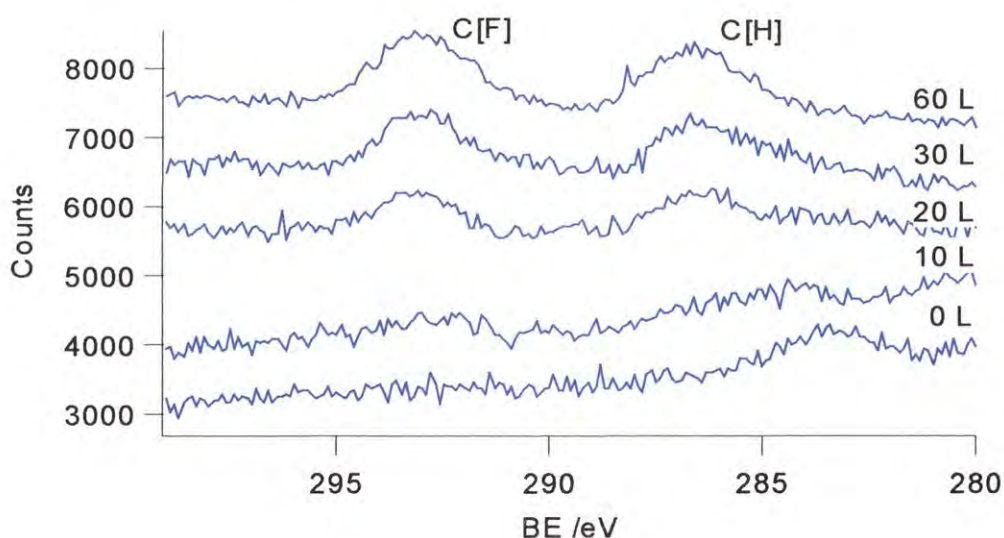


Figure 5.15 The XPS spectra of the C 1s region as a function of TFET exposure on GaAs(100) – (4x1) at 111 K. — spectra are referenced either to the Ga 3d peak at 19.5 eV (0 – 20 L) or C[F] 293.0 eV peak (30 – 60 L).

Figure 5.15 shows the C 1s region as a function of TFET exposure. A peak in this region at ~ 283 eV is also observed which is due to As Auger transitions. This peak affected the C 1s peak position and intensity (The interference could not be eliminated by changing the anode from Al to Mg as Ga Auger peaks interfere with the C 1s peak when using a Mg anode).

For the clean surface, the C 1s region consists of the prominent As Auger peaks at 283.5 eV. These As Auger peaks decrease, as the exposure of TFET increases, similar to the As 3d peak. After 20 L, two C 1s features become distinguishable from the Auger peaks occurring at 293.2 and 286.5 eV with a FWHM of 1.7 and 1.9 eV, respectively. The peak at 293.2 eV observed in the C 1s spectrum is due to chemically shifted C 1s peak due to adsorbed fluorine at the carbon sites, denoted C[F], while the peak at 286.5 eV corresponds to hydrogenated carbon, C[H]. With increasing TFET exposures, these C 1s features increase in size and at coverage >60 L, when the As 3d and Ga 3d photoemission peaks are completely attenuated, and multi-layers of TFET are expected to have formed on the surface. It should be noted that these peaks may contain contributions from the surface species $\text{CF}_3\text{CH}_2\text{SH}$, $\text{CF}_3\text{CH}_2\text{S-}$ and/or $\text{CF}_2=\text{CH}_2$ with the latter two species forming in the first monolayer.

The S 2p XPS region shown in Figure 5.16 is characterised by one photoemission feature after TFET exposure. The use of peak fitting software indicates that this feature consists of several states. Based on previous analysis of H_2S adsorption on $\text{GaAs}(100)^{43}$, three peaks at 160.7, 161.7 and 162.4 eV were fitted. These states relate to atomic S bonded to Ga site (S(I)), S-As or HS-Ga states (they occur at the same BE values, S(II) or HS(I)) and HS-bonded to As sites (HS(II)), respectively. The peaks were optimised and additional peaks were added if necessary to produce a good fit. In some cases, when the peaks were optimised no area was observed for one of the three original states and hence that state was considered not to be populated.

The S $2p_{3/2}$ peaks, at the low coverage of 10 L, were fitted at 160.7, 161.7 and 163.5 eV indicating that S(I) and S(II) or HS(I) are formed. The peak at 163.5

eV is believed to be due to thiolate formation ($\text{CF}_3\text{CH}_2\text{S}^-$) (defined as RS(I)) and this assignment is discussed in detail in the following paragraph. As shown in Figure 5.16, the two low BE states are not included on the graph as they are not as intense as the RS(I) species and a more detailed analysis can be found in Appendix B, Table B2. At 20 L, two new sulphur states are formed, occurring at 164.5 and 162.4 eV (HS(II)) while the HS(I) state disappears. The peak at 164.5 eV has been assigned to intact thiol ($\text{CF}_3\text{CH}_2\text{SH}$) (defined as RSH(I) , see below). The HS(II) state increases in intensity as the TFET exposure increases from 20 L to 30 L, while the S(I) state remains constant. Between 30 and 60 L, the peak at 164.6 eV becomes dominant indicating multi-layer formation.

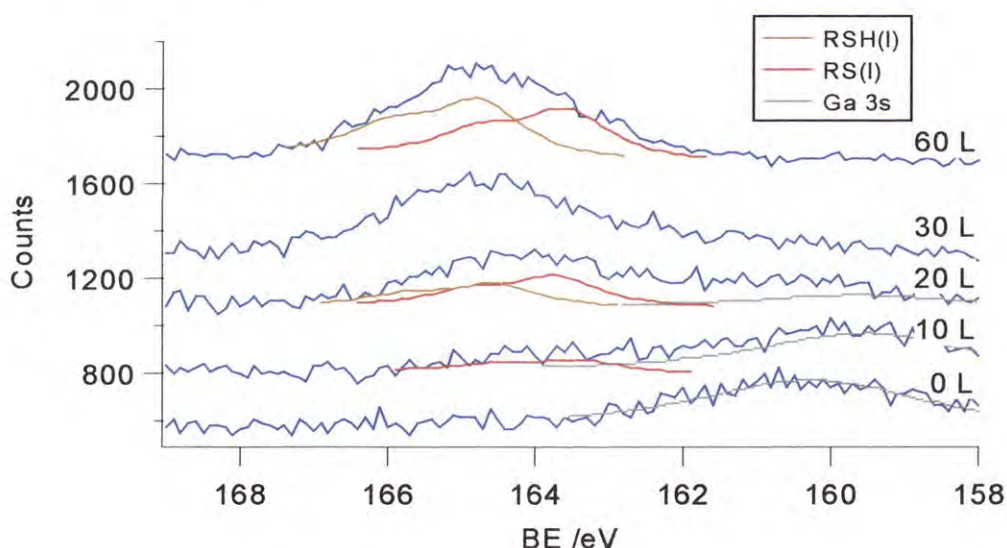


Figure 5.16 The XPS spectra of the S 2p region as a function of TFET exposure on GaAs(100) – (4x1) at 111 K. Only the most intense species are indicated and a more detailed analysis can be found in Table B2, Appendix B. — spectra are referenced either to the Ga 3d peak at 19.5 eV (0 – 20 L) or C[F] 293.0 eV peak (30 – 60 L).

There are no XPS studies of fluorinated thiols in the literature to compare with, with only hydrocarbon thiols previously studied. Hydrocarbon thiolate species have been reported on a number of surfaces with a binding energy range of 162 – 163 eV.^{22, 35, 36, 37, 38} The difference of 0.5 eV in the measured value of 163.5

eV in this study and those reported in the literature may be due to differences in electronegativity.^{36, 39} Elements that are lower in electronegativity to sulphur result in lower BE values. For example, atomic sulphur binds to both Ga and As sites. Ga (1.6)⁴⁰ has a lower electronegativity than As (2.0)⁴⁰ and hence the XPS peak-maximum for Ga-S occurs at lower binding energy compared to As-S.⁴³ If the species attached to sulphur are more electronegative, this results in a shift to higher BE values. For example, multi-layer hydrocarbon thiols and sulphonate species occur at 163 – 164 eV^{35, 37} and 167 – 168 eV, respectively.^{36, 41} Oxygen (3.5)⁴⁰ is more electronegative than hydrocarbons (~2.5)⁴⁰ and this shifts the BE to higher values. In the case of CF₃CH₂S-, fluorine atoms (4.0)⁴⁰ affect the sulphur, shifting the peak to higher BE values of ~ 0.5 eV. The same reason can be used to infer that the peak at 164.5 eV is due to CF₃CH₂SH since it is 1.0 eV greater than hydrocarbon thiols. The value of 164.5 eV is also consistent with thiols that are terminated by an electron withdrawing group e.g. HO₂CC(CH₂)₁₅SH (165 eV).⁴²

There is some interference in the S 2p region at low exposures, due to the Ga 3s peak, which cannot be removed by changing the X-ray anode. On a cleaned GaAs(100) surface, the Ga 3s peak occurs at 160.5 eV and this peak shifts to lower binding energy of 159.6 eV upon TFET adsorption due to TFET reacting with the surface Ga. The Ga 3s peak is not detected after exposing the surface to 20 L. The interference of the Ga 3s peak is not as problematic as the As Auger peaks in the C 1s region and can be factored out using peak fitting software.

Following exposure of TFET, the F 1s region consists of one photoemission feature (Figure 5.17). At 10 L, the F 1s feature comprises of three peaks

occurring at 688.4, 687.1 and 683.2 eV. Each peak can be identified based on literature values. The peak at 688.4 eV is indicative of CF_3 groups neighbouring a heteroatom such as S and based on this has been assigned as $\text{CF}_3\text{CH}_2\text{S}^-$.^{8, 28, 30} The peak at 687.1 eV is characteristic of $\text{CF}_2=\text{CH}_2$ ^{28, 30} while 683.2 eV is consistent with chemisorbed fluorine³⁰.

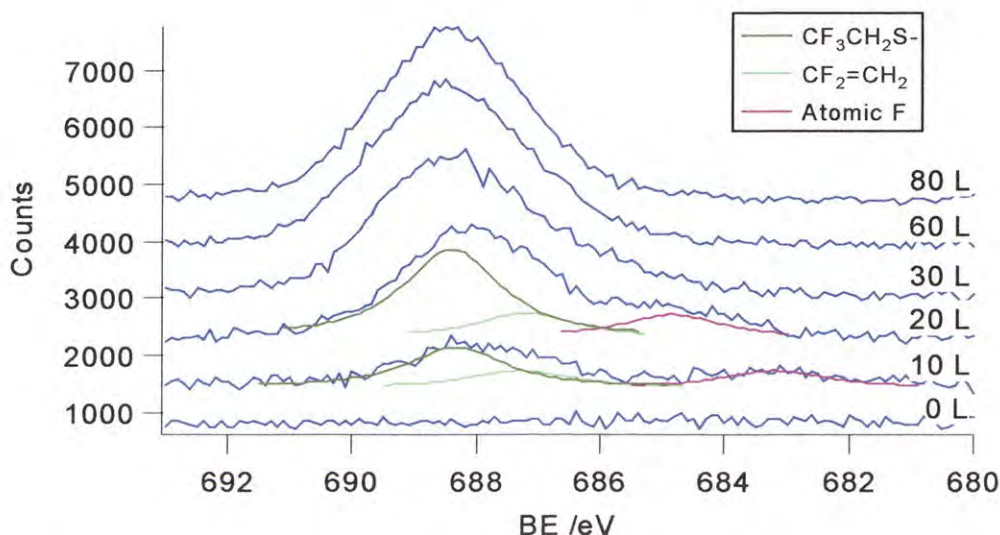


Figure 5.17 The uptake of TFET on GaAs(100) – (4x1) monitored using the F 1s XPS region at 111 K. — spectra are referenced either to the Ga 3d peak at 19.5 eV (0 – 20 L) or C[F] 293.0 eV peak (30 – 80 L).

After aliquot dosing of 20 L of TFET, the peak at 683.2 eV shifts to 684.8 eV. Further dosing of TFET (30 L) results in the loss of the chemisorbed fluorine (684.8 eV) state. The disappearance of chemisorbed fluorine peak indicates that the onset of multi-layer adsorption has occurred. Between 40 and 60 L, the peaks at 688.4 eV becomes dominant. This peak at multi-layer coverage is most likely to be due to $\text{CF}_3\text{CH}_2\text{SH}$ with the resolution of the spectrometer unable to distinguish between the thiol and thiolate species

Both the Ga and As 3d XPS substrate regions were monitored as the TFET exposure was increased (Figure 5.18). For an initially clean surface, a single peak was fitted to give binding energy maxima for As 3d peak of 40.7 eV. The

Ga 3d photoemission feature occurs at 19.5 eV. As discussed in Appendix B, the data analysis involved internally referencing each region to either the Ga state at 19.5 eV (0 – 30 L) or the C[F] state at 293.0 eV (40 – 60 L).

When 10 L of TFET is exposed to the surface, the As peak diminishes and shifts to 41.4 eV with a further shift to 42.0 eV at 20 L. This new peak can be attributed to several possibilities, including AsS,⁴³ AsF or elemental As.^{44, 45, 46, 47, 48, 49, 50} All three forms of arsenic occur at similar BE values at ~ 1 eV from the As(-Ga) peak.⁵¹ Between 20 and 30 L, there is a shift of +0.4 eV in the Ga 3d spectrum indicating the dominance of the GaS state. The photoemission features of Ga and As 3d decrease as a function of TFET exposure with no trace of either state after 60 L. It should be noted that the peak at 33.9 eV is due to the F 2s photoemission peak.

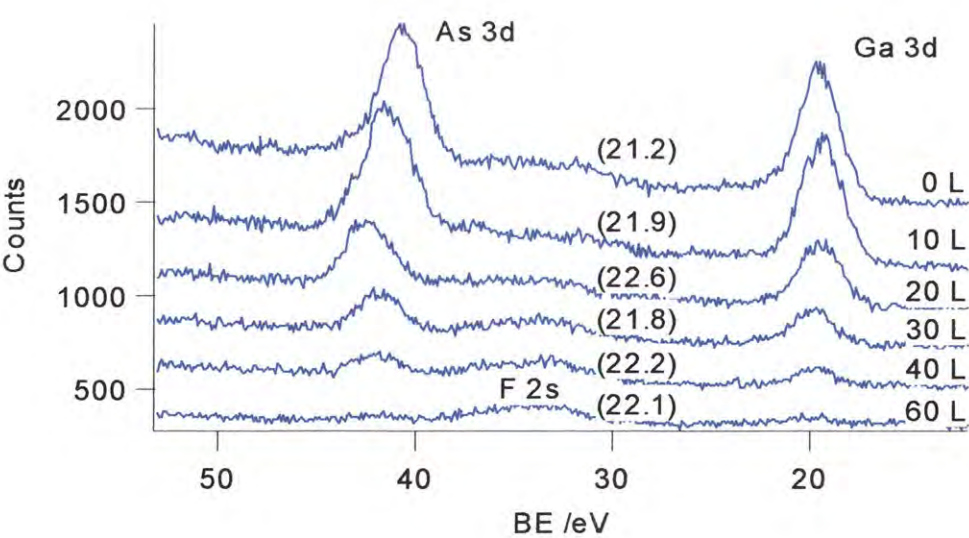


Figure 5.18 The XPS spectra of the As and Ga 3d region as a function of TFET uptake on GaAs(100) – (4x1) at 111 K. The difference between the As and Ga 3d peaks is included in parentheses. — spectra are referenced either to the Ga 3d peak at 19.5 eV (0 – 20 L) or C[F] 293.0 eV peak (30 – 60 L).

5.2.4 Thermal Desorption of TFET Layers Studied Using XPS

The thermal stability of the multi-layer formation of TFET on GaAs(100) was monitored using XPS.

Only two temperatures, 111 and 165 K were corrected for charging by referencing the spectra to the C[F] peak at 293.0 eV. Detection of C[F] and unambiguous assignment of As or Ga 3d peaks at higher temperatures could not be determined with the remaining spectra left unshifted.

The C 1s and S 2p regions both can contain interference from the As Auger and Ga 3s peaks, respectively. This interference at low concentrations of TFET makes assignment of these species difficult at high temperatures when the substrate peaks become more prominent.

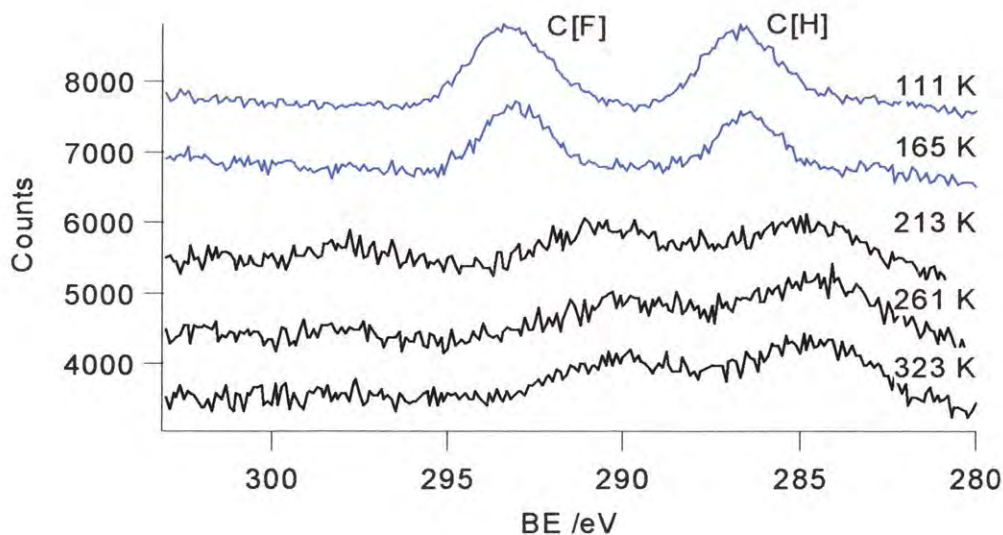


Figure 5.19 The thermal stability of TFET (100 L at 111 K) while monitoring the C 1s XPS region. — spectra are referenced to the C[F] 293.0 eV peak (111 & 165 K). — spectra remain unshifted (213 – 323 K).

At 111 K, the C 1s region contains two photoemission features centred at 293.2 eV (*i.e.* C[F]) and 286.6 eV (*i.e.* C[H]) with an FWHM of 2.1 and 2.3, respectively (Figure 5.19). Heating the substrate beyond 213 K results in the As Auger peaks becoming dominant and no further information can be obtained.

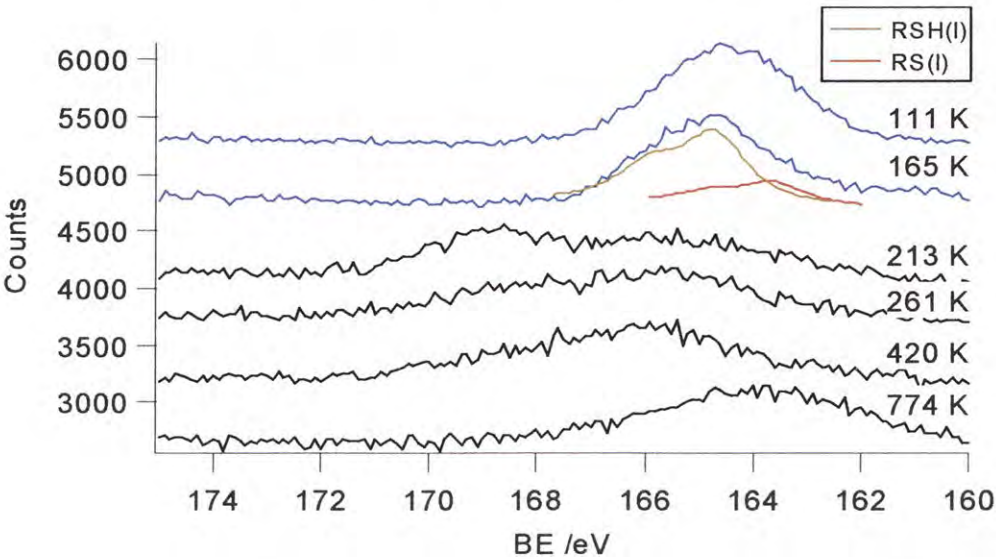


Figure 5.20 The thermal stability of TFET multi-layers (100 L at 111 K) while monitoring the S 2p XPS region. — spectra are referenced to the C[F] 293.0 eV peak (111 & 165 K). — spectra are unshifted (213 – 774 K)

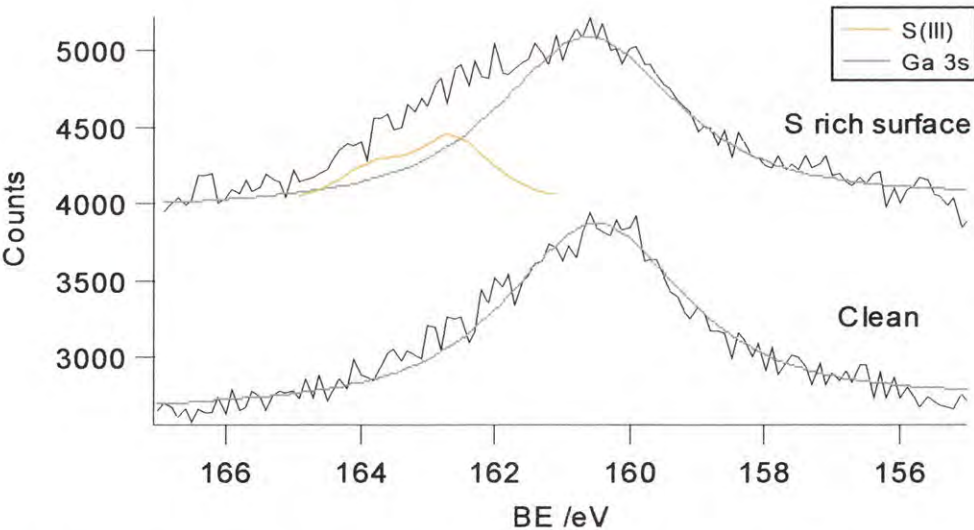


Figure 5.21 Monitoring of S 2p and Ga 3s XPS region for the clean GaAs (100) – (4x1) surface and a surface treated with three cycles of 100 L exposure of TFET followed by annealing to 670 K to deposit a layer of sulphur.

At multi-layer coverage, two sets of doublets ($2p_{3/2}$ and $2p_{1/2}$) were fitted to the S 2p XPS photoemission feature. The $2p_{3/2}$ peaks occur at 164.5 eV (*i.e.* RSH(I)) and 163.4 eV (*i.e.* RS(I)) (Figure 5.20). When the substrate is heated to 165 K, two new peaks are observed at 162.5 eV (*i.e.* HS(II)) and 160.8 eV (*i.e.* S(I)). Heating the surface to 213 K results in the decrease in these peaks and appearance of a broad shoulder at lower BE which continues to grow as a function of temperature. This peak is the Ga 3s peak, which becomes detectable as the surface layers desorb. The data indicate that the sulphur concentration decreases as the temperature is increased, although a sulphur state remains on the surface at 774 K which is discussed in more detail below.

The S 2p region was scanned using an increased dwell time to increase the sensitivity and confirm that sulphur remains on the surface even after annealing the substrate to 770 K as observed in the AES experiments. The main objective of this experiment was to confirm that sulphur does remain on the surface with repeated cycles of dose-annealing consistent with AES experiments. The GaAs surface was cleaned and then excessively dosed with TFET for 100 L, followed by heating the surface to 670 K. This dosing-annealing procedure was repeated twice more. After the third time, the S 2p region was scanned (Figure 5.21). The clean surface in the S 2p region has one peak, which is due to Ga 3s (160.5 eV). Following the dosing-annealing technique, a shoulder was detected on the Ga 3s feature. By internal referencing the Ga 3s peak to 160.5 eV, a doublet was fitted using peak fitting software with the S $2p_{3/2}$ peak occurring at 162.5 eV (defined as S(III), this is different to HS(II) and this difference will be explained further in the discussion).

Monitoring the F 1s region upon TFET multi-layer formation shows a single peak at 688.4 eV (Figure 5.22) after peak fitting the 111 K spectrum. This peak position is similar in value to that observed for a multi-layer coverage in the uptake experiments (§ 5.3.3) and corresponds to condense $\text{CF}_3\text{CH}_2\text{SH}$ layers. When the surface is heated to 165 K, two new peaks are observed at 687.1 and 684.7 eV due to $\text{CF}_2=\text{CH}_2$ and chemisorbed fluorine, respectively. Further heating beyond 213 K results in reduction of the F 1s concentration until 420 K when no signal is detected.

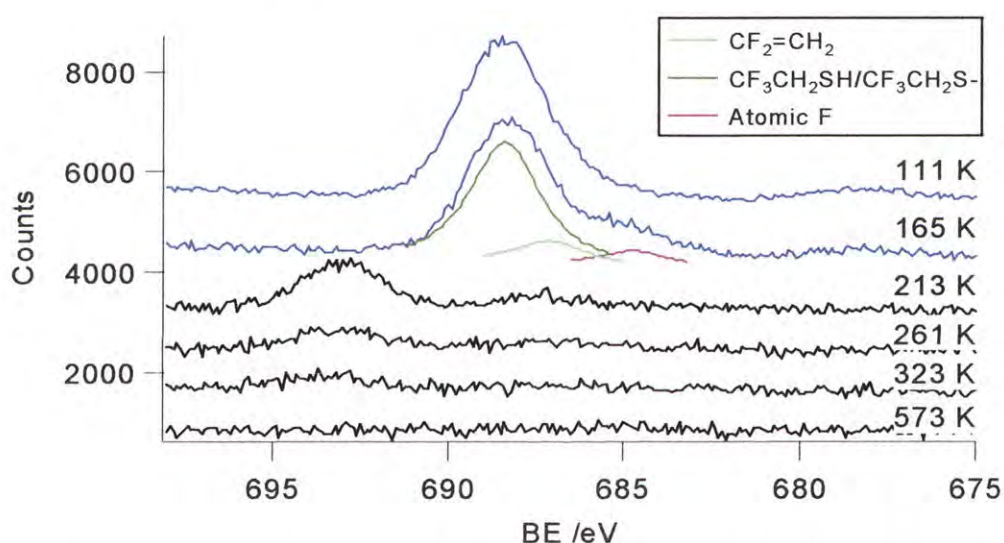


Figure 5.22 The thermal stability of TFET (100 L at 111 K) while monitoring the F 1s XPS region. — spectra are referenced to the C[F] 293.0 eV peak (111 & 165 K). — spectra remain unshifted (213 – 573 K)

For multi-layer coverage of TFET, no substrate peaks in the Ga or As 3d XPS regions were detected. The two peaks are first observed after heating the surface to 213 K (Figure 5.23). Both peaks gradually increase in intensity as a function of temperature. The difference between the As and Ga 3d peaks at 213 K is 22.1 eV and reduces as a function of temperature to a final value of 20.5 eV at 774 K. This latter difference is significantly different to the value obtained for a clean surface of 21.4 eV and suggests that annealing to 774 K does not

result in a return to the clean surface. This confirms the LEED results that the surface is chemically altered even after heating to annealing temperatures.

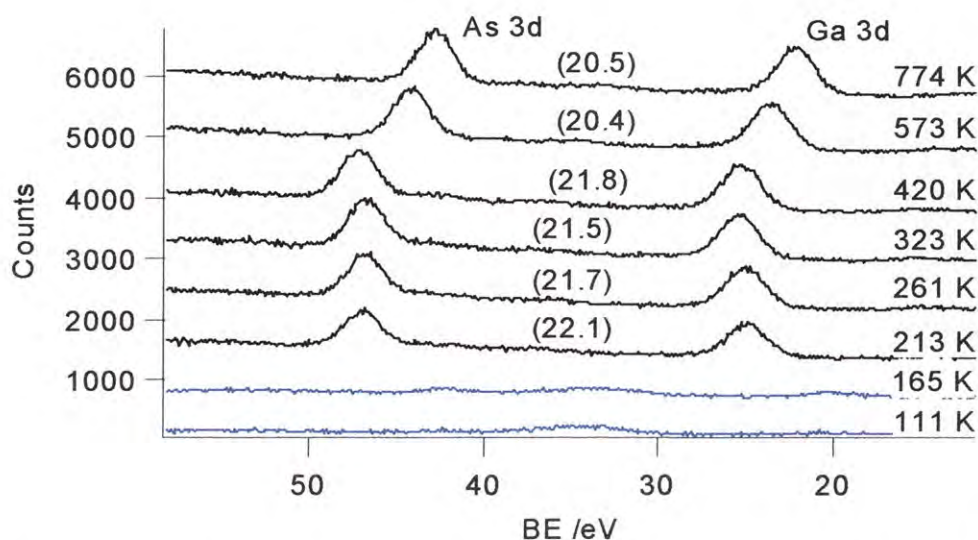


Figure 5.23 The thermal stability of TFET multi-layers (100 L at 111 K) while monitoring the As and Ga 3d XPS region. The difference between the As and Ga 3d peaks is included in parentheses. — spectra are referenced to the C[F] 293.0 eV peak (111 & 165 K). — spectra are unshifted (213 – 774 K).

5.2.5 Electron Irradiation of TFET Monitored by XPS

A multi-layer coverage of TFET was electron irradiated with the AES gun for 10 minutes followed by XPS monitoring of all the expected regions. This study was used to study the kinetics of electron dissociation of the TFET layer. The XPS peaks are referenced to the C[F] peak for 107 and 273 K and after electron irradiation with the remaining spectra left unshifted.

Prior to electron irradiation of the surface, the C 1s region consists of two photoemission features that occur at 293.2 (i.e. C[F]) and 286.7 eV (i.e. C[H]) with a FWHM of 1.8 and 1.9 eV, respectively (Figure 5.24 (a)). Following electron irradiation, the two photoemission features broaden with a FWHM of 2.5 eV observed for both peaks indicating the formation of new species. The

C[F] peak is more affected by irradiation with a decline of 25 % of the peak area while the C[H] peak area increases slightly by 6 %. Heating the substrate to 273 K results in continued broadening of the C[F] peak to a FWHM of 2.7 eV while interference with the As Auger peaks begins to affect the analysis of the C[H] peak.

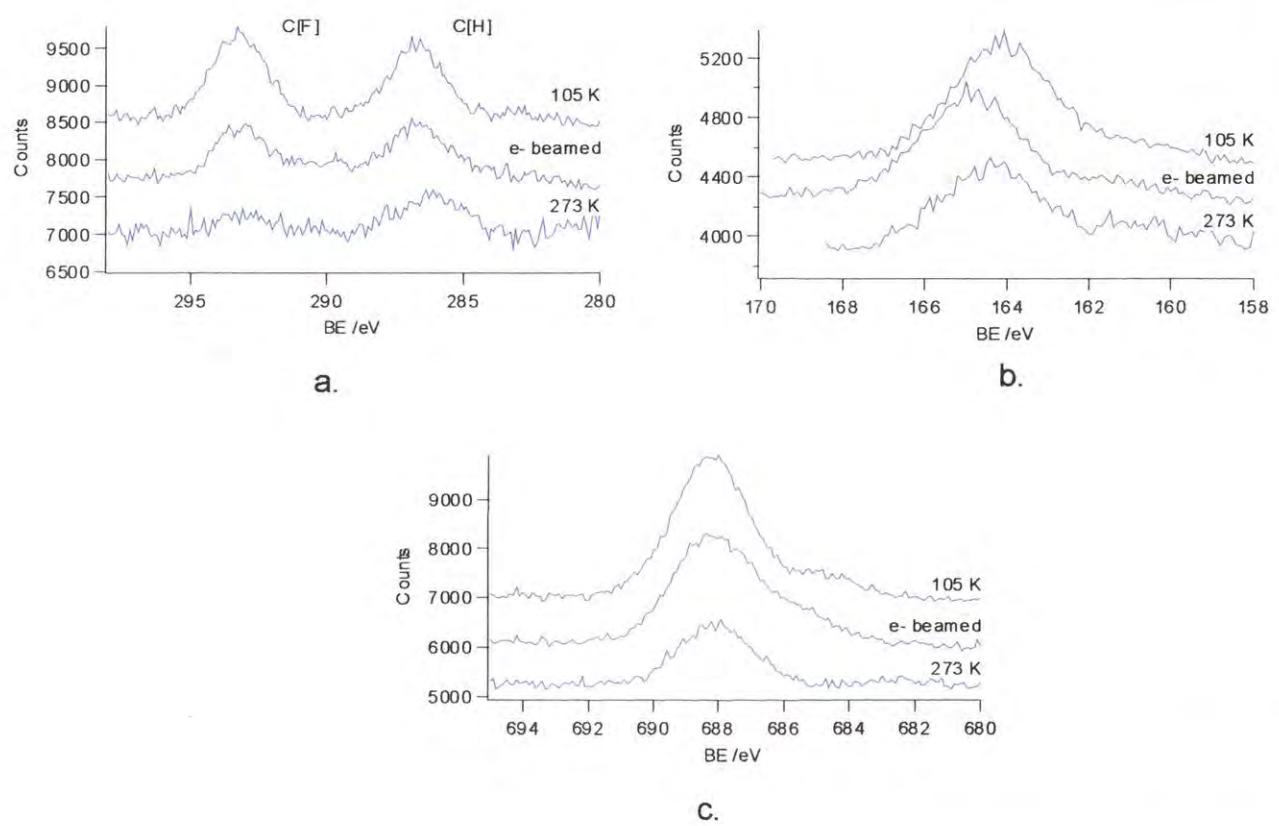


Figure 5.24 The XPS of the thermal stability of TFET (100 L at 105 K) on GaAs(100) – (4x1) after electron irradiating the surface for 10 minutes while observing (a) the C 1s region, (b) the S 2p region and (c) the F 1s region. — spectra are referenced to the C[F] 293.0 eV peak (107 K, e-beamed & 273 K). — spectra are unshifted (371 – 751 K).

After electron irradiation, the S 2p photoemission feature has a net reduction of 7 % (Figure 5.24 (b)). The four peaks before electron irradiation occur at 164.3

(RSH(I)), 163.5 (RS(I)), 162.5 (HS(II)) and 160.8 eV (S(I)). The S(I) state increases by 23 % (from a peak area of 423 to 521), the HS(II) state decreases by 52 % (from a peak area of 519 to 251) while the RSH(I) and RS(I) states decrease slightly (3597 to 3444). Electron irradiation causes charging of the RSH(I) and RS(I) states resulting in a shift to higher BE of 164.9 and 163.9 eV, respectively. After heating to 273 K, the two states return to the original values prior to electron irradiation.

Studying the F 1s region before and after electron irradiation reveals some interesting chemistry. Upon multi-layer formation, three peaks, at 688.4, 686.9 and 684.1 eV, are observed (Figure 5.24 (c)). The electron irradiation of the surface leads to an overall reduction in the fluorine concentration of 11 %. The two higher binding energy peaks are reduced by 19 % (from a peak area of 10249 to 8276) while the peak at 684.1 eV increases by 94 % (759 to 1470).

5.3 Discussion

The most significant discovery in this study is that TFET undergoes several competing reactions on GaAs(100) which desorb subsequently forming an alkane (CF_3CH_3), an alkene ($\text{CF}_2=\text{CH}_2$) and a coupling product ($\text{CF}_2=\text{CHCH}_2\text{CF}_3$). This study widens the known chemistry of thiols on semiconductor surfaces.

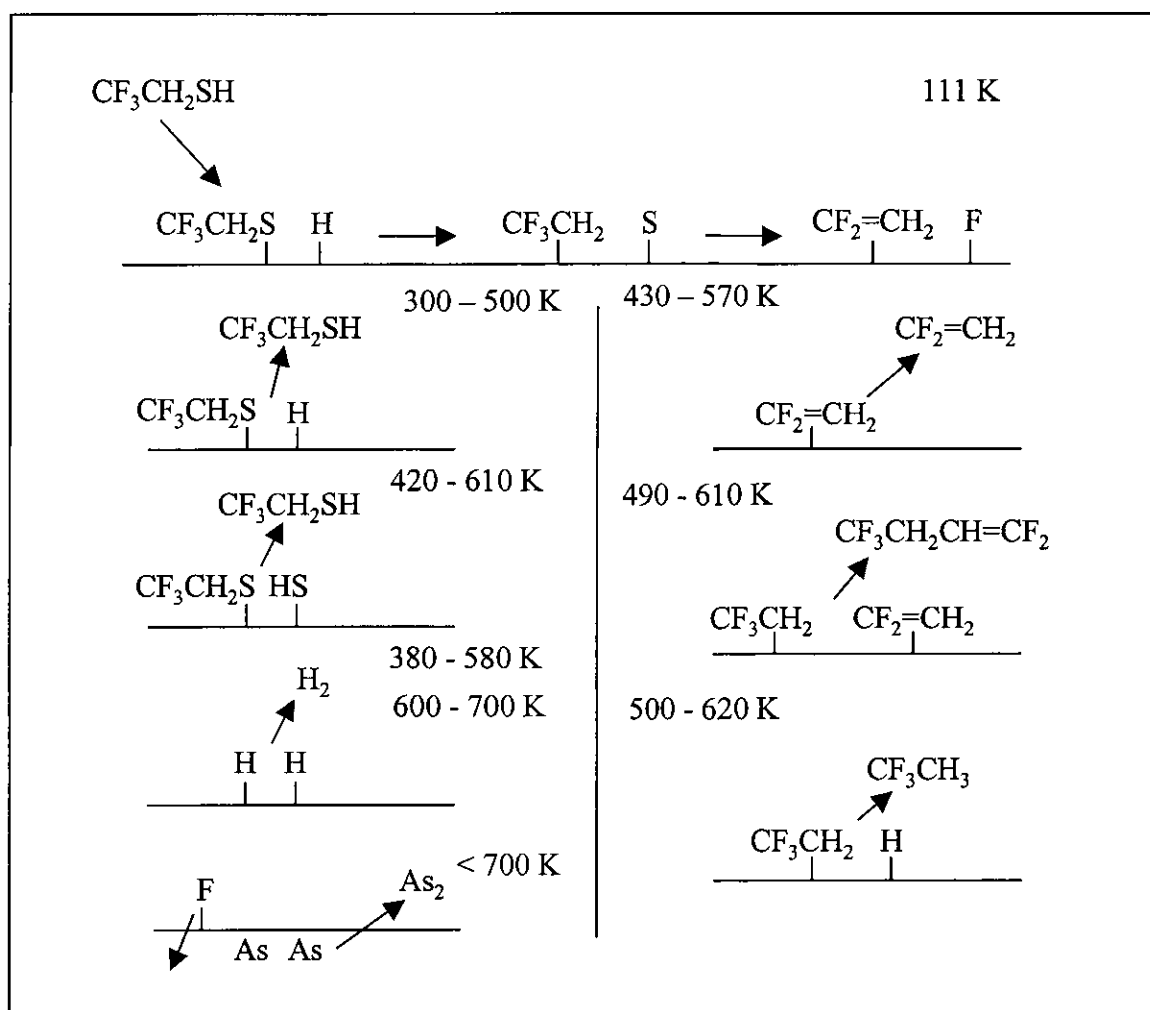
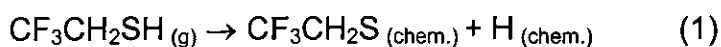
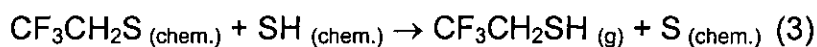
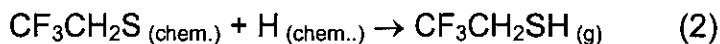


Figure 5.25 The reaction scheme of TFET adsorption on GaAs (100)-(4x1).

Figure 5.25 shows the reaction profile of TFET decomposition on the surface and the resulting reactions.



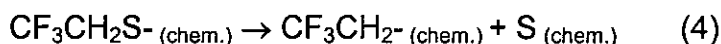
When TFET adsorbs on GaAs(100) – (4x1), the S-H bond dissociates, forming the thiolate species ($\text{CF}_3\text{CH}_2\text{S}-$) and chemisorbed hydrogen as outlined in reaction (1). The XPS data show that 100 % dissociation of TFET occurs (*i.e.* 162.8 eV peak or RS(I)) at 111 K for a low coverage (10 L). The scission of the S-H bond occurs at this low temperature is known for a number of thiols including ethanethiol on $\text{Mo}(110)^{22}$, $\text{Au}(110)^6$ and $\text{Ag}(110)^6$, $\text{CF}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{SH}^{21}$ and $\text{CH}_3\text{CH}=\text{CHSH}^{35}$ on $\text{Mo}(110)$. This dissociation is reversible and state I in the TPD $\text{CF}_3\text{CH}_2\text{SH}$ spectra is the reverse of reaction (1) where surface hydrogen and $\text{CF}_3\text{CH}_2\text{S}-$ species recombine:



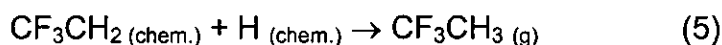
The high-temperature desorption peak for $\text{CF}_3\text{CH}_2\text{SH}$ is due to thiolate species combining with hydrogen atoms attached to surface sulphur atoms *via* reaction (3). Although this combination reaction is expected to be kinetically second order, the peaks shift to higher temperatures at higher coverage. This shift is due to the stabilising forces of sulphur on the surface. As the TFET coverage is increased, the amount of atomic sulphur is increased which stabilises either the reactants or the intermediates of reaction (2). Therefore state II requires higher temperatures to desorb from the surface. Hence, the peak-maxima in the TPD spectra for state II shift to higher temperatures for increasing coverage. Similar observations have been reported for ethanethiol adsorption on GaAs(100).¹⁰

As a result of this phenomena, Singh *et al.* observed the formation of H_2S on GaAs(100).¹⁰ In order for hydrogen sulphide to form, high concentrations of both surface hydrogen and sulphur are required with no H_2S formed at low sulphur

concentrations.^{6, 10} Conversely, in this study no H₂S was detected and this is suggested to be due predominantly to the low concentration of hydrogen atoms on the surface.

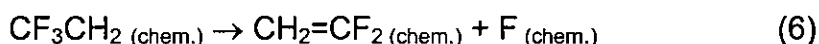


Additional decomposition of the CF₃CH₂S⁻ species occurs *via* C-S bond scission. This reaction pathway can lead to a number of processes. Hydrogen reduction of the resulting CF₃CH₂⁻ species leads to the formation of 1,1,1-trifluoroethane (CF₃CH₃):



It would be expected that 1,1,1-trifluoroethane is formed by the reaction of CF₃CH₂⁻ species with neighbouring hydrogen atoms (see reaction (5)) as was confirmed by the isotope scrambling experiments when co-adsorbed deuterium and TFET react on the surface to desorb CF₃CH₂D. The detection of CF₂CH₂D containing deuterium incorporation confirms that surface bound hydrogen atoms take part in the formation of CF₃CH₃ as in reaction (5).

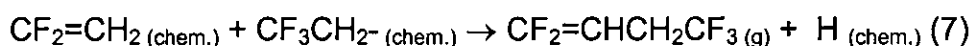
1,1-Difluoroethene is formed by β-fluoride elimination of the alkyl species on the surface resulting in chemisorbed CF₂=CH₂:



There is evidence that this β-fluoride elimination reaction occurs even at 111 K with the F 1s XPS data showing the presence of CF₂=CH₂ (687.0 eV) and the by-product chemisorbed F (683.2 eV). This low-temperature dissociation is not unusual, with ethene formation occurring on Ni(100) between 120 – 140 K.⁵² Furthermore, C-F bond scission occurs below 200 and 160 K for CF₃CH₂I

adsorption on Si(100)²⁰ and CF₃I on Cu(111)²⁷, respectively. The relatively low temperatures for C-F bond cleavage indicate that C-F bond dissociation requires a small activation energy and hence has quite a facile bond activation. This facility can be related to the thermodynamics of the system. Difluoroethene has a lower thermoneutrality compared to ethene since the Ga-F and C-F bonds are similar in energy and CF₂=CH₂ ($\Delta H_f = -18.5 \text{ kJ mol}^{-1}$) is relatively stable compared to CH₂=CH₂ ($\Delta H_f = +3.0 \text{ kJ mol}^{-1}$).^{23, 53, 54}

The alkene-coupling product, CF₂=CHCH₂CF₃, is postulated to be formed by the so-called olefin insertion mechanism observed in catalysis, in particular the Ziegler-Natta of higher hydrocarbons. The CF₂=CH₂ forms *via* the β -fluoride elimination inserts into the adsorbed CF₃CH₂- groups. Followed by loss of hydrogen to form the coupling product, CF₂=CHCH₂CF₃ as shown in (7). In order for the coupling reaction to occur and form 1,1-difluorobutene, CF₂=CH₂ has to remain on the surface and not immediately desorb upon formation. Other studies have reported that alkenes remain bonded to the surface after formation.^{29, 55}



Alternative coupling mechanisms to form CH₃CH₂CH=CF₂, including alkyl coupling of an ethyl and CF₃CH₂- species followed by HF elimination, have been dismissed. The by-product HF was not detected by TPD. Furthermore, the activation barrier to direct coupling to form CF₃CH₂CH₂CF₃ is increased as a result of substitution of an electron-withdrawing group such as fluorine and hence direct coupling would be unexpected.¹⁹

Molecular hydrogen desorption was also reported with the primary source of hydrogen on the surface from the dissociation of the S-H bond when TFET initially adsorbs on the surface. The only other source is from the hydride elimination of the coupling product and this is relatively small compared to the predominant source of S-H bond scission.

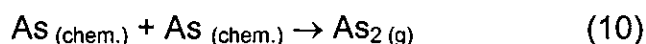


Hydrogen evolves from the surface through two different channels *via* reaction (8). The low-temperature state at 450 K is indicative of H₂ desorption from Ga-rich sites.³² The higher temperature state, centred at 680 K, suggests hydrogen desorption from arsenic sites.³² This indicates that there is a change in surface stoichiometry during surface reactions which is attributed to the role that chemisorbed fluorine plays on etching the surface.

The adsorption of XeF₂ on GaAs has been studied by several groups and it has been found that fluorine reacts with the surface to initially form GaF.^{44, 56, 57} Subsequent fluorination generates GaF₂ and GaF₃ in the near-surface region and simultaneously the diffusion of As to the surface. Simpson *et al.* determined that the arsenic on the surface contains no fluorine and was in an elemental form and quite possibly As₂ as reported in this study.⁴⁴ Fluorine diffuses into the bulk and forms GaF, GaF₂ and GaF₃ species below the surface.⁴⁴ Diffusing into the sub-surface, the fluorine atoms are not available at the surface for fluorine reductive reactions to occur (*i.e.* CF₃CH₂F is not observed).

Although no GaF_x species were detected *via* TPD spectroscopy, XPS data shows that elemental fluorine was detected on the surface for high temperatures. Since XPS probes the bulk layers whereas TPD is only

monitoring what is desorbing from the surface then the F1s in XPS confirms that fluorine goes into the bulk and either stays there or desorbs as GaF spontaneously and does not get detected by the mass spectrometer during TPD scans. However, the formation of the etch product As₂ is directly related to the migration of chemisorbed fluorine (formed from the β-fluoride elimination reaction) into the sub-surface layer and displacement of arsenic to the surface (see reaction (9)). The surface arsenic desorbs from the surface *via* reaction (10) at lower temperatures to the incongruent melting point of bulk GaAs.



There is a wide array of chemisorbed fluorine states observed in the F 1s XPS data, in particular when heating a multi-layer of TFET. Shifts in the chemisorbed fluorine BE value are probably the result of occupying different surface sites, for example, arsenic, sub-surface and/or defect sites. Similarly, chemisorbed fluorine is observed to migrate to other binding sites at high temperatures when CF₃I is adsorbed on Ru(100), resulting in several different BE values for atomic fluorine.³⁰

This layer of sulphur at high temperatures is due to the S(III) state. In the thermal desorption experiments, the S(III) state remains at 773 K. This state has been assigned to dimerised sulphur on arsenic sites. Previous work has shown that a peak at 161.6 eV occurs for dimerised sulphur on Ga sites at high temperatures.⁴³ Based on previous electronegativity arguments described in § 5.2.3, then S(III) at 162.5 eV is likely to be dimerised sulphur on As rich sites. Furthermore, the presence of hydrogen desorption from As sites at high

temperatures indicates that the movement of surface species onto the migrated arsenic can occur. Moreover, the presence of the elemental sulphur on the surface at 774 K explains why annealing alone is insufficient to restore the clean surface and argon bombardment is necessary to remove the surface sulphur.

5.4 Conclusion

In conclusion the adsorption of TFET produces some very interesting chemistry on GaAs(100)-(4x1). XPS data shows that TFET dissociates to form $\text{CF}_3\text{CH}_2\text{S}$ - species and chemisorbed hydrogen at 111 K. This S-H bond scission is a reversible process, with a TPD peak observed at 438 K. $\text{CF}_3\text{CH}_2\text{SH}$ also desorbs at higher temperatures due to the combination of $\text{CF}_3\text{CH}_2\text{S}$ - species with hydrogen from HS- species.

Further dissociation occurs at 111 K, to form CF_3CH_2 - species and atomic sulphur. β -Fluorine elimination resulting in conversion of the alkyl group to $\text{CF}_2=\text{CH}_2$. The olefin remains bonded to the surface. CF_3CH_3 evolves from the surface by hydrogen reduction of CF_3CH_2 - species.

Further reactions of the CF_3CH_2 - groups and $\text{CF}_2=\text{CH}_2$ produce $\text{CF}_2=\text{CHCH}_2\text{CF}_3$. Although the possible coupling mechanism has been discussed at length, further studies are required to confirm this process. One experiment that could substantiate this process is the coadsorption of $\text{CH}_3\text{CH}_2\text{SH}$ and $\text{CF}_2=\text{CH}_2$. If $\text{CF}_2=\text{CHCH}_2\text{CH}_3$ is formed from the combination of these two species, this would confirm the outlined insertion mechanism.

Chemisorbed hydrogen combines to form hydrogen gas and depending on the surface chemistry, results in desorption at two different temperatures. The low-temperature state is due to H_2 evolving from gallium sites while the higher temperature state is the result of H_2 desorption from arsenic sites. Arsenic is displaced to the surface at higher temperatures due to fluorine diffusing into the sub-surface layers to form GaF_x species.

SECTION C

$\text{CF}_3\text{CH}_2\text{I}$ ADSORPTION ON GaAs(100)

5.5 Results

5.5.1 TPD Analysis of 1,1,1-Trifluoroethane Iodide

The study of the desorption of individual species was conducted by dosing a clean GaAs(100) – (4x1) surface with 1,1,1-trifluoroethane iodide (TFEI). During TPD scans of varying coverage of TFEI, only three fluorocarbon products were detected in this study, the parent ion $\text{CF}_3\text{CH}_2\text{I}$, $\text{CF}_2=\text{CH}_2$ and $\text{CF}_2=\text{CHCH}_2\text{CF}_3$. The only other gaseous product observed was As_2 .

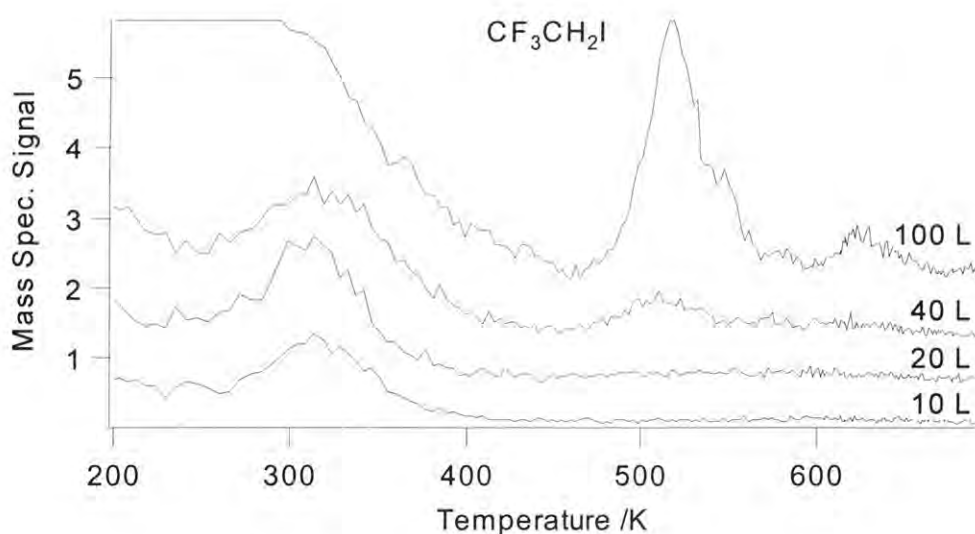


Figure 5.26 The TPD spectra of the molecular ion, $\text{CF}_3\text{CH}_2\text{I}$ ($m/z=210$) as a function of TFEI exposure on GaAs(100) – (4x1) at 100 K. The temperature ramp is 10 K s^{-1} .

The molecular ion $\text{CF}_3\text{CH}_2\text{I}$ ($m/z = 210$) was monitored as a function of TFEI exposure and the spectra are shown in Figure 5.26. One peak is observed at 500 K due to recombinative molecular desorption. It should be noted that the high temperature peak is only detected after population of the lower temperature state. This indicates that there is an activation process requiring

initial population of the physisorption state before occupation of the 500 K state can occur and is observed in the 100 L spectrum which contains a large temperature peak due to the presence of multi-layers on the surface for this exposure. An activation process is confirmed when adsorption at 300 K results in no desorption of $\text{CF}_3\text{CH}_2\text{I}$ at any coverage. Also noteworthy is that this state shifts to higher temperatures with increasing exposures, with the peak observed at 520 K for 100 L TFEI. Applying the Redhead equation to this state with pre-exponential factor of 10^{13} s^{-1} and a heating rate of 10 K s^{-1} gives an activation energy of 140 kJ mol^{-1} .

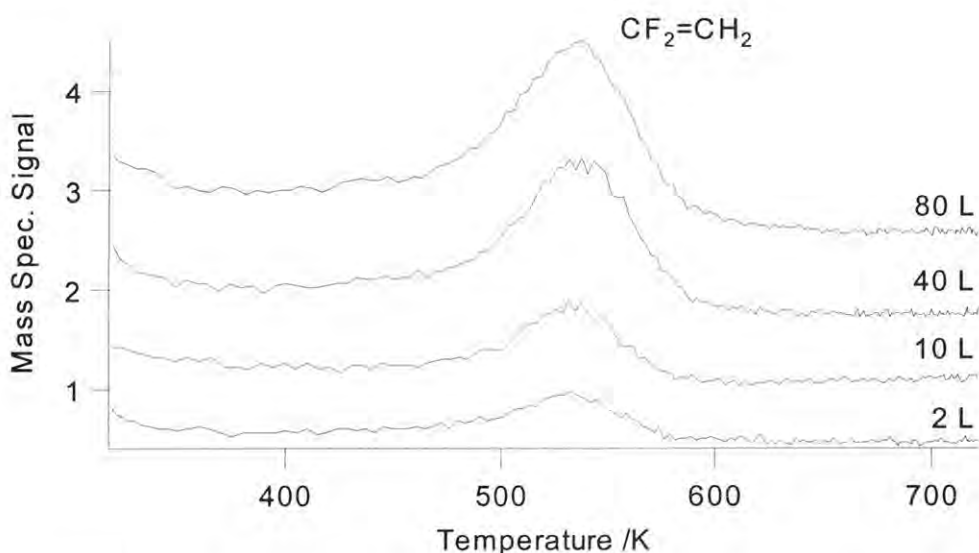


Figure 5.27 The TPD spectra of the uptake of TFEI on GaAs(100) – (4x1) monitoring $\text{CF}_2=\text{CH}_2$ ($m/z = 64$) at 300 K. The temperature rate is 10 K s^{-1} .

The β -fluoride elimination reaction product, $\text{CF}_2=\text{CH}_2$, desorbs from the surface at 550 K from adsorption of TFEI at 300 K (Figure 5.27). The peak-maxima at 550 K shifts slightly to higher temperatures as the exposure of TFEI increases. Using the Redhead equation with a pre-exponential factor of 10^{13} s^{-1} and a heating rate of 10 K s^{-1} gives an activation energy of 132 kJ mol^{-1} for this state.

The identity of $\text{CF}_2=\text{CH}_2$ was confirmed by monitoring the ion trace $\text{CF}=\text{CH}_2$ ($m/z = 45$ amu) fragment (see Appendix B, §B1 for spectra).

Other ion currents were monitored including CF_3CH_3 ($m/z=84$ amu), H_2 ($m/z=2$ amu), HI ($m/z=128$ amu) and HF ($m/z=20$ amu). None of these species were detected with the CF_3CH_3 and CH_3CF_2^+ (*i.e.* the most abundant fragment of CF_3CH_3) ion signals being identical to the $\text{CF}_3\text{CH}_2\text{I}$ TPD trace. Nor was fluorine reduction of the alkyl group to form $\text{CF}_3\text{CH}_2\text{F}$ ($m/z = 102$) detected.

The coupling products $\text{CF}_3\text{CH}_2\text{CH}_2\text{CF}_3$ ($m/z = 166$ amu) and $\text{CF}_2=\text{CHCH}_2\text{CF}_3$ ($m/z = 146$ amu) were monitored. Only the alkene-coupling product was detected with a broad desorption feature in the temperature range 400 to 500 K, with a peak maximum shifting to higher temperatures as a function of TFEI exposure. The spectra obtained are not included since their quality were not high enough to be reproduced here. However the work on TFEI reactions, in particular the detection of coupling products was pursued by a Research Fellow in the group (Dr N. Kemp) who detected desorption of both the $\text{CF}_3\text{CH}_2\text{CH}_2\text{CF}_3$ and $\text{CF}_2=\text{CHCH}_2\text{CF}_3$ coupling products. These studies have been recently published and here only the summary of these results is provided.⁵⁸

Desorption of $\text{CF}_2=\text{CHCH}_2\text{CF}_3$ occurred as a broad feature spanning from 390 to 530 K. The peak maximum increases slightly with increasing exposure similarly to the slight shift in the $\text{CF}_2=\text{CH}_2$ desorption profile. In the case of $\text{CF}_3\text{CH}_2\text{CH}_2\text{CF}_3$ the desorption traces also show a broad peak spanning from 425 to 580 K with a peak maximum at ~ 510 K for low exposures. As the TFEI exposure is increased, the peak shifts to lower temperatures indicative of a second-order process. In addition the $\text{CF}_3\text{CH}_2\text{CH}_2\text{CF}_3$ peak intensity was ~ 4

times less intense than $\text{CF}_2=\text{CHCH}_2\text{CF}_3$ species, implying that the rate constant for the formation of the latter product is much higher.

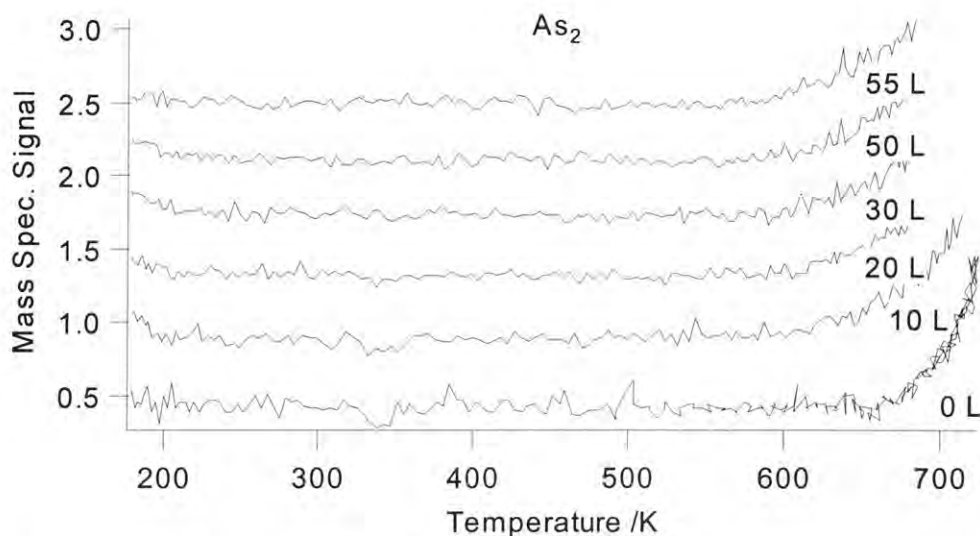


Figure 5.28 The TPD spectra of the uptake of TFEI on GaAs(100) – (4x1) monitoring As_2 ($m/z=150$). Between each experiment, the surface was heated to 700 K, instead of the usual annealing temperature of 770 K to allow the accumulation of etch species on the surface. The exposures represent the overall amount of TFEI used. The temperature ramp is 10 K s^{-1} .

As_2 desorption was detected by performing the experiments as outlined for the TFET TPD study (§ 5.2.1). Figure 5.28 shows a similar shift in the As_2 peak to lower temperatures indicating evidence of etching. No iodine or fluorine containing desorption products other than $\text{CF}_3\text{CH}_2\text{I}$ were observed. Etch products such as GaI_x , AsI_x , GaF_x and AsF_x ($x = 1 - 3$) were monitored but not detected due to low sensitivity. Additional research on this adsorption system conducted in the group does show lower halides are detected. GaI desorption was detected at 560 K while GaF was observed to desorb at 490 K. It should be noted that the GaF peak was 4 times less intense than the GaI desorption peak. AsF desorption occurred as a doublet with a peak maxima at 480 and 530 K while AsI desorption showed a single peak centred at 550 K.

5.5.2 Adsorption of TFEI Monitored Using XPS

The three regions associated with TFEI were monitored, C 1s, F 1s and I 3d, as a function of TFEI exposure. The substrate regions (As and Ga 3d) were also examined. The spectra were referenced to the Ga 3d peak maximum at 19.5 eV (0 – 30 L) and the C[F] peak at 293.0 eV (40 – 200 L) as discussed in Appendix B.

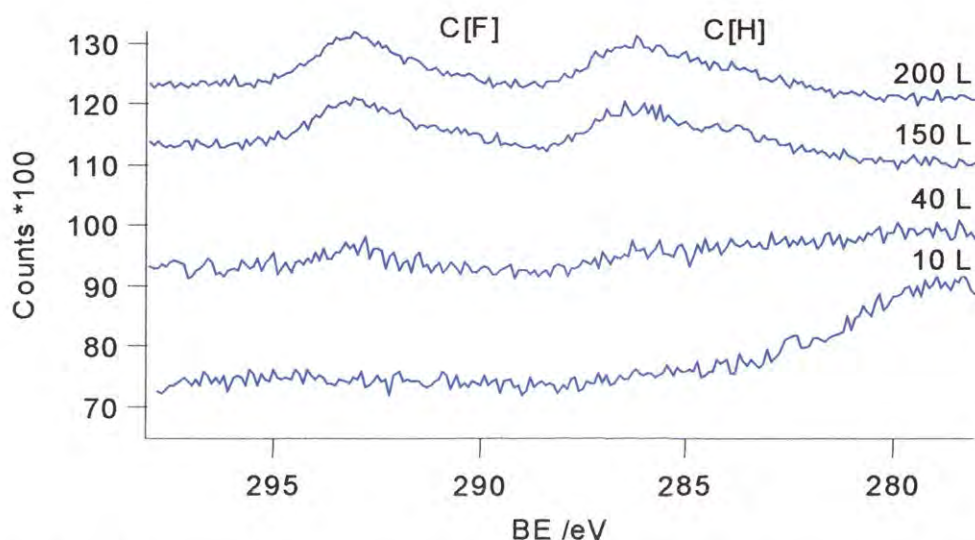


Figure 5.29 The uptake of TFEI on GaAs(100) – (4x1) monitoring the C 1s XPS region adsorbed at 107 K. All spectra are referenced to either the Ga 3d peak at 19.5 eV (10 L) or C[F] 293.0 eV peak (40 - 200 L).

The C[F] state at 293.0 eV is first observed when the surface is exposed to 40 L of TFEI (Figure 5.29). The C[H] peak detected at 286.5 eV is not discernable at low exposures because of interference from the As Auger peak. However, it is observed and discernable in the 150 L spectrum and for higher exposures. The I 3d and F 1s regions suggest that each individual feature is composed of several overlapping states, corresponding to $\text{CF}_3\text{CH}_2\text{I}$, CF_3CH_2^- and/or $\text{CF}_2=\text{CH}_2$.

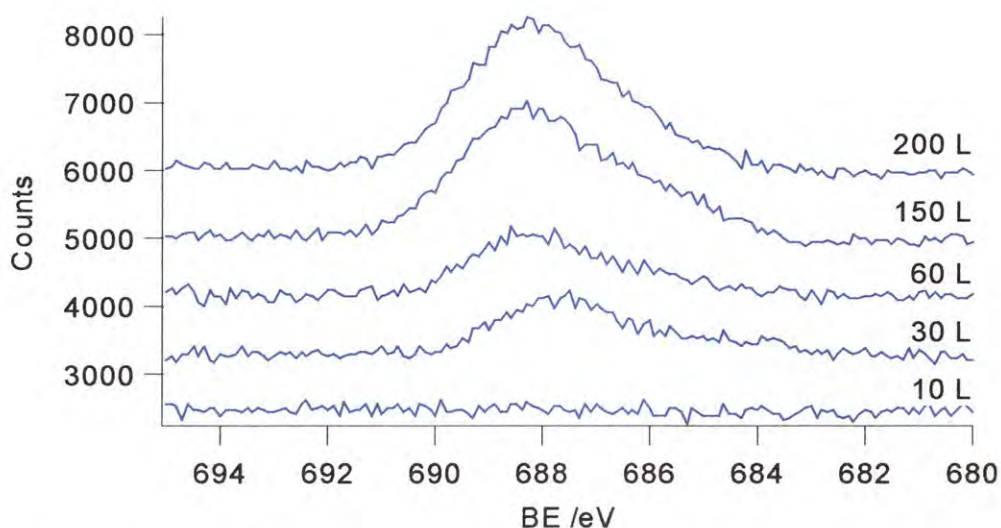


Figure 5.30 The XPS spectra of TFEI on GaAs(100) – (4x1) monitoring the F 1s region adsorbed at 107 K. All spectra are referenced to either the Ga 3d peak at 19.5 eV (10 – 30 L) or C[F] 293.0 eV peak (60 - 200 L).

Figure 5.30 shows the F 1s region as a function of increasing TFEI exposure. An asymmetric peak is first observed at 30 L, consisting of three peaks at 688.0, 687.1 and 685.0 eV. The highest BE state is assigned to F in the molecular $\text{CF}_3\text{CH}_2\text{I}$ since this is similar in value to CF_3I on various surfaces.^{8, 28, 30} The 687.1 eV peak is consistent with $\text{CF}_2=\text{CH}_2$ ^{28, 30} and this state occurs at the same value reported in this chapter for $\text{CF}_2=\text{CH}_2$ (see §5.3.3) formed from reaction of TFET on GaAs(100). The final state at 685.0 eV is due to chemisorbed fluorine. TFET adsorption shows a similar peak, the result of shifted chemisorbed fluorine.

In the I 3d region, two doublets are observed at 30 L with the $3d_{5/2}$ components in the two peaks being at 620.5 and 617.8 eV (Figure 5.31). The peak at 620.5 eV is consistent with reported values for alkyl iodides^{8, 28, 30, 55} (*i.e.* corresponds to $\text{CF}_3\text{CH}_2\text{I}$) and is the iodine state with the highest concentration, comprising 80 % of the total iodine on the surface. The remaining iodide at 617.8 eV is assigned to elemental iodide. As the exposure of TFEI is increased to 40 L, the

peaks shift to 621.2 and 619.2 eV, respectively, indicative of multi-layer formation.

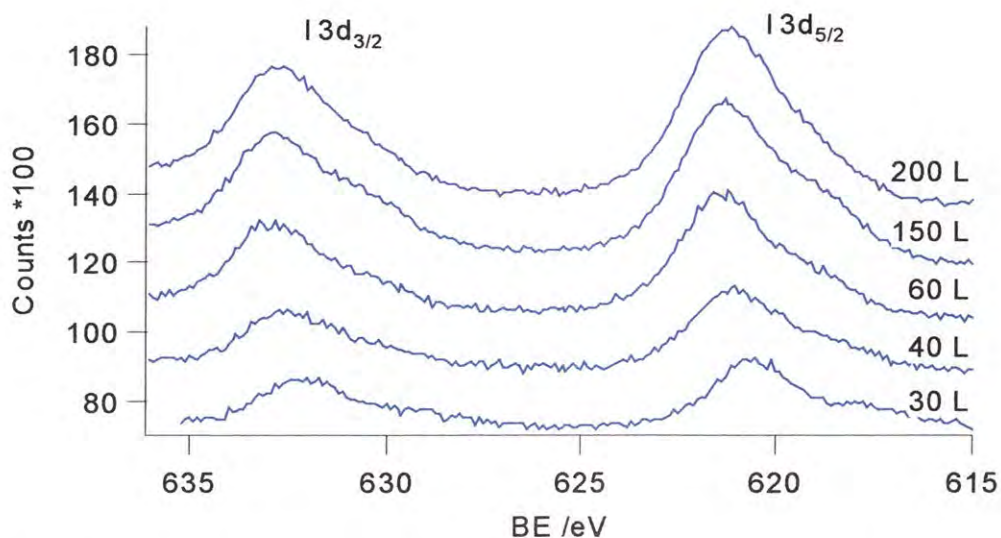


Figure 5.31 XPS study of TFEI on GaAs(100) – (4x1) monitoring the I 3d region adsorbed at 107 K. All spectra are referenced to either the Ga 3d peak at 19.5 eV (30 L) or C[F] 293.0 eV peak (40 - 200 L).

The substrate region shows two peaks occurring at 41.0 and 19.5 eV for a clean surface (Figure 5.32). Adsorption results in a shift to 42.1 eV for the As 3d peak. Shifting to 42.6 eV at 30 L, the As 3d peak remains at this value for additional exposures of 40 and 60 L. For Ga 3d, there is a shift to 20.3 eV for 40 L, followed by 20.6 eV at 60 L. These shifts to higher BE at higher coverage have been assigned to GaI and AsI bonds. These peaks decrease as a function of TFEI coverage until disappearing at an exposure of 150 L.

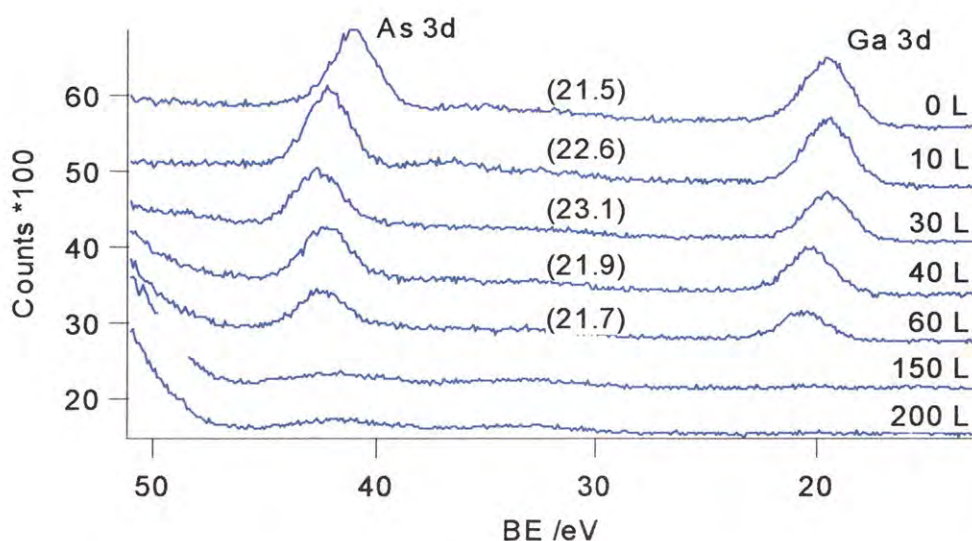


Figure 5.32 The XPS study of the uptake of TFEI on GaAs(100) monitoring the Ga and As 3d regions adsorbed at 107 K. The difference between the As and Ga 3d peaks is included in parentheses. All spectra are referenced to either the Ga peak 3d at 19.5 eV (0 – 30 L) or C[F] 293.0 eV peak (40 - 200 L).

The difference between the two substrate peaks is typical of adsorption on GaAs and correlates with the adsorption of TFET on GaAs(100) (see § 5.3.3).

5.5.3 Thermal Desorption of TFEI Observed Using XPS

The surface was saturated with TFEI followed by monitoring of the Ga 3d, As 3d, C 1s, F 1s and I 3d as a function of temperature. The spectra are left unshifted.

At 107 K, the C 1s region contains two photoemission features each with a FWHM of 2.1 eV (Figure 5.33). As the surface is heated, the carbon states reduce in intensity until neither state is detected above the noise level after 185 K with As Auger peaks in the region also dominating the whole spectrum.

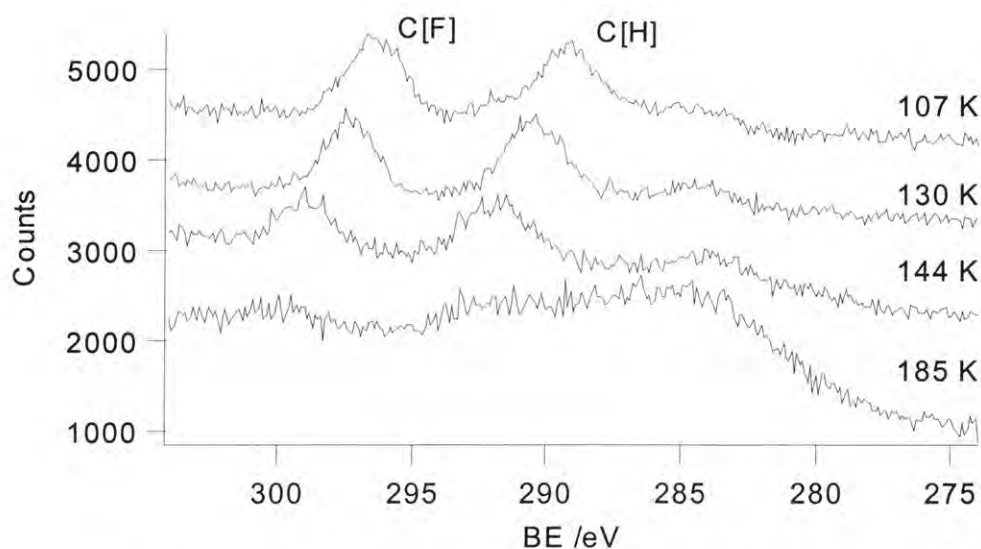


Figure 5.33 The thermal stability of TFEI (100 L at 107 K) on GaAs(100) – (4x1) monitored using the C 1s XPS region. The spectra are left unshifted.

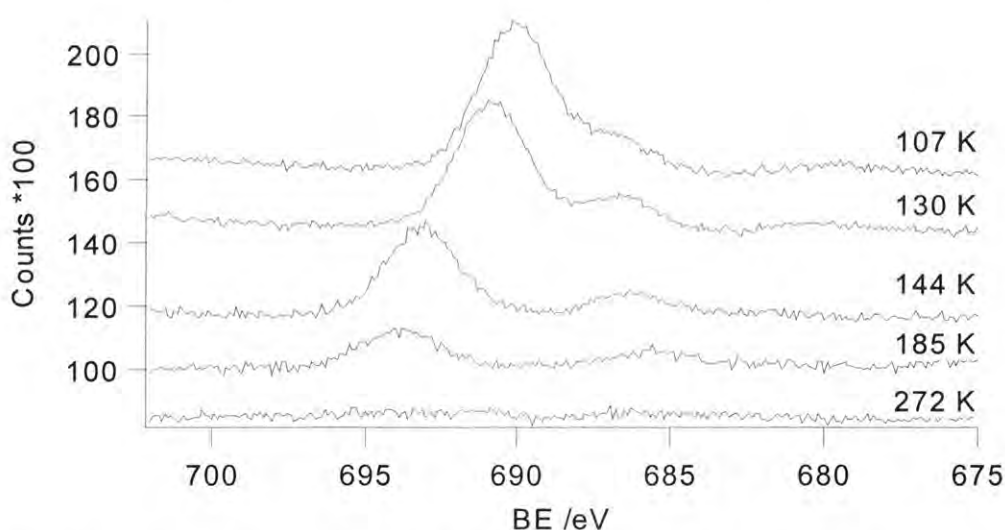


Figure 5.34 The thermal desorption study of TFEI (100 L at 107 K) on GaAs(100) – (4x1) observed using the F 1s XPS region as a function of substrate temperature. The spectra remain unshifted.

At a multi-layer coverage of TFEI, the F 1s region consists of one major photoemission feature and a small shoulder (Figure 5.34). As the substrate is heated, these two features separate and shift further and further apart until no fluorine is detected at 272 K.

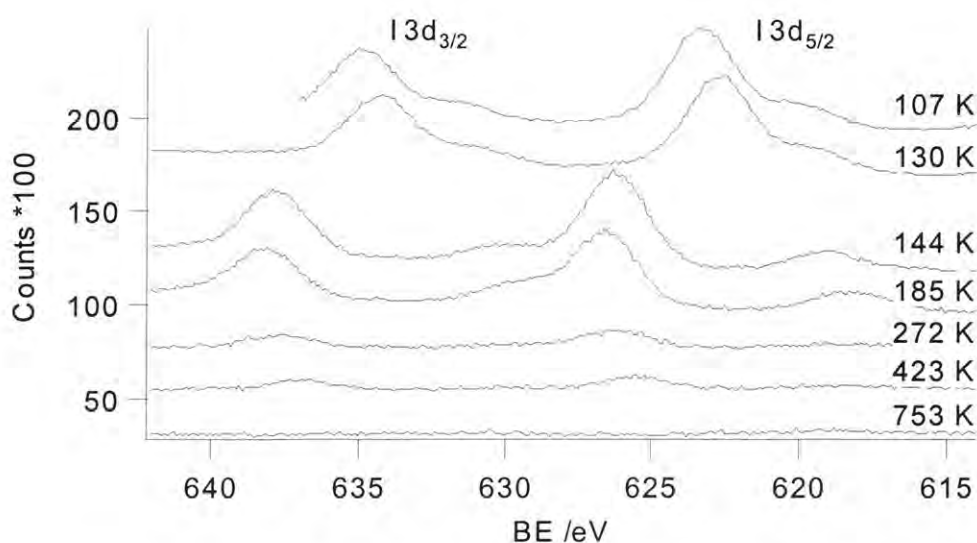


Figure 5.35 The XPS spectra of the I 3d region monitoring the thermal stability of TFEI (100 L at 107 K) on GaAs(100) – (4x1). The spectra remain unshifted.

The I 3d region behaves similarly to the F 1s region with two photoemission features observed for both the I 3d_{5/2} and 3d_{3/2} component (Figure 5.35). The smaller of the two is a shoulder that shifts to lower BE as a function of increasing temperature and may be the result of atomic iodine migrating to other sites such as defect or As sites. At 144 K, there is sufficient separation that the 3d_{3/2} component of the smaller peak begins to overlap with the 3d_{5/2} component of the larger peak. Heating to 272 K results in significant loss of iodine with only one peak observed. Iodine is maintained at this concentration until 569 K where no iodine is detected at higher temperatures.

Low temperature adsorption results in several I 4d photoemission features (Figure 5.36) in the As and Ga region. When the surface is heated to 185 K, the Ga and As 3d peaks are detected with both peaks gradually increasing as a function of increasing temperature. The difference between the As and Ga 3d peaks is initially 23.0 eV. This high value may have contributions from the I 4d photoemission feature and result in a higher value for the As 3d peak and

hence a larger difference. At 272 K, the difference of 21.7 eV steadily decreases to 19.5 eV at 753 K.

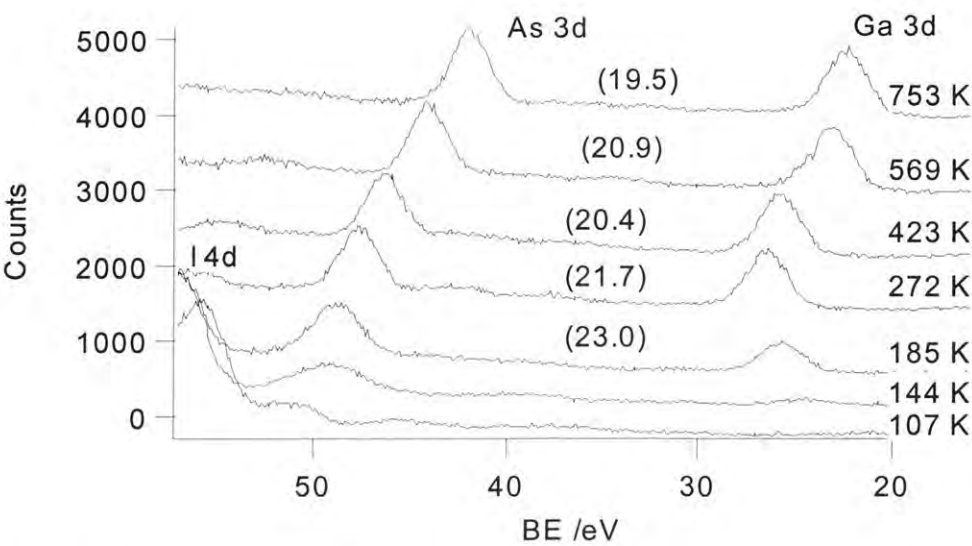


Figure 5.36 The thermal stability of TFEI (100 L at 107 K) on GaAs(100) – (4x1) monitoring the Ga and As 3d XPS region. The difference between the As and Ga 3d peaks is included in parentheses. The spectra remain unshifted.

5.6 Discussion

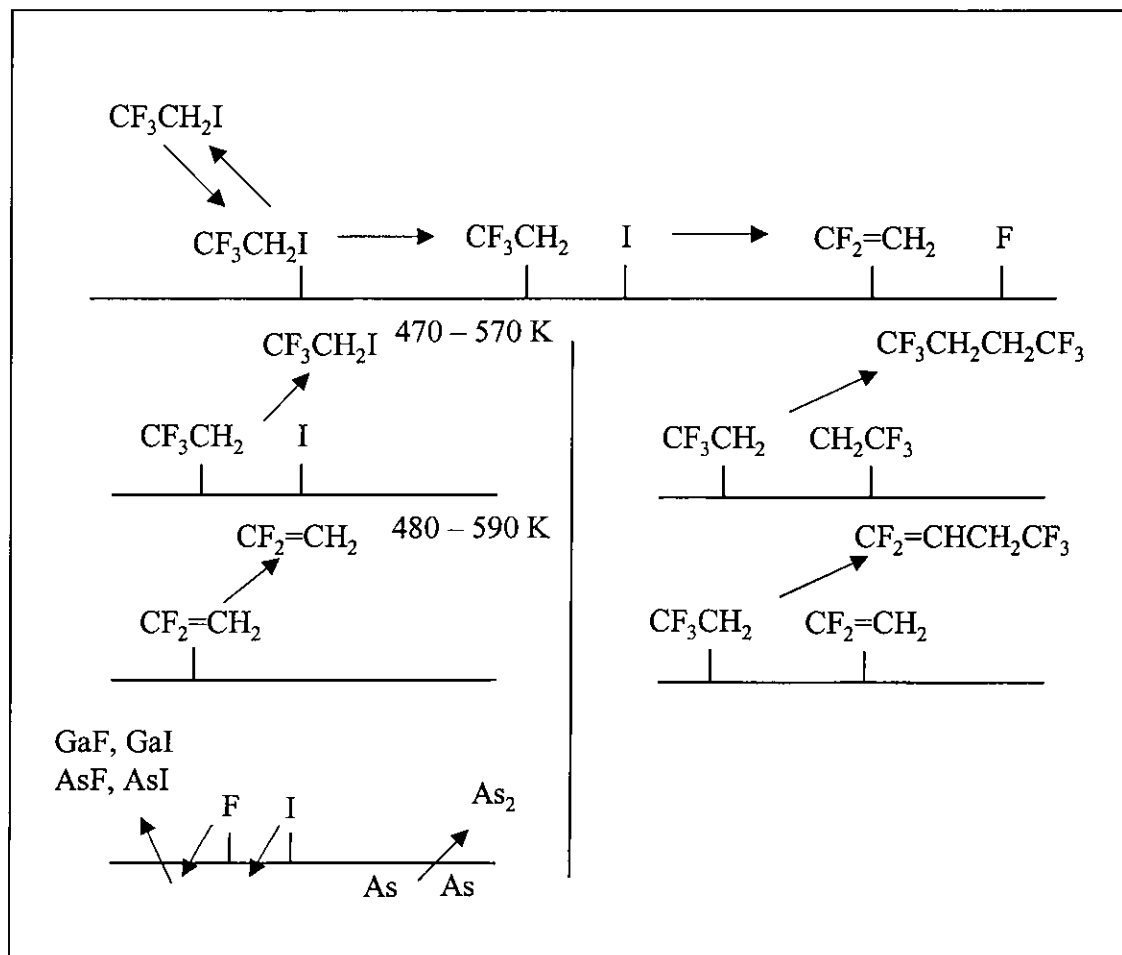


Figure 5.37 The reaction mechanism for TFEI adsorbed on GaAs(100) – (4x1).

This section discusses the reaction of CF₃CH₂I on GaAs(100). The reaction schematic is outlined in Figure 5.37. In summary, CF₃CH₂I absorbs on the surface both molecularly and dissociatively at 107 K. At this adsorption temperature, the population of a higher temperature chemisorbed state for TFEI is possible which is not available at room temperature adsorption. Adsorption at 300 K results in the formation of CF₂=CH₂, CF₂=CHCH₂CF₃ and CF₃CH₂CH₂CF₃. The β-fluoride elimination process produces chemisorbed fluorine that migrates to the sub-surface to generate GaF_x species. Fluorine and

iodine migration displaces arsenic to the surface and the elementary arsenic desorbs at lower temperatures to the congruent melting point.



Initially, TFEI adsorbs molecularly on the surface at 107 K with the C-I bond dissociating for a small minority (20 % based on I 3d_{5/2} analysis) (see reaction (1)). The presence of intact CF₃CH₂I even at low coverage (30 L) where there are sites available indicates that island formation may be prevalent. This is consistent with CF₃I adsorption on Ag(111) where the majority of the C-I bonds remain undissociated at low coverage, evidence of island formation.⁸ Island formation of iodine is observed when CH₃I and CH₃CH₂I adsorbs on Ag(111),^{2, 3} CH₃CH₂I on Pt(111)⁵⁹ and molecular iodine on GaAs(100)⁶⁰.

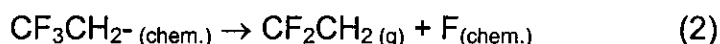
Desorption of CF₃CH₂I physisorbed layer occurs ~200 K in the TPD spectra. Similarly, a great portion of the iodine signal is lost in the XPS spectra between 185 and 272 K, indicating that physisorption occurs in this temperature range which is in agreement with the TPD data.

The dissociation of CF₃CH₂I results in the formation of CF₃CH₂- and chemisorbed iodine (reaction (1)). Another desorption state of TFEI is observed at 500 K, the peak maximum shifts to higher temperatures at higher exposures. This state is more than likely the result of recombinative desorption. At high coverage, there is a significant coverage of chemisorbed iodine which creates a highly populated surface. The shift in the chemisorption peak at 500 K for higher exposures may be linked to several factors. Iodination of the surface at varying levels has been reported to shift TPD peaks.⁶³ Higher and higher temperatures

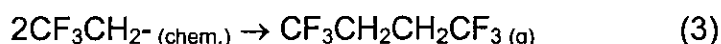
may be necessary as the coverage increases for the iodine to migrate to the periphery of the alkyl island and then recombine.

This shifting-phenomenon is also detected in the $\text{CF}_2=\text{CH}_2$ TPD spectra with the peak maxima shifting to higher temperatures as a function of coverage indicating formation much later and hence desorbing at a higher temperature. Similar shifts to higher desorption temperatures as the coverage increases occur when CH_3I , $\text{CH}_3\text{CH}_2\text{I}$ and $\text{CH}_3\text{CH}_2\text{CH}_2\text{I}$ adsorb on copper surfaces and have been attributed to site blocking by chemisorbed iodine.^{61, 62, 63}

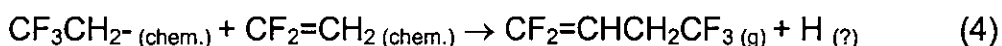
No reaction process results in chemisorbed hydrogen adsorption on the surface and this is evident with the lack of CF_3CH_3 , HF , HI and H_2 observed during the TPD studies. Nor is CF_3CH_3 formed when $\text{CF}_3\text{CH}_2\text{I}$ reacts with $\text{Ag}(111)$,¹⁹ or $\text{Si}(100)$,²⁰ agreeing with the results presented here. The only dissociative reaction pathway available for the CF_3CH_2^- species on $\text{Ag}(111)$ ^{19, 24} and $\text{Si}(100)$ ²⁰ is β -fluorine elimination to form $\text{CF}_2=\text{CH}_2$, similarly to the observations on $\text{GaAs}(100)$.



The predominance of $\text{CF}_2=\text{CH}_2$ formation *via* β -fluoride elimination is consistent with adsorption of TFEI on $\text{Si}(100)$ ²⁰ and $\text{Ag}(111)$ ^{16, 19}. Although this is the case, coupling reactions can also take place for adsorption of TFEI on $\text{GaAs}(100)$. $\text{CF}_3\text{CH}_2\text{CH}_2\text{CF}_3$ is formed *via* direct second order coupling of the adsorbed CF_3CH_2^- species:



The major coupling product is $\text{CF}_2=\text{CHCH}_2\text{CF}_3$, the formation of which shows first order reaction kinetics. The reason for this is that the formation of this product is reaction limited relying on the 1st order formation of $\text{CF}_2=\text{CH}_2$ followed by insertions of this species into the carbon-surface bond of CF_3CH_2 -groups to yield $\text{CF}_3\text{CH}_2\text{CH}=\text{CF}_2$. The fate of the β -hydrogen in the elimination process is unknown at the present time and further investigations are warranted in this aspect of the study.



The formation of fluorinated alkyl coupling product is different from that on $\text{Ag(III)}^{16, 19}$ or Si(100)^{20} where TFEI was shown to yield only $\text{CF}_2=\text{CH}_2$ as the reaction product. Whilst the result is not unusual for Si(100) , not known to facilitate coupling reactions, it was unexpected for Ag(111) which is known to form exclusively coupling products. In the latter case it is postulated that an electron withdrawing group (e.g. F or CF_3) at the β position increases the kinetic barrier to direct coupling and hence β -fluorine elimination becomes the dominant pathway.^{16, 25} Jenks *et al.* found for CH_3I and $\text{CH}_3\text{CH}_2\text{I}$ reactions on copper surfaces that alkyl reduction reactions such as C-C coupling are adversely affected by chemisorbed iodine.⁶³ In this study the presence of halides on the surface or as substituents did not affect the coupling reactions observed. In fact two coupling products are observed to form whereas with TFET (§ 5.2 and 5.3) only one coupling product ($\text{CF}_2=\text{CHCH}_2\text{CF}_3$) was formed.

As noted in the results section the removal of iodine, formed during dissociative adsorption of TFEI, occurs *via* the formation of volatile GaI and AsI . This suggests that the iodine interacts with both the surface Ga atoms and the

subsurface As atoms which are accessible due to the nature of the gallium rich (4x1) surface the experiments were conducted on (§ 3.2.1).

The formation of GaF and AsF were also detected. The fluorine is liberated *via* β -fluoride elimination of the adsorbed CF_3CH_2^- species. The elemental fluorine reacts with the surface Ga and subsurface As atoms to form GaF and AsF, respectively. It should be noted that AsF, like AsI, does not desorb to the same extent as the corresponding GaF and GaI. This could be related to the fact that the substrate that the experiments were conducted on was a gallium-rich surface. However, previous investigations of etching of GaAs with fluorine from XeF_2 show that fluorine predominantly diffuses into the bulk to disrupt the Ga-As bonds. Thus:



The removal of volatile etch products GaI, GaF (major) and AsI, AsF (minor) creates a As-rich surface where As atoms from the bulk migrate to the surface and form chemisorbed As_2 . Heating to temperatures greater than 700 K causes desorption of these dimers and returns the surface to the original gallium rich state.

5.7 Conclusions

TFEI adsorbs on GaAs(100) at 107 K molecularly. Dissociation occurs below room temperature to form CF_3CH_2^- and I species. The CF_3CH_2^- groups undergo a series of competing reactions. The major pathway is the formation of $\text{CF}_2=\text{CH}_2$ via β -fluoride elimination. The accompanying disproportionation product, $\text{CF}_3\text{CH}_2\text{F}$, is not observed and this is due to the fluorine required for this process becoming unavailable by the formation of etch products with reactions either with the surface or subsurface atoms occurring to form GaF and AsF. Direct coupling of CF_3CH_2^- species also occurs to form $\text{CF}_3\text{CH}_2\text{CH}_2\text{CF}_3$ by a second order process. Furthermore, $\text{CF}_2=\text{CHCH}_2\text{CF}_3$ is formed by the olefin insertion of $\text{CF}_2=\text{CH}_2$ into adsorbed CF_3CH_2^- species followed by loss of hydrogen. Etch products AsF, AsI, GaF, GaI and As_2 desorb at high temperatures. The removal of these etch products restores the surface to the original gallium-rich stoichiometry.

SECTION D

THE IMPORTANCE OF THE CO-ADSORBED SPECIES

The aim of this study of alkyl coupling reactions, using TFET and TFEI was to investigate the effect of the co-adsorbed species, if any, on the reaction products formed. In both cases, dissociation of the molecule occurred on the surface to generate CF_3CH_2^- species. For TFET, CF_3CH_2^- species react to produce $\text{CF}_2=\text{CH}_2$, CF_3CH_3 , $\text{CF}_2=\text{CHCH}_2\text{CF}_3$ and H_2 while for TFEI, the CF_3CH_2^- groups react to form $\text{CF}_2=\text{CH}_2$, $\text{CF}_2=\text{CHCH}_2\text{CF}_3$ and $\text{CF}_3\text{CH}_2\text{CH}_2\text{CF}_3$. Both molecules react on the surface to produce etch products. Obviously the co-adsorbed species does influence the chemistry and reaction products formed.

Paul *et al.* determined that fluorine leads to destabilisation of the transition state and/or stabilisation of the initial state, reducing the rate of coupling.²⁵ Wu *et al.* observed that CF_3CH_2^- alkyl coupling has the highest activation barrier and coupling was not observed when CF_3CH_2^- is formed from CH_2 and CF_3 on $\text{Ag}(111)$.^{16, 19} Instead, β -fluoride elimination occurs and forms 1,1-difluoroethene.^{16, 19} In addition, cross-coupling of $\text{CF}_3\text{CH}_2\text{I}$ and $\text{CH}_3\text{CH}_2\text{CH}_2\text{SH}$ on $\text{Cu}(100)$ ⁶⁴ produces $\text{CF}_3\text{CH}_2\text{CH}_2\text{CH}_3$ while $\text{CH}_3\text{CH}_2\text{I}$ and $\text{CF}_3\text{CH}_2\text{CH}_2\text{I}$ couple on $\text{Ag}(111)$ to produce $\text{CF}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$.²⁵

On $\text{GaAs}(100)$ fluorine substitution does not affect the rate constant for CF_3CH_2^- coupling and the reason for this is as follows. Previous investigations of $\text{CF}_3\text{CH}_2\text{I}$ were studied on $\text{Ag}(111)$ where the elemental fluorine remains on the surface and influences the CF_3CH_2^- reactions. On $\text{GaAs}(100)$, fluorine (for both TFET and TFEI) and the iodine (only TFEI) diffuse into the bulk thereby

reducing their surface concentration. In addition, the formation of stable and volatile Ga and As halides ensure that the halogens do not influence the CF_3CH_2 - reactions, in particular coupling reactions.

In the case of TFET the concentration of surface fluorine is not expected to be high at only one time. Yet the rate constant for the coupling process is low and only one coupling product $\text{CF}_2=\text{CHCH}_2\text{CF}_3$ is formed. This is because decomposition of $\text{CF}_3\text{CH}_2\text{S}$ results in adsorbed S which blocks surface sites and prevents further reactions. However, sulphur is known to stabilise alkyl groups and this is the more important factor than site-blocking. Thus the CF_3CH_2 - groups remain longer on the surface and increase the rate constant for the coupling process as observed for insertion of $\text{CF}_2=\text{CH}_2$ into adsorbed CF_3CH_2 - species to form $\text{CF}_2=\text{CHCH}_2\text{CF}_3$.

In summary this chapter on alkyl reactions have shown that the effect of the co-adsorbed species does influence the chemical reactions that the CF_3CH_2 - species undergo.

5.8 References

1. L. G. Maidanovskaya, I. A. Kirovskaya, V. P. Balaganskaya, *Ser. Khim.*, **185** (1965), 124
2. X-L. Zhou, F. Solymosi, P. M. Blass, K. C. Cannon, J. M. White, *Surf. Sci.*, **219**, (1989), 294
3. X-L. Zhou, J. M. White, *Cat. Lett.*, **2**, (1989), 375
4. X-L. Zhou, P. M. Blass, B. E. Koel, J. M. White, *Surf. Sci.*, **271**, (1992), 452
5. X-L. Zhou, J. M. White, *J. Phys. Chem.*, **95**, (1991), 5575
6. D. M. Jaffey, R. J. Madix, *Surf. Sci.*, **311**, (1994), 159
7. C. J. Jenks, A. Paul, L. A. Smoliar, B. E. Bent, *J. Phys. Chem.*, **98**, (1994), 572 F
8. M.E. Castro, L. A. Pressley, J. Kiss, E. D. Pylant, S. K. Jo, X.-L. Zhou, J. M. White, *J. Phys. Chem.*, **97**, (1993), 8476
9. A. Szabo, S. E. Converse, S. R. Whaley, J. M. White, *Surf. Sci.*, **364**, (1996), 345
10. N. K. Singh, D. C. Doran, *Surf. Sci.*, **422**, (1999), 50
11. N. K. Singh, A. Bolzan, J. S. Foord, H. Wright, *Surf. Sci.*, **409**, (1998), 272
12. M. J. Overett, R. Oliver Hall, J. R. Moss, *Coord. Chem. Rev.*, **206-207**, (2000), 581
13. N. N. Greenwood, A. Earnshaw, *Chemistry of the Elements*, (1995), Cambridge, UK, 293
14. E. T. Fitzgerald, J. S. Foord, *J. Phys.: Condens. Matter*, **3**, (1991), S347
15. J-L. Lin, C-M. Chiang, C. J. Jenks, M. X. yang, T. H. Wentzlaff, B. E. Bent, *J. Catal.*, **147**, (1994), 250
16. H-J. Wu, H-K. Hsu, C-M. Chiang, *J. Am. Chem. Soc.*, **121**, (1999), 4433
17. J. E. Fieberg, A. Szabo, J. M. White, *J. Chem. Soc., Faraday Trans.*, **92**, (1996), 4739
18. J. G. Forbes, A. J. Gellman, *J. Am. Chem. Soc.*, **115**, (1993), 6277
19. A. Paul, A. J. Gellman, *Langmuir*, **11**, (1995), 4433
20. J-L. Lin, J. T. Yates, Jr., *J. Vac. Sci. Technol. A*, **13**, (1995), 178
21. M. E. Napier, C. M. Friend, *Langmuir*, **12**, (1996), 1800
22. J. T. Roberts, C. M. Friend, *J. Phys. Chem.*, **92**, (1988), 5205
23. M. E. Napier, C. M. Friend, *J. Phys. Chem.*, **99**, (1995), 8750

24. H-J. Wu, C-M. Chiang, *J. Phys. Chem. B*, **102**, (1998), 7075
25. A. Paul, A. J. Gellman, *J. Am. Chem. Soc.*, **117**, (1995), 9056
26. R. G. Jones, N. K. Singh, *Vacuum*, **38**, (1988), 213
27. Y-C. Hou, C-M, Chiang, *J. Am. Chem. Soc.*, **121**, (1999), 8116
28. Z-M. Liu, X-L. Zhou, J. Kiss, J. M. White, *Surf. Sci.*, **286**, (1993), 233
29. I. Kovacs, F. Solymosi, *J. Phys. Chem. B*, **101**, (1997), 5397
30. M. B. Jensen, U. Myler, C. J. Jenks, P. A. Thiel, E. D. Pylant, J. M. White, *J. Phys. Chem.*, **99**, (1995), 8736
31. S. M. Francis, P. A. Goulding, M. E. Pemble, *Vacuum*, **41**, (1990), 909
32. J. R. Creighton, *J. Vac. Sci. Technol. A*, **8**, (1990), 3984
33. *Eight Peak Index Mass Spectra*, 4th Ed., The Mass Spectrometry Group, (1991), Cambridge, UK
34. C. T. Foxon, J. A. Harvey, B. A. Joyce, *J. Phys. Chem. Solids*, **34**, (1973), 1693
35. B. C. Wiegand, C. M. Friend, P. Uvdal, M. E. Napier, *Surf. Sci.*, **355**, (1996), L311
36. T. Ishida, N. Choi, W. Mizutani, H. Tokumoto, I. Kojima, H. Azebara, H. Hokari, U. Akiba, M. Fujihira, *Langmuir*, **15**, (1999), 6799
37. D. G. Castner, K. Hinds, D. W. Grainger, *Langmuir*, **12**, (1996), 5083
38. Y-H. Lai, C-T. Yeh, S-H. Cheng, P. Laio, W-H. Hung, *J. Phys. Chem. B*, **106**, (2002), 5438
39. G. Kaindl, T-C. Chiang, D. E. Eastman, F. J. Himpsel, *J. Phys. Rev. Lett*, **45**, (1980), 1808
40. *Chemistry*, 3rd Ed., J. C. Bailar, Jr., T. Moeller, J. Kleinberg, C. O. Guss, M. E. Castellion, C. Metz, Harcourt Brace Jovanovich, Publishers, (1989), 226-227
41. J. Chatain, *Handbook of X-ray Photoelectron Spectroscopy*, Perkin-Elmer Corporation, (1993)
42. C. W. Sheen, J-X. Shi, J. Martensson, A. N. Parikh, D. L. Allara, *J. Am. Chem. Soc.*, **114**, (1992), 1514
43. S. Conrad, D. R. Mullins, Q. -S. Xin, X. -Y. Zhu, *Surf. Sci.*, **382**, (1997), 79
44. W. C. Simpson, P. R. Varekamp, D. K. Shuh, J. A. Yarmoff, *J. Vac. Sci. Technol. A*, **13**, (1995), 1709

45. P.R. Varekamp, W. C. Simpson, D. K. Shuh, T. D. Durbin, V. Chakarian, J. A. Yarnoff, *Phys. Rev. B*, **50**, (1994), 14267
46. A. B. McLean, L. J. Terminello, F. R. McFeely, *Phys. Rev. B*, **40**, (1989), 11778
47. P. K. Larsen, J. H. Neave, J. F. von der Veen, P. J. Dobson, B. A. Joyce, *Phys. Rev. B*, **27**, (1983), 4966
48. A. D. Katnani, H. W. Sang, Jr., P. Chiaradia, R. S. Bauer, *J. Vac. Sci. Technol. B*, **3**, (1985), 608
49. F. van der Veen, P. K. Lauren, J. H. Neave, B. A. Joyce, *Solid State Commun.*, **49**, (1984), 351
50. G. P. Schwartz, G. J. Gaultieri, G. W. Kammlott, B. Schwatz, *J. Electrochem. Soc.*, **126**, (1979), 1739
51. L. R. Williston, I. Bello, W. M. Lau, *J. Vac. Sci. Technol. A*, **11**, (1993), 1242
52. S. Tjandra, F. Zaera, *Surf. Sci.*, **289**, (1993), 255
53. *JANAF Thermochemical Tables*, 2nd ed.; National Bureau of Standards; Gaithersburg, MD, 1971
54. *CRC Handbook of Chemistry and Physics*, 70th ed.; CRC: Boca Raton, FL, 1990; pp F191 – 198, D67
55. I. Kovacs, F. Solymosi, *J. Phys. Chem.*, **97**, (1993), 11056
56. W. C. Simpson, J. A. Yarnoff, *Annu. Rev. Phys. Chem.*, **47**, (1996), 527
57. H. Nienhaus, W. Monch, *Appl. Surf. Sci.*, **104/105**, (1996), 95
58. N. T. Kemp, N. Paris, N. Singh, *J. Vac. Sci. Technol. A*, In press
59. S. Wehner, J. Kuppers, *J. Chem. Phys.*, **111**, (1999), 3218
60. P. R. Varekamp, M. C. Hakansson, D. K. Shuh, J. Kanski, L. Ilver, Z. Q. He, J. A. Yarnoff, U. O. Karlsson, *Vacuum*, **46**, (1995), 1231
61. A. Pai, C. J. Jenks, B. E. Bent, *Surf. Sci.*, **261**, (1992), 233
62. C. J. Jenks, M. Xi, M. X. Yang, B. E. Bent, *J. Phys. Chem.*, **98**, (1994), 2152
63. C. J. Jenks, B. E. Bent, F. Zaera, *J. Phys. Chem. B*, **104**, (2000), 3017
64. P. Gatland, *Hon. Thesis*, University of New South Wales, Sydney, 2000

CHAPTER VI

XPS AND TPD STUDIES OF TiCl_4 ADSORPTION ON $\text{Pt}(111)$

In this chapter, the results of experiments to study the adsorption and thermal stability of titanium tetrachloride on $\text{Pt}(111)$ will be reported. The results are used to discuss the implications for TiCl_4 as a titanium precursor, in particular for TiN deposition.

6.1 Introduction

Titanium tetrachloride is a good source material for titanium-based industries in the fields of hard coatings and catalysis. This titanium precursor has been used to deposit a number of coatings including TiN ^{1, 2, 3, 4, 5}, TiSi_2 ^{6, 7, 8, 9} and TiC ,¹⁰ and is also used as one of the key components in the Ziegler-Natta catalyst for the growth of long chain organic molecules.^{11, 12} The results presented in this chapter concentrate on the use of titanium tetrachloride as a source for TiN growth.

Whilst TiCl_4 has been successful in the deposition of Ti, albeit at high temperatures, the reactions by which TiCl_4 converts to elemental titanium is not well understood. For example, in some cases of the deposition of TiN, traces of chlorine are also found in films which cause adhesion problems, especially with stainless steel and refractory substrates such as tungsten carbide.¹³ Chlorine incorporation into the films is not understood and it would be desirable to elucidate the TiCl_4 reaction mechanisms so as to engineer optimum growth condition which will yield quality, chlorine free titanium layers.

6.1.1 Adsorption of Titanium Tetrachloride

Only a limited number of investigations have been reported on the interaction of titanium tetrachloride on a single crystal surface. Mendicino and Seebauer studied the interaction of TiCl_4 on $\text{Si}(100)^{14}$, while Chen *et al.* studied TiCl_4 on $\text{W}(100)^{18}$. At a low coverage, complete dissociation of TiCl_4 occurs on $\text{Si}(100)$ with only one desorption product, SiCl_2 , detected.¹⁴ The remaining surface titanium diffuses into the bulk.¹⁴ As the silicon surface is exposed to a higher coverage of TiCl_4 , molecular TiCl_4 desorbs with SiCl_2 and some SiCl_4 also detected in the TPD spectra.¹⁴ The complete removal of chlorine from the surface in the form of SiCl_2 occurs after heating the substrate to 950 K.¹⁴ This desorption temperature corresponds to the growth temperature at which good quality TiSi_2 films are deposited.^{14, 15} A further study shows that the hydrogen atoms in SiH_4 (the silicon source for TiSi_2 growth) are not effective at removing the bulk of the chlorine from the surface via HCl abstraction reactions.¹⁵ Therefore, chlorine removal (in the form of SiCl_2 desorption) is the limiting step for the lowering of the growth temperature of TiSi_2 films. Furthermore, these results show the importance of surface chemistry studies to improve industrial processes.

The adsorption of titanium tetrachloride on $\text{W}(100)$ was studied by Chen *et al.*¹⁸ Adsorbing on the surface molecularly, TiCl_4 subsequently desorbs from the surface at 170, 225 and 455 K.¹⁸ The 170 K state is the result of multi-layer formation while the TPD peak at 225 K is due to desorption of chemisorbed molecular state and/or TiCl_3 and Cl recombination.¹⁸ Heating the substrate further results in the conversion of Ti^{4+} to Ti^{3+} .¹⁸ The third TiCl_4 state evolves in

this temperature range and is due to a disproportionation reactions with one possible pathway outlined in (1).¹⁸



Titanium and chlorine on the surface are not detected after heating the substrate to 2000 K and 1500 K, respectively.¹⁸ This desorption temperature for chlorine is consistent with the deposition temperature for the growth of good quality Ti-based coatings. For example, deposition of TiC using TiCl_4 and propane (as carbon source) on tungsten occurs at ~ 1300 K.¹⁰ This result is similar to reports of Mendicino *et al.*¹⁴ and shows that chlorine desorption is the limiting step for lowering the deposition temperature for the growth of Ti-based coatings.

Titanium tetrachloride weakly adsorbs on Au foil and MgCl_2 thin films at liquid nitrogen temperatures.^{11, 12, 16} Sublimation of the TiCl_4 layer is the only desorption product observed. Chemical activation of this layer for these surfaces can be obtained by electron irradiation with a mixed TiMgCl_x phase detected for the latter surface and the reduction of the Ti^{4+} species on the former.^{11, 16}

6.1.2 Aims

The aims of this study of TiCl_4 on Pt(111) are to:

1. Investigate the adsorption, thermal stability and the reaction products of TiCl_4 on Pt(111) using the technique of TPD spectroscopy.

2. To investigate the bonding characteristics of TiCl_4 on $\text{Pt}(111)$ using XPS, in particular, identification of the oxidation states of Ti following adsorption and thermal decomposition.

6.2 Results

6.2.1 TPD Study of TiCl_4 on $\text{Pt}(111)$

The uptake and desorption behaviour of titanium tetrachloride on $\text{Pt}(111)$ was studied using TPD spectroscopy. A number of species were monitored by TPD spectroscopy: TiCl_x where $x = 0 - 4$ ($m/z = 48, 83, 118, 153, 188$ amu), Cl ($m/z=35$) and Cl_2 (70 amu)). All species detected showed desorption features in the spectra. However, only Ti and Cl showed desorption features at high temperatures.

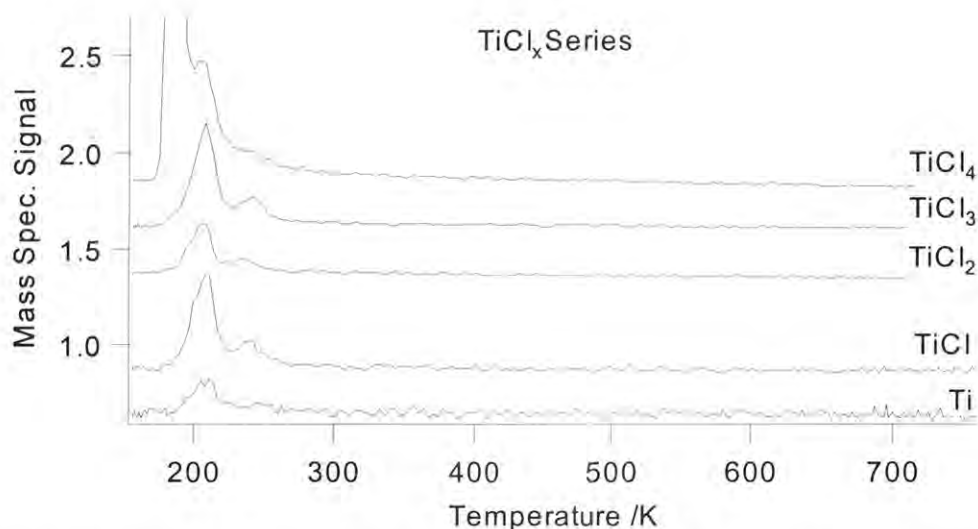


Figure 6.1 The TPD spectra of the adsorption of TiCl_4 on $\text{Pt}(111)$ whilst monitoring Ti ($m/z = 48$) for 1 L and TiCl ($m/z = 93$), TiCl_2 ($m/z = 118$), TiCl_3 ($m/z = 153$), and TiCl_4 ($m/z = 188$) for 4 L at 130 K. The surface was heated to 196 K before each TPD experiment to remove the physisorption peak with the exception of the TiCl_4 where it is included for clarity. Heating rate is 10 K s^{-1} .

The desorption of TiCl_x ($x = 1 - 4$) was investigated for a 4 L exposure of titanium tetrachloride (Figure 6.1). A spectrum tuned to Ti ($m/z = 48$) is also included in Figure 6.1 for comparison at a lower coverage of 1 L. All five spectra show two peaks occurring at 210 and 242 K, assigned $\alpha_1\text{-TiCl}_4$ and $\alpha_2\text{-TiCl}_4$,

respectively. A lower temperature peak is also observed at 188 K in the TiCl_4 spectrum due to physisorbed TiCl_4 . The other spectra also contain this low-temperature peak, however, it was desorbed prior to the TPD experiment to clarify the positions of the other low-temperature states. The three peaks have an activation energy for desorption of 45.6, 51.4 and 59.4 kJ mol^{-1} , respectively, after applying the Redhead equation with a heating rate of 9 K s^{-1} . The desorption state of 45.6 kJ mol^{-1} corresponds to the literature value of heat of sublimation of 46 kJ mol^{-1} (*i.e.* from the sum of the heats of fusion and evaporation of titanium tetrachloride at 298 K^{17}).

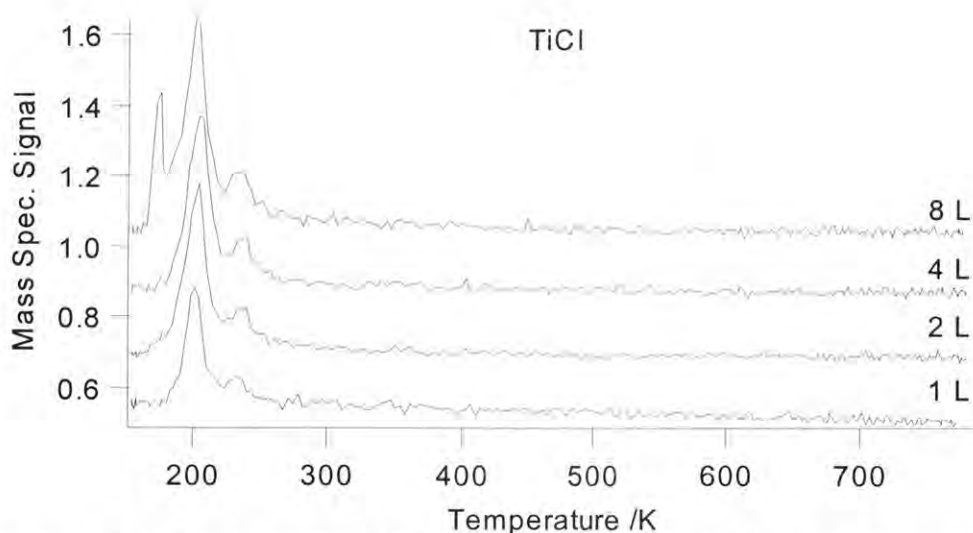


Figure 6.2 The TPD spectra of the uptake of TiCl_4 on $\text{Pt}(111)$ whilst monitoring TiCl ($m/z = 93$). The surface was heated to 196 K before each TPD experiment to remove the physisorption peak. Heating rate is 10 K s^{-1} .

The uptake of TiCl_4 plot monitoring TiCl is shown in Figure 6.2. The peaks at 210 K corresponds to molecular desorption of TiCl_4 while the 242 K peak corresponds to recombinative desorption of TiCl_3 and Cl or molecular desorption from defect sites. As the TiCl_4 exposure is increased, the 210 K peak remains constant, indicating 1st order desorption and molecular desorption. The

desorption energies of these states agree with TiCl_4 desorption from $\text{W}(100)^{18}$ and the higher temperature state, as identified in that paper, may be due to TiCl_4 desorption from defect sites. For a greater exposure of titanium tetrachloride between 8 and 20 L, no additional peaks were detected in the TPD spectra of TiCl and hence were not included. This result was confirmed when the TiCl_x (where $x = 2 - 4$) species were monitored.

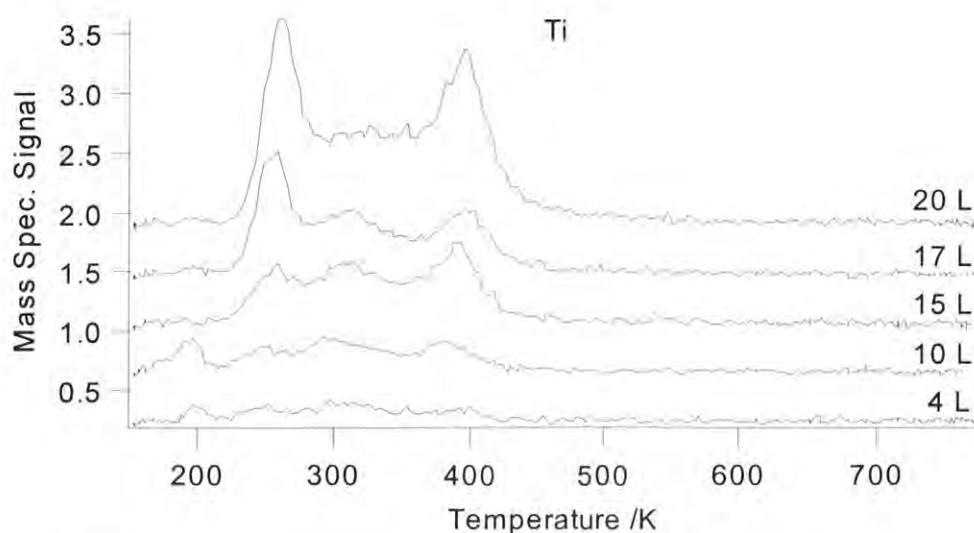


Figure 6.3 The TPD spectra of Ti ($m/z = 48$) monitored after the adsorption of TiCl_4 on Pt(111) at 130 K followed by heating to 196 K to remove the physisorption peak. Heating ramp is 10 K s^{-1} .

The desorption of Ti was monitored after heating the dosed substrate to 197 K to remove the physisorbed species. High temperature peaks are observed for higher exposures of titanium tetrachloride (Figure 6.3) occurring at 250, 305 and 393 K at an exposure of 4 L. All three peaks increase as a function of titanium tetrachloride exposure. The appearance of the 250 K peak in all five spectra of TiCl_x where $x = 0-4$ indicates that it is the $\alpha_2\text{-TiCl}_4$ desorption product. The small shift to higher temperature of 250 K instead of 242 K is an anomaly due to the effect of the presence of the higher temperature peaks. The peak at 305 K reaches saturation at 17 L and shows an apparent shift to higher temperatures

with increasing exposures of TiCl_4 . Levelling out at 20 L, the peak at 393 K shows an apparent shift to higher temperatures. The peaks at 305 and 393 K have been assigned as the $\gamma_1\text{-Ti}$ and $\gamma_2\text{-Ti}$ products, respectively. The two higher temperature peaks have a desorption energy of 75.6 and 98.2 kJ mol^{-1} , respectively, when applying Redhead's equation with a heating rate of 9 K s^{-1} .

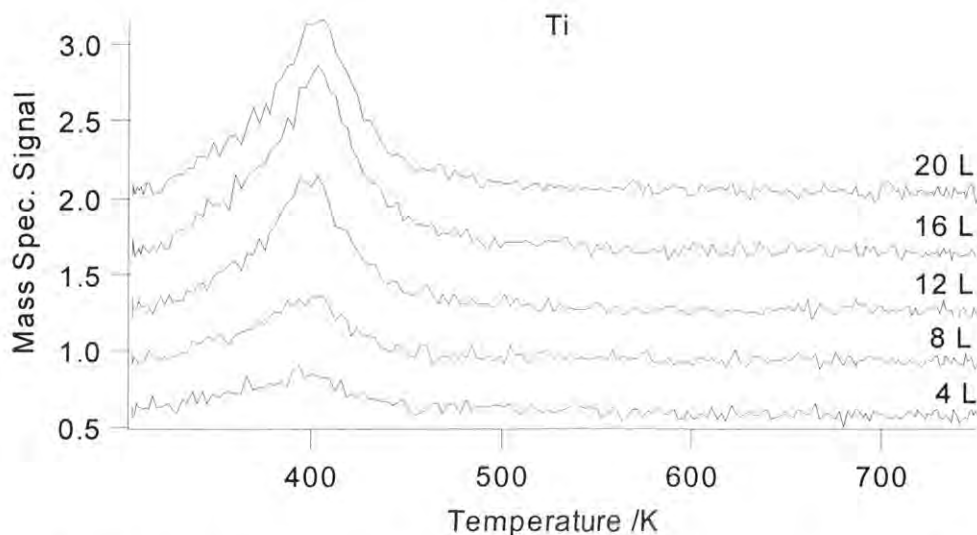


Figure 6.4 The TPD spectra of TiCl_4 adsorbed on Pt(111) at an elevated temperature of 300 K whilst monitoring Ti ($m/z = 48$). Heating rate is 10 K s^{-1} .

The highest temperature state of Ti in Figure 6.2 was monitored following adsorption at 300 K when this was the only state expected that would become populated. The TPD spectra in Figure 6.4 are dominated by one peak occurring at 400 K. The peak-maximum remains constant as a function of titanium tetrachloride exposure. This observation indicates that the low temperature peaks affects the 400 K state such that there is an observed shift to higher temperatures when the surface is exposed to titanium tetrachloride at lower temperatures. Furthermore, this shows that kinetic order information is difficult to obtain from Figure 6.3 with the lower temperature peaks influencing the peak maxima.

The desorption of molecular and atomic chlorine was also studied to provide information about the nature of chlorine on the surface. There is only one peak at ~ 190 K due to mass spectrometer fragmentation of TiCl_4 . (Figure 6.5). The peaks expected from $\alpha\text{-TiCl}_4$ states are not present due to the dominance of the ~ 190 K peak which eclipsed the small signal from the chemisorbed states.

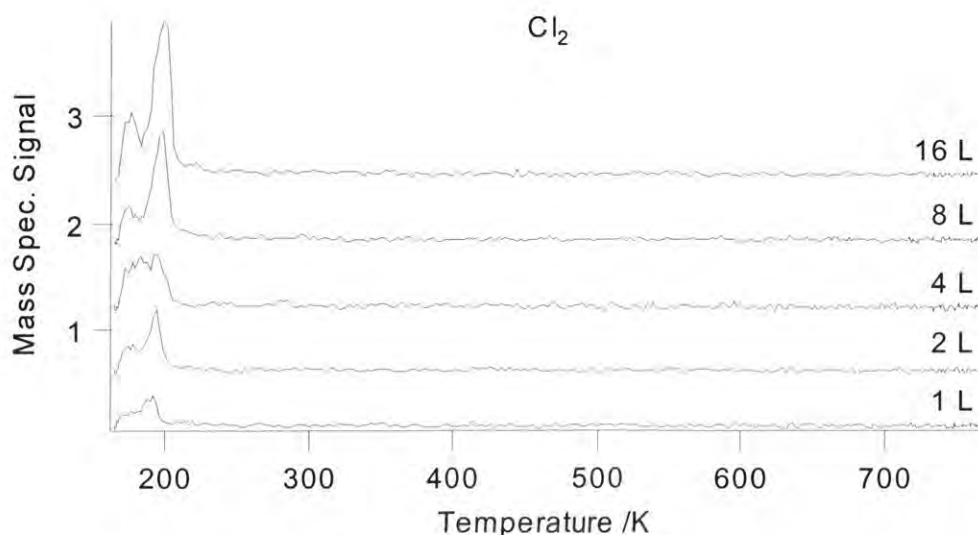


Figure 6.5 The TPD spectra of the uptake of TiCl_4 on Pt(111) monitoring Cl_2 ($m/z = 70$) at 130 K. Heating ramp is 10 K s^{-1} .

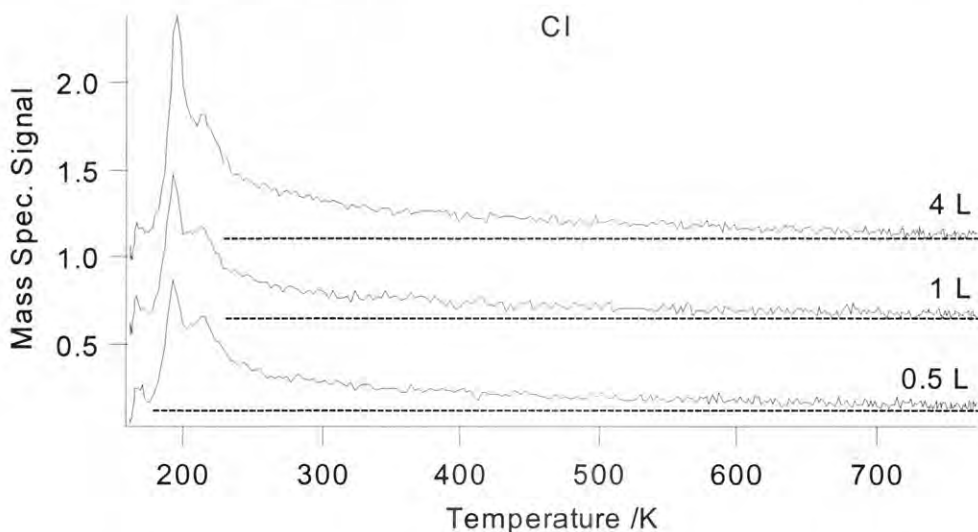


Figure 6.6 The uptake of TiCl_4 on Pt(111) at 150 K monitoring Cl ($m/z = 35$) using TPD spectroscopy. Heating rate is 10 K s^{-1} .

Desorption profiles monitoring Cl ($m/z = 35$) were acquired as a function of TiCl_4 exposure (Figure 6.6). Two peaks were detected at 196 and 217 K. These two peaks are due to mass spectrometer fragmentation of the multi-layer desorption and the α_1 - TiCl_4 desorption state, respectively. As the substrate temperature increases, the Cl spectra do not immediately return to a stable baseline as observed in other spectra presented in this chapter. Instead, the Cl signal is only gradually restored to a flat baseline over a wide temperature range. This sloping background may indicate that there is gradual desorption of atomic chlorine from the surface for a broad temperature range. A dashed line has been inserted under each spectrum to highlight this feature.

Furthermore, the species PtCl ($m/z = 230$ amu) were monitored but no evidence of corrosion was observed.

The effect of an applied bias to the substrate was studied to determine the level of electron-induced dissociation of the titanium tetrachloride layer. Stray electrons from the mass spectrometer and the ion gauge can cause electron induced dissociation in adsorbed layers, particularly in the halogen-metal bonds. This has been reported for the decomposition of titanium tetrachloride layers on MgCl_2 thin films by electron irradiation.^{11, 16} Experiments were conducted by monitoring TiCl_x ($x = 1 - 4$) while applying a bias of -100 V to the sample. This bias repelled any stray electrons, preventing electron-induced dissociation of the titanium tetrachloride layer. The resulting spectra showed no difference to those spectra presented in Figure 6.1. Therefore, no electron-induced dissociation was detected.

6.2.2 XPS Thermal Desorption Studies

The surface was initially exposed to a multi-layer coverage of titanium tetrachloride (100 L). The surface was heated successively to higher temperatures to thermally dissociate the layers. XPS was used to monitor the Pt 4f, Ti 2p and Cl 2p binding energy regions.

The Pt 4f region consists of a pair of peaks ($4f_{7/2}$, $4f_{5/2}$) due to spin-orbit coupling, separated by 3.3 eV (Figure 6.7). The peak area of the Pt 4f photoemission feature increases as a function of temperature due to desorption of first the multi-layers and then the mono-layer. The largest increase in Pt 4f signal is in going from 113 to 273 K, indicating that multi-layer desorption is complete by 273 K. After heating the surface to 473 K, the peak area plateaux out.

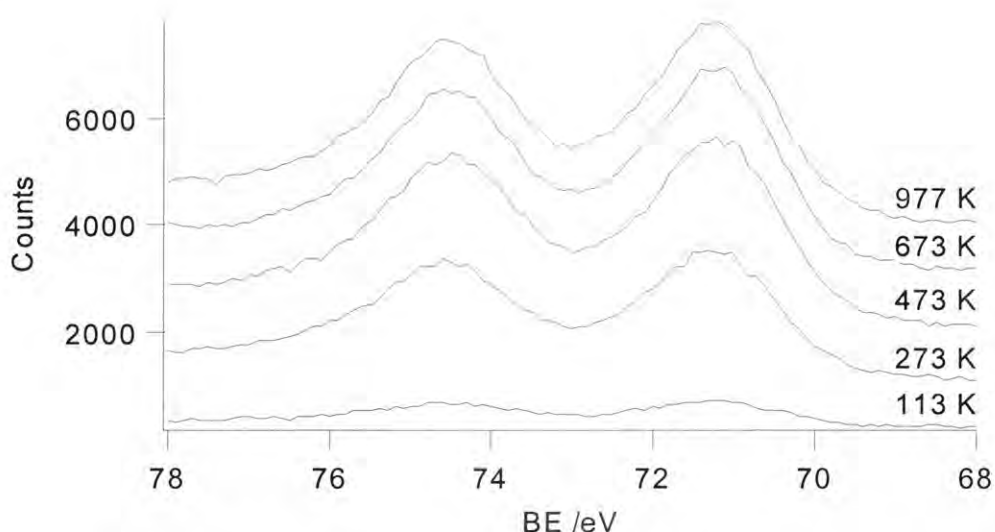


Figure 6.7 The thermal stability of a multi-layer coverage of titanium tetrachloride (100 L at 113 K) observed using the Pt 4f XPS region. Spectra are referenced to the Pt $4f_{5/2}$ peak at 71.0 eV.

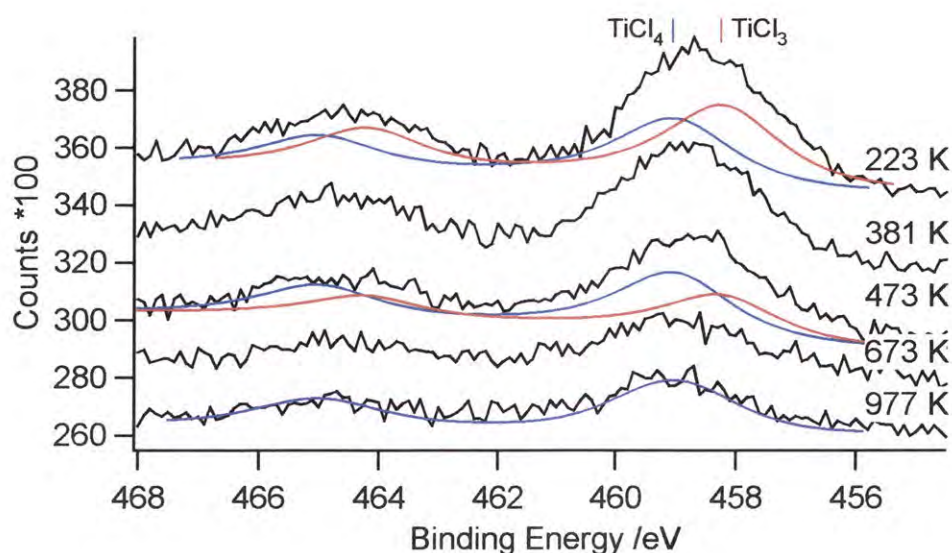


Figure 6.8 The thermal desorption study of TiCl_4 (100 L at 113 K) on Pt(111) monitoring the Ti 2p XPS region as a function of temperature with the line indicating the positions of the TiCl_4 and TiCl_3 species. Spectra are referenced to the Pt $4f_{5/2}$ peak at 71.0 eV.

Figure 6.8 shows XP spectra monitoring the Ti 2p region. At 223 K, the peak maxima occur at 458.7 eV ($2p_{3/2}$) and 464.8 eV ($2p_{1/2}$). Each spectrum has contributions from TiCl_4 , TiCl_3 and Ti species based on $2p_{3/2}$ literature values of 459.0 for TiCl_4 , 458.2 eV for TiCl_3 and 455.0 eV for Ti.¹⁸ The surface initially begins with a TiCl_x layer and decomposition leads to the formation of TiCl_3 and TiCl_x ($x = 0,1$) by 900 K. Figure 6.9 shows the total Ti signal (area under all peaks) plotted as a function of substrate temperature. Two distinct regions are observed; $T < 500$ K where TiCl_4 exists predominantly and $T > 500$ K where TiCl_4 decomposes into TiCl_x ($x = 0 - 3$). Comparison of Figure 6.9 with the total Cl peak area shown in Figure 6.11 leads to the conclusion that there is a sharp decrease at ~ 500 K and this decrease is due to desorption of TiCl_x species. In Figure 6.11, it is observed that by 500 K Cl concentration has decreased by 80 % indicating desorption and possible decomposition of TiCl_x species. Furthermore, no loss of Ti concentration is observed in the XPS spectra for

temperatures greater than 573 K. This observation is consistent also with TPD analysis where no peaks were detected in any of the spectra above 500 K.

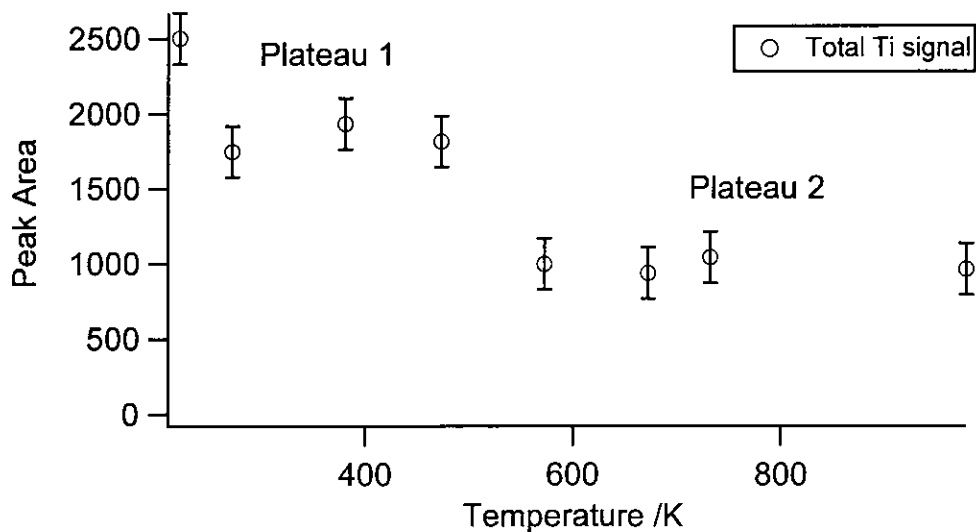


Figure 6.9 The total XPS Ti [O] signal for the XPS thermal desorption experiments plotted as a function of temperature.

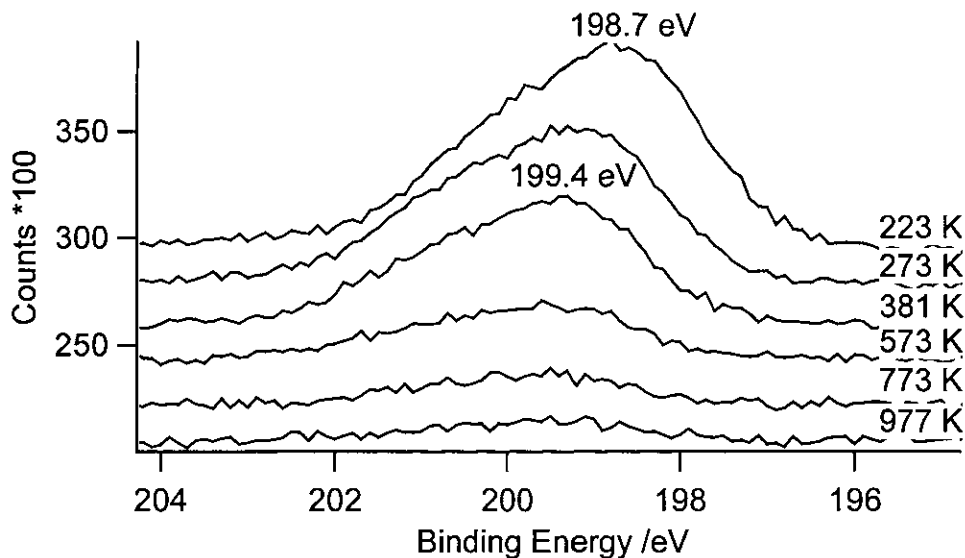


Figure 6.10 The thermal stability of TiCl_4 (100 L at 113 K) on Pt(111) observed using the Cl 2p XPS region.

The Cl 2p region contains one photoemission feature (Figure 6.10). The photoemission feature area and maximum position were recorded for each spectrum. At 223 K, the feature-maximum is 198.7 eV and as the surface is heated to 381 K, the peak shifts to 199.4 eV. This maximum does not shift

further when heated. The area of the photoemission feature is reduced and when the area is plotted as a function of temperature with an exponential decay observed (Figure 6.11).

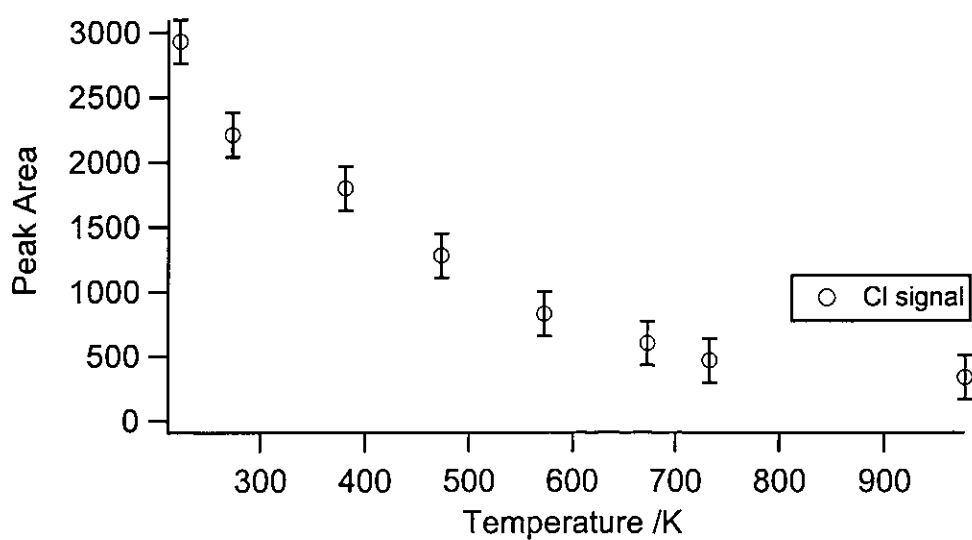


Figure 6.11 The total Cl XPS [O] signal for the XPS thermal desorption experiments plotted as a function of temperature.

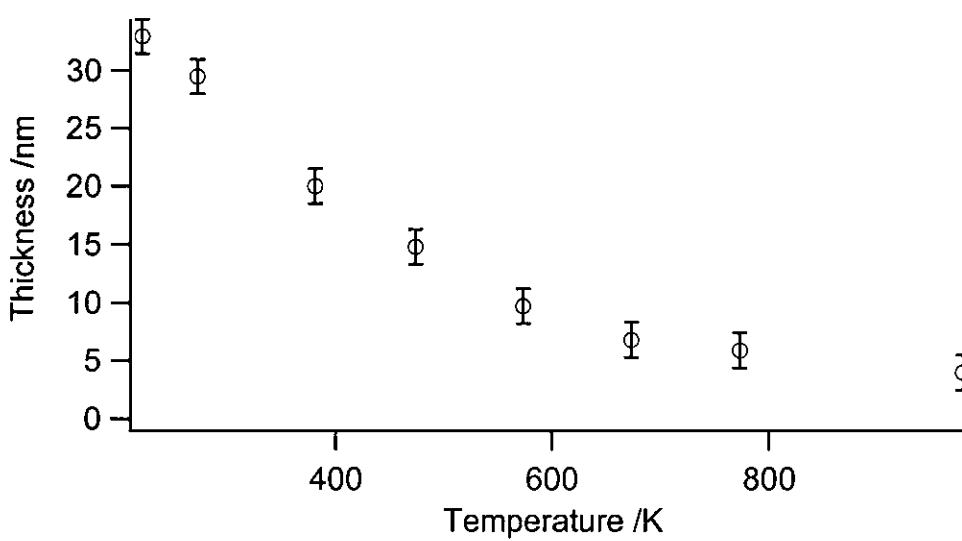


Figure 6.12 The thickness of the TiCl₄ layer as a function of temperature.

The thickness of the TiCl₄ layer was determined using the inelastic mean free path of Pt (1.90 nm), Ti (4.42 nm) and Cl (4.93 nm) assuming the surface consisted of a surface layer of TiCl₄ on Pt(111) substrate. Wagner sensitivity factors were used and the result is plotted in Figure 6.12. The graph shows that the loss of titanium occurs as the temperature is increased.

6.3 Discussion

The results presented in this chapter indicate that the mechanism of titanium tetrachloride adsorption proceeds through the following pathways, outlined in Figure 6.13.

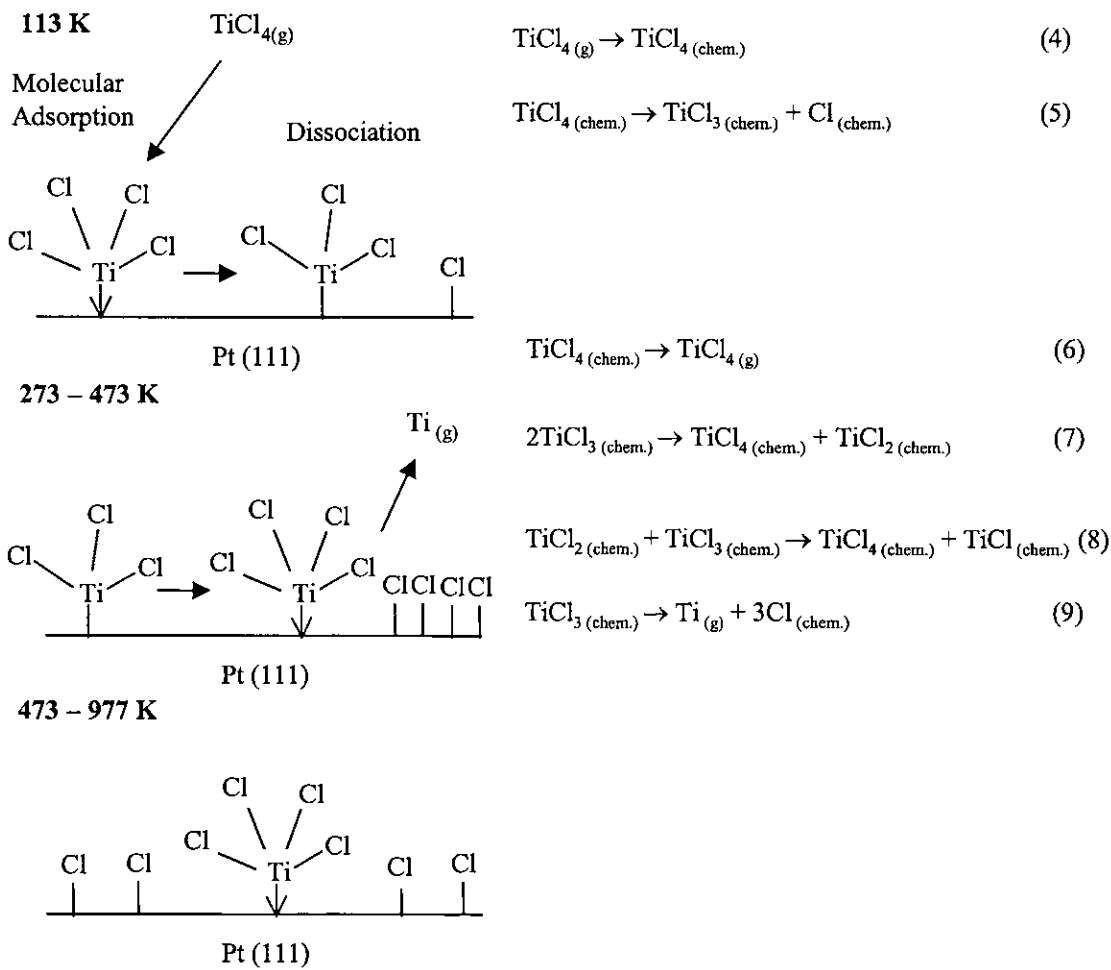


Figure 6.13 Reaction scheme proposed for titanium tetrachloride adsorption on Pt(111).

In summary, TiCl_4 adsorbs molecularly on Pt(111) at 113 K (4). Heating the surface to 190 K results in desorption of the physisorbed TiCl_4 species (6). Further heating results in competition between molecular desorption of the $\alpha_{1,2}$ - TiCl_4 and dissociation to form $\text{TiCl}_{3(\text{chem.})}$ and $\text{Cl}_{(\text{chem.})}$. These species decompose further to desorb $\gamma_{1,2}$ -Ti via possible disproportionation and/or

dissociation pathways outlined in (5, 7-9). Heating the surface beyond 473 K, results in irreversibly bonded TiCl_4 which is still detected on the surface at 977 K.

The exact kinetics for the formation of the $\alpha_2\text{-TiCl}_4$ state is undetermined as the $\alpha_1\text{-TiCl}_4$ state obscures the peak maxima in the TiCl_x (where $x = 1 - 4$) TPD spectra. Furthermore, the $\gamma_{1,2}\text{-Ti}$ states may alter the peak maxima for $\alpha_2\text{-TiCl}_4$ peak when monitoring Ti during TPD. This presents a problem as to the nature of desorption as to whether it is molecular or recombinative desorption. Chen *et al.* observed a similar peak for TiCl_4 adsorption on $\text{W}(100)^{18}$ and assigned the $\alpha_2\text{-TiCl}_4$ state to molecular desorption of TiCl_4 from defect sites. Without any other clear evidence, isotope scrambling experiments are required involving co-adsorption of TiCl_4 with atomic ^{37}Cl . Since maintaining of the natural 3:1 ratio between the ^{35}Cl and ^{37}Cl would indicate molecular desorption while a higher ratio of ^{37}Cl indicates recombination.

There is significant evidence to suggest that the γ -states are due to atomic titanium desorption from the surface and is not the result of fragmentation of the TiCl_x species. The $\gamma_{1,2}\text{-Ti}$ states do not occur in the TPD spectra monitoring TiCl_x species (where $x = 1 - 4$). Nor can these states be attributed to atomic titanium formed by electron-induced dissociation of TiCl_x species as no change was noted in the TPD spectra of TiCl_x when a negative bias was applied. The mechanism for the formation of $\gamma_{1,2}\text{-Ti}$ may be through a series of disproportionation reactions and/or dissociation process. The disproportionation pathway proceeds *via* TiCl_3 species disproportionating to form TiCl_4 and TiCl_2 species. TiCl_2 species are not very stable and rapidly decay to form atomic

chlorine and the desorption product Ti as outlined in reactions (7-8). Reacting by disproportionation has been reported for TiCl_4 adsorption on $\text{W}(100)^{18}$ and for the decomposition of solid TiCl_3 and TiCl_2 .¹⁹ Alternatively, the dissociation mechanism involves successive loss of Cl until no chlorine remains bonded to Ti with the Ti ejected from the surface in the process (see reaction (9)). Both mechanisms involve loss of TiCl_3 , a species detected by XPS between 223 and 573 K, the temperature range within which the $\gamma_{1,2}$ -Ti states are formed. It is not until 573 K where there is a shift to higher BE indicating that TiCl_3 species no longer remain on the surface at a significant amount above this temperature. This observation provides further evidence that TiCl_3 species play an important role in Ti generation. Therefore, both processes are likely, giving rise to the two states, γ_1 -Ti and γ_2 -Ti, observed. For more conclusive proof as to the exact mechanism, synchrotron radiation studies are required to isolate the different oxidation states.

For temperatures 573 K and up to 977 K, Ti^{4+} species are favoured with the Ti 2p XPS spectra showing a shift to 459.1 eV. Under certain conditions, the Ti^{4+} state has been reported to be favoured over other oxidation states, especially Ti^{3+} . Boffa *et al.* reported that all the Ti^{3+} species are converted to Ti^{4+} when titanium oxide films containing a mixture of $\text{Ti}^{4+}/\text{Ti}^{3+}$ species are heated in an oxygen atmosphere.²⁰ This conversion is due to a reduction in the wetting of the Pt surface by the oxide as less oxide is coordinated to the Pt surface and more to the Ti group. A similar effect may be present in this study with the large amounts of chlorine both on the surface and in the gas-phase, the result of γ -Ti desorption, wetting the surface. It is not uncommon for titanium halides to increase the wetting of the surface and TiF_3 has been used to lower the contact

angle of Cu-Sn alloys.²¹ Therefore higher temperatures are needed to desorb more chlorine such that the concentration on the surface is reduced sufficient for reduction of the Ti^{4+} species to occur.

The presence of Ti^{4+} indicates a high coordination of chlorine which is known to inhibit the growth of Ti-based coatings. As reported for titanium tetrachloride adsorption on $\text{Si}(100)^{14}$ and $\text{W}(100)^{18}$, both studies show that the co-precursors (*i.e.* C_3H_8 for TiC and SiH_4 for TiSi_4) are, for the most part, ineffective at removing chlorine with thermal desorption the best mechanism for chlorine loss. Therefore, based on this information and due to the lingering amount of chlorine on the surface at 977 K, deposition of Ti-based coatings are limited to temperatures greater than 977 K when depositing such material on Pt.

6.4 Conclusions

Titanium tetrachloride, a common precursor used in industry for TiN deposition, adsorbs initially molecularly. This form desorbs molecularly from the α_1 -state and α_2 -state likely as the result of recombinative TiCl_3 and Cl desorption. Successive heating results in dissociation of TiCl_4 on Pt(111) to form TiCl_3 and atomic chlorine. Heating results in disproportionation and/or dissociation reactions to generate TiCl_4 and Ti. Atomic Ti is the only Ti-containing high temperature desorption product observed and its desorption results in a large accumulation of chlorine on the surface. This effect causes increased wetting of the surface which can be alleviated by either conversion of TiCl_x species into TiCl_4 or direct Cl desorption. As found with other studies of TiCl_4 on single crystal surfaces, chlorine desorption is the rate-limiting step for TiN formation.

Future work could involve reactions of co-adsorbed TiCl_4 and a range of nitrogen source (e.g. ammonia, hydrazine) or reactions of TiCl_4 with industrial surfaces such as TiN coated platinum. The former would provide information about which nitrogen source is the most effective at abstracting the chlorine. Such studies can lead to better production of CVD materials. The use of industrial surfaces can also improve TiN production by analysing the effect of the TiCl_4 as the film thickness increases and the properties of the surface reflect the deposited material.

6.5 References

1. J. B. Price, J. O. Borland, S. Selbrede, *Thin Solid Films*, **236** (1993), 311
2. M. Ritala, M. Leskela, E. Rauhala, P. Haussalo, *J. Electrochem. Soc.*, **142**, (1995), 2731
3. A. Sherman, *J. Electrochem. Soc.*, **137**, (1990), 1892
4. P. Motte, M. Proust, J. Torres, Y. Gobil, Y. Morand, J. Palleau, R. Pantel, M. Juhel, *Microelectronic Engineering*, **50**, (2000), 369
5. R. I. Hegde, R. W. Fiodalice, P. J. Tobin, *Appl. Phys. Lett.*, **62**, (1993), 2326
6. J. Lee, R. Reif, *J. Electron. Mater.*, **20**, (1991), 331
7. G. J. Reynolds, C. B. Cooper III, P. J. Garczi, *J. Appl. Phys.*, **65**, (1989), 3212
8. J. Mercier, J. L. Regolini, D. Bensahel, *J. Electron. Mater.*, **19**, (1990), 253
9. K. Saito, T. Amazawa, Y. Arita, *Jpn. J. Appl. Phys.*, **29**, (1990), L185
10. E. A. Hauptfear, L. D. Schmidt, *J. Electrochem. Soc.*, **140**, (1993), 1793
11. E. Magni, G. A. Somorjai, *Surf. Sci.*, **345**, (1996), 1
12. E. Magni, G. A. Somorjai, *Appl. Surf. Sci.*, **89**, (1995), 187
13. J-H. Boo, C. H. Heo, Y. K. Cho, J-G. Han, *J. Vac. Sci. Technol. A*, **18**, (2000), 1590
14. M. A. Mendicino & E. G. Seebauer, *Surf. Sci.*, **277**, (1992), 89
15. M. A. Mendicino & E. G. Seebauer, *J. Electrochem. Soc.*, **140**, (1993), 1786
16. S. H. Kim, G. A. Samorjai, *J. Phys. Chem.*, **106**, (2002), 1386
17. Ed. D. R. Lide, *Chemical Handbook of Chemistry and Physics*, (1992), CRC Press, Boca Raton, FL
18. W. Chen, J. T. Roberts, *Surf. Sci.*, **359**, (1996), 93
19. F. A. Cotton, G. Wilkinson, *Advanced Inorganic Chemistry*, 4th Ed., (1980), Wiley, New York, USA
20. A. B. Boffa, H. C. Galloway, P. W. Jacobs, J. J. Benitez, J. D. Batteas, M. Salmeron, A. T. Bell, G. A. Somorjai, *Surf. Sci.*, **326**, (1995), 80
21. 254-255: Y. V. Naidich, V. P. Krasovsky, *Pro. 2nd Int. Conf. on High Temperature Capilarity*, Cracow (Poland) 29 June – 2 July, ed. N. Eustathopoulos & N. Sobczak, published by Foundry Research Institute (Cracow), (1998), 87

APPENDIX A

XPS DATA FOR Cl_2 ADSORPTION ON CVD DIAMOND

The following data is the raw XPS data found in Chapter 4 that has not been referenced based on the initially clean carbon 1s peak as well as some spectra that was absent in Chapter 4 to save space but may be of interest.

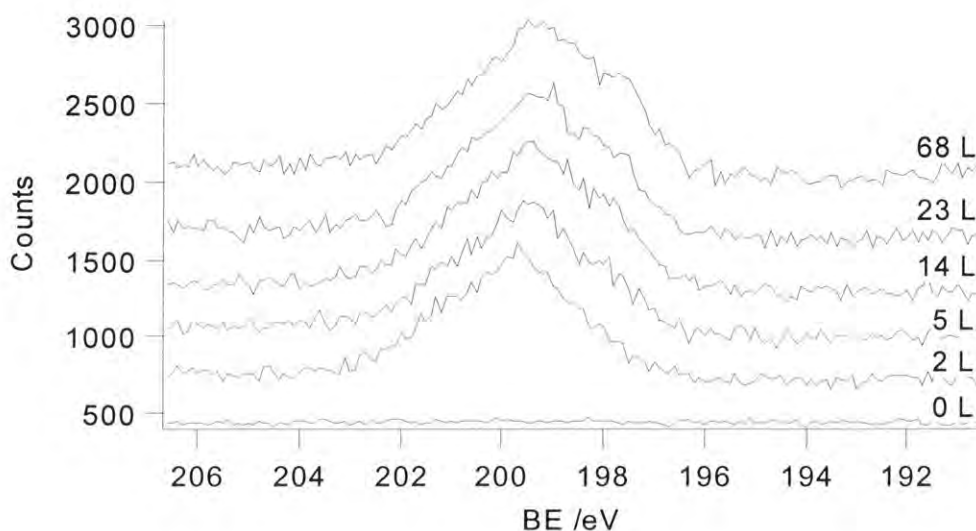


Figure A1 The Cl 2p XPS spectra monitoring the uptake of molecular chlorine on CVD diamond surface.

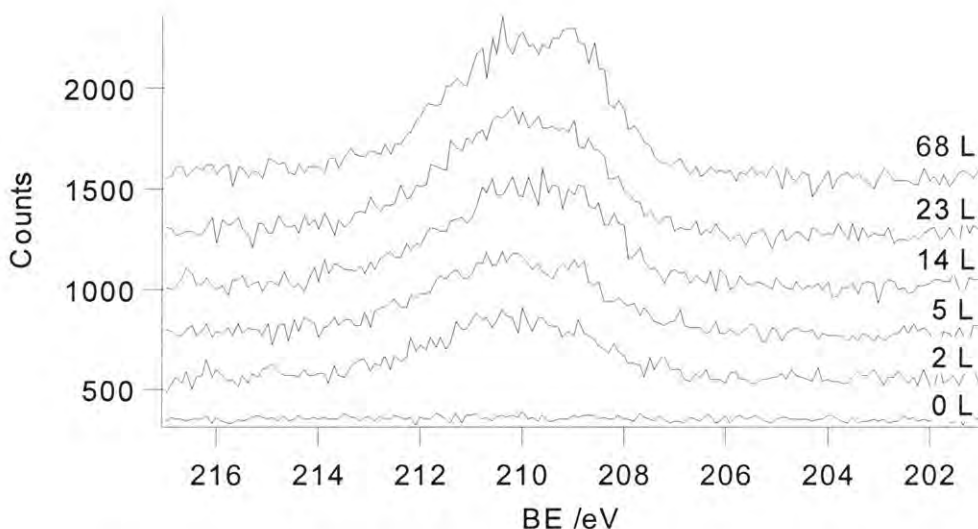


Figure A2 The uptake of Cl_2 on a hydrogen-terminated ($P_{\text{H}_2} = 1.0 \times 10^{-4}$ for 20 minutes) CVD diamond surface observed using the Cl 2p XPS region.

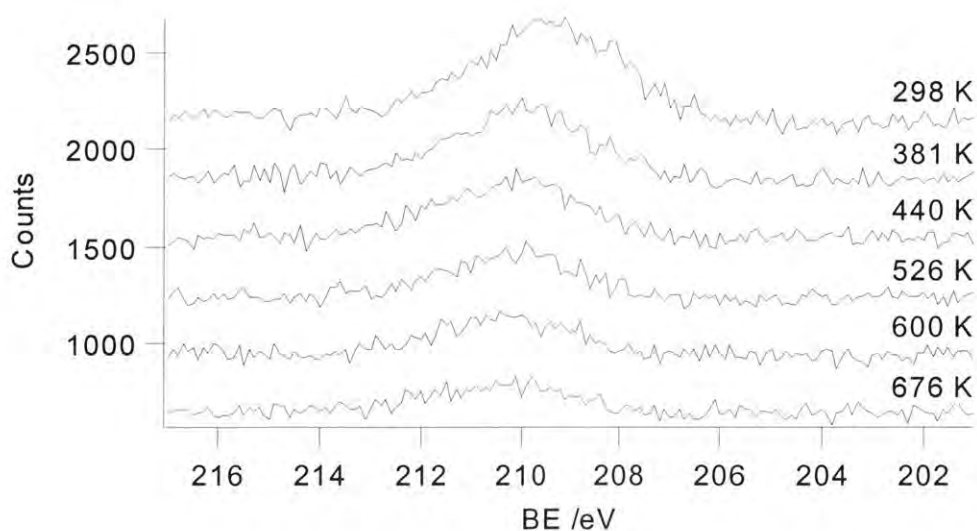


Figure A3 The thermal stability of a saturated chlorinated diamond surface (Cl_2 exposure is 23 L at 298 K) monitored using the Cl 2p XPS region.

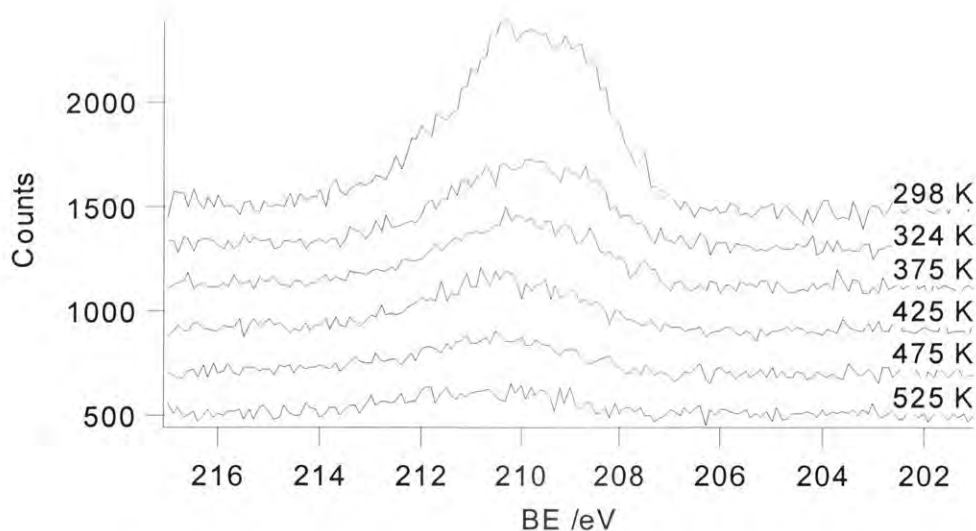


Figure A4 The thermal desorption of chlorine (Cl_2 exposure is 23 L at 298 K) from a hydrogen-terminated CVD diamond surface ($P_{\text{H}_2} = 1.0 \times 10^{-4}$ for 20 minutes) observed using the Cl 2p XPS region.

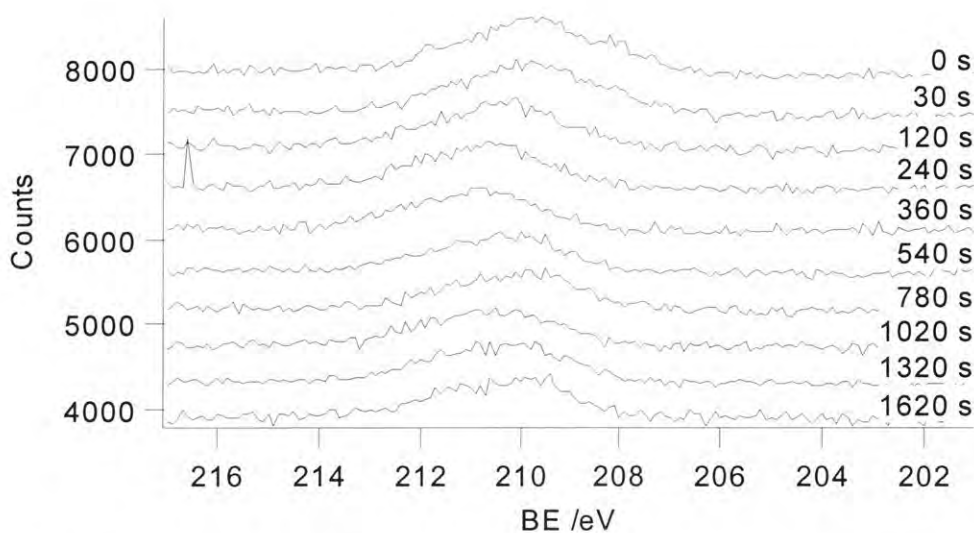


Figure A5 The etching of the chlorine layer (Cl_2 exposure is 23 L at 298 K) on CVD diamond as a function of atomic hydrogen exposure time using a constant H_2 pressure of 1.0×10^{-7} mbar and monitoring the Cl 2p XPS region.

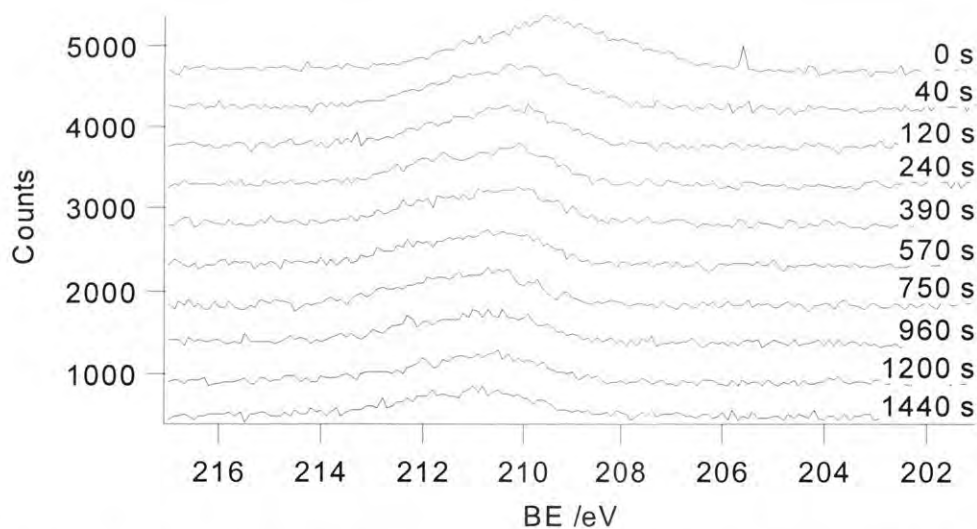


Figure A6 The Cl 2p XPS spectra showing the saturation chlorine layer (Cl_2 exposure is 27 L at 298 K) as it is exposed to atomic hydrogen ($P_{\text{H}_2} = 1.0 \times 10^{-6}$ mbar) for the periods indicated.

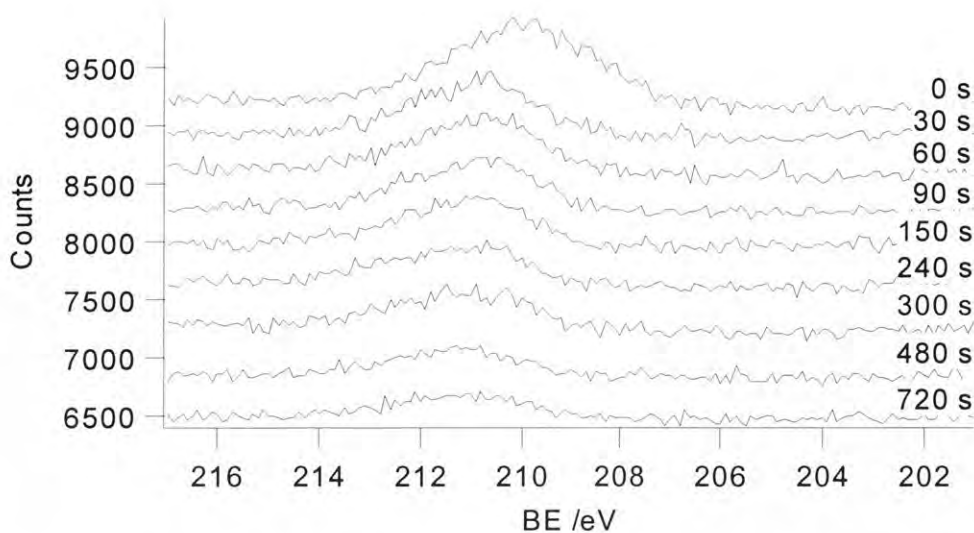


Figure A7 Etching of the chlorine coverage (Cl_2 exposure is 23 L at 298 K) on CVD diamond by atomic hydrogen ($P_{\text{H}_2} = 1.0 \times 10^{-5}$ mbar) for the times indicated and observed using the Cl 2p XPS region.

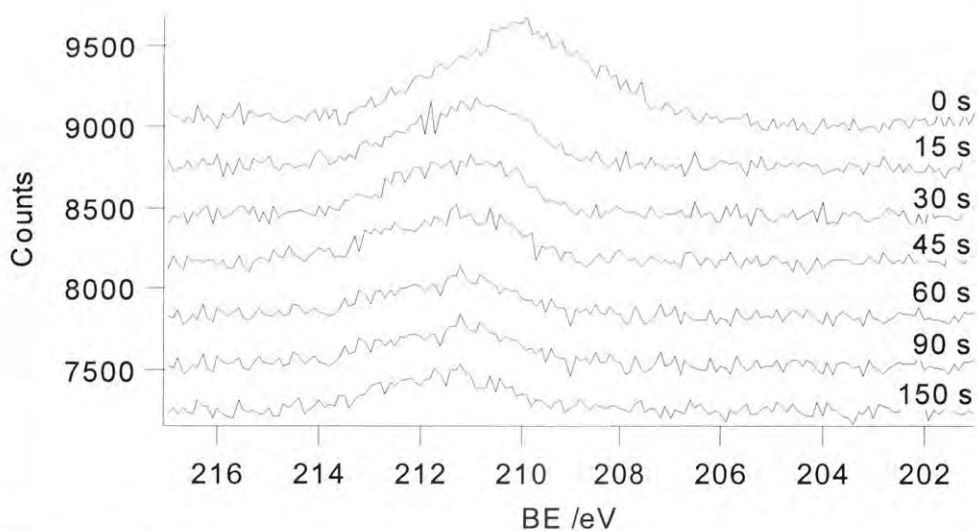


Figure A8 Cl 2p XPS spectra for surface chlorine (Cl_2 exposure is 30 L at 298 K) on CVD diamond after it is exposed to atomic hydrogen ($P_{\text{H}_2} = 1.0 \times 10^{-4}$ mbar) for the times indicated.

APPENDIX B

ANALYSIS OF XPS DATA FOR TFET AND TFEI ON GaAs(100)

B1 TPD Fragmentation Spectra

The mass spectra from the literature were used to decide which fragment was the most intense and which fragments contained no contributions from other products. The literature mass spectra were obtained from the Eight Peak Index¹ or NIST Chemistry WebBook² on-line and these spectra are provided in B2 although some products such as $\text{CF}_3\text{CH}_2\text{CH}_2\text{CF}_3$ are not available, as the spectra do not exist in the literature. The TPD spectra of the fragment ions that were used to confirm the identity of the products are provided below for completeness.

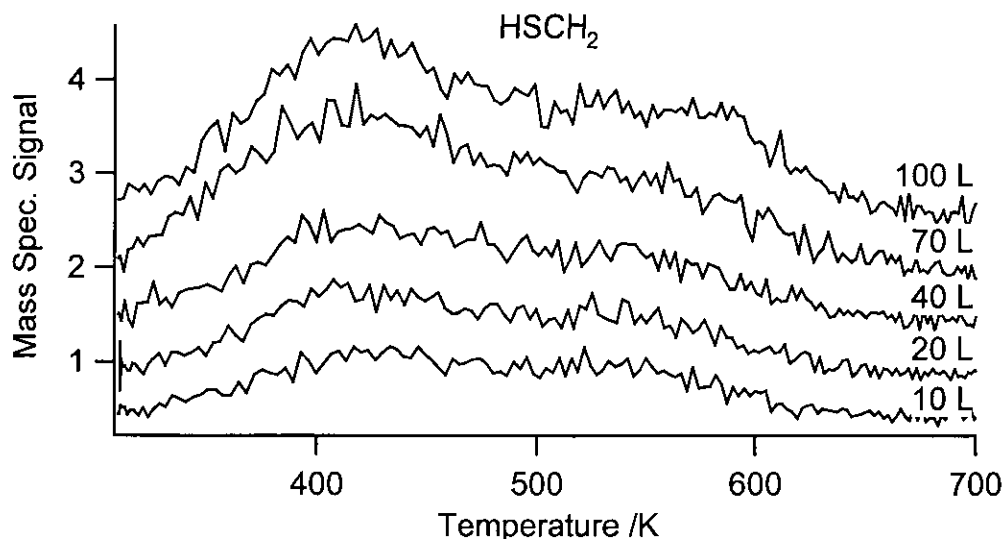


Figure B1 The TPD spectra of the uptake of TFET on GaAs (100) - (4x1) monitoring $m/z = 47$ amu (CH_2SH), a fragment of the parent ion $\text{CF}_3\text{CH}_2\text{SH}$ at 300 K. The temperature ramp is 10 K s^{-1} .

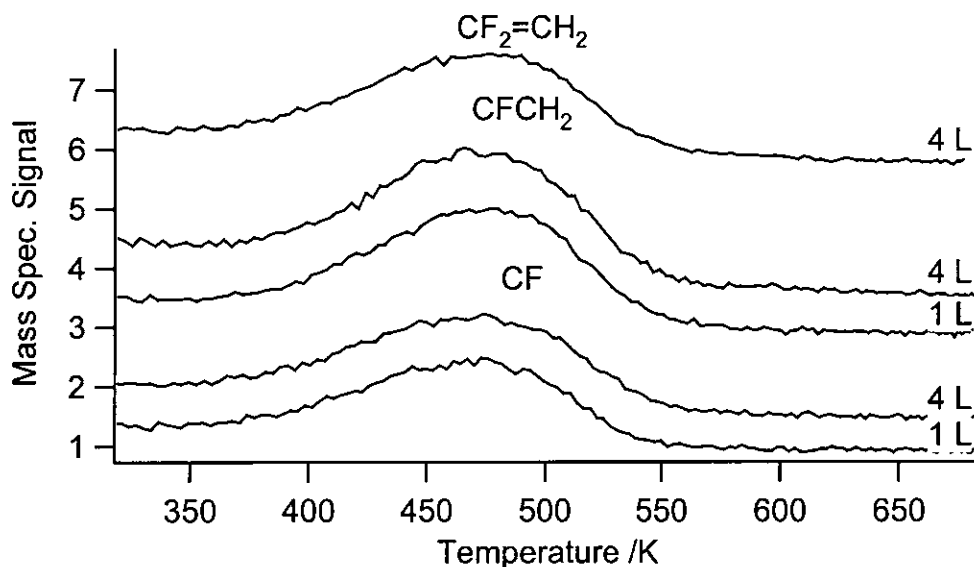


Figure B2 The TPD spectra of the uptake of TFET on GaAs (100) - (4x1) monitoring $m/z = 45$ and 31 amu, fragments of the parent ion $\text{CF}_2=\text{CH}_2$. The temperature ramp is 15 K s^{-1} . There is a slight discrepancy between the T_{max} from Figure 5.9 (500 K) and one's above (475 K) which may due may factors such as a different GaAs sample, heating rate and/or position of the thermocouple. This is confirmed when compared to the spectrum of $\text{CF}_2=\text{CH}_2$ using the same conditions. Regardless, all three spectra are consistent in peak shape and T_{max} , confirming that 45 and 31 are fragments of $\text{CF}_2=\text{CH}_2$.

B2 Mass Spectra of the Different Products Detected in Chapter 5

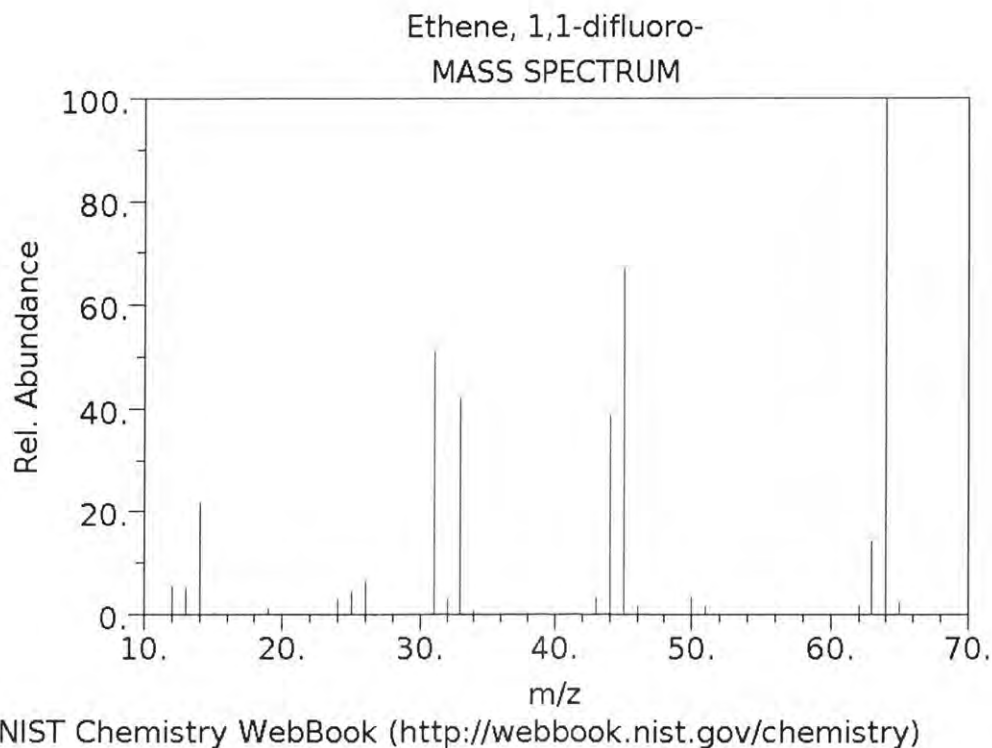


Figure B3 Literature mass spectrum of 1,1,1-difluoroethene.²

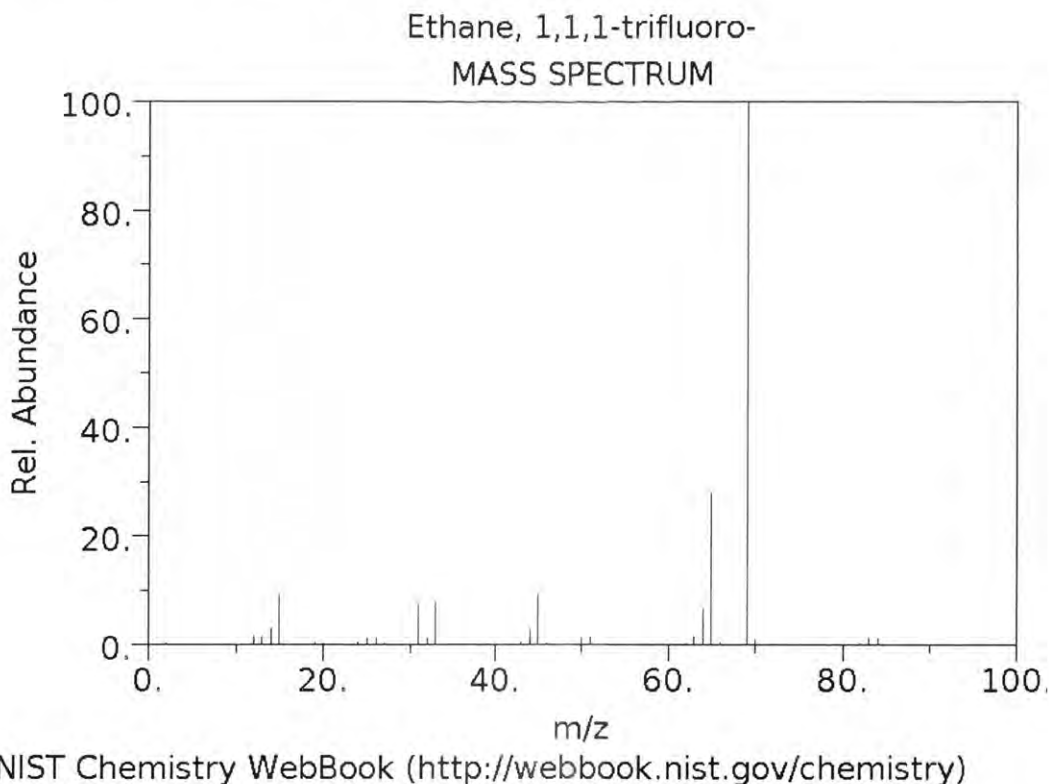
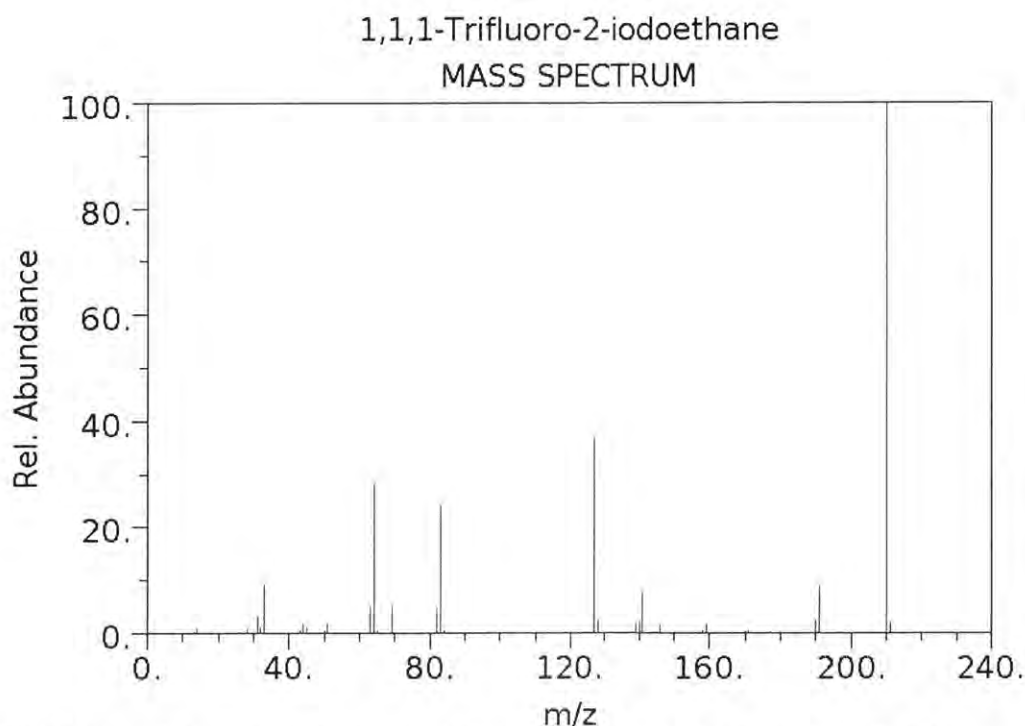


Figure B4 Literature mass spectrum of 1,1,1-trifluoroethane.²



NIST Chemistry WebBook (<http://webbook.nist.gov/chemistry>)

Figure B5 Literature mass spectrum of 1,1,1-trifluoro-2-iodoethane.²

B3 XPS Peak Fitting

During XPS data acquisition, there was a large amount of charging on the surface, this does affect the XPS spectra and in some cases shifting the spectra by +8 eV. As outlined in the diamond analysis (see § 4.2), band bending is the result of adsorbates on the surface causing a flattening of the conduction and valence band edge in the surface region. In the diamond study, there are only two adsorbates (chlorine and hydrogen) that affect the band edge and the band bending can be qualitatively assigned in that case. As will be outlined in the result and discussion sections of this chapter, there are at least four different species (e.g. $\text{CF}_3\text{CH}_2\text{SH}$, $\text{CF}_3\text{CH}_2\text{I}$, $\text{CF}_3\text{CH}_2\text{S}^-$, $\text{CF}_2=\text{CH}_2$, atomic F, S, I and/or H) on the surface and it is difficult to quantitatively assign the charging over the distribution of species with great accuracy. Furthermore, differential charging can also result with non-uniformed charging of surface causing shifting of

differing values for each region such that applying a single correction value no longer work. And unlike metal surfaces, semiconductors do not have a Fermi edge to calibrate with.

Hence, establishing an absolute binding energy scale is difficult due to charging and ambiguities in the placement of the Fermi edge. One method that is well established in the literature is the use of an internal standard such as Ga(-As) 3d or As(-Ga) 3d peak.^{3, 4, 5, 6, 7, 8} The Ga and As 3d peaks are less surface sensitive compared to the corresponding 2p peaks since the photoemission 3d electrons have an escape depth of $\sim 80 \text{ \AA}$.³ In the present study, the Ga(-As) 3d peak at 19.5 eV is chosen as the internal standard. This peak has been found to be the most reliable for several reasons.

For a clean GaAs surface, the Ga 3d and As 3d peaks are composed of several peaks. These include a set of doublets due to the bulk and surface states with the doublet contribution the result of spin-orbit coupling with a separation of 0.7 and 0.5 eV typically employed for As and Ga, respectively, when peak fitting.⁹ The surface state for Ga occurs +0.3 eV from the bulk while for As it is -0.4 eV.^{6, 8} When an adsorbate bonds to the surface, these surface states are replaced by chemical states. The position of the Ga-S chemical state is at the same BE value as the surface state whereas the As-S state is +0.6 eV from the bulk state.⁸ Because of the limits of the spectrometer, such detail cannot be deconvoluted from this data and usually this in depth analysis is reserved for XPS studies using synchrotron radiation.

Therefore, in this study, the Ga and As 3d peaks are approximated by using one single peak. If the As 3d peak is used as the internal reference, there will

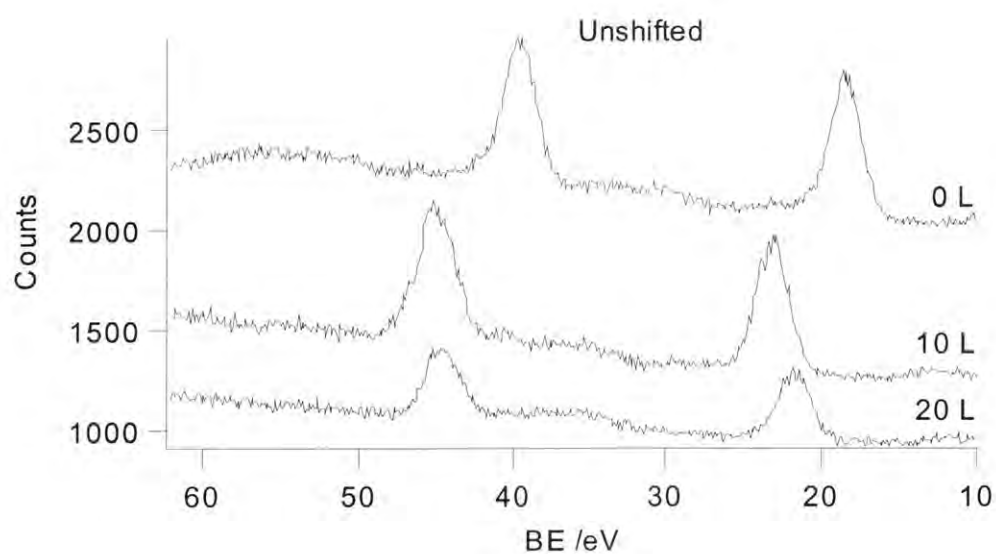
be systematic error associated with using a single peak since the surface and chemical states are separated by 0.9 eV and opposite sides of the bulk peak. Adsorption will result in shifts in the As 3d peak to higher binding energy that are not mirrored by the other regions. Conversely, the surface and Ga-S states (which make up most of the chemisorption states for simple adsorption of TFET and similarly applied for TFEI) for Ga 3d occur at the same position and should not be affected for the uptake of TFET and TFEI for sub-monolayer and monolayer coverage. Hence, the Ga 3d peak at 19.5 eV is used for such conditions as the internal standard.

For multi-layer coverage, the ratio of surface/adsorbate sites to bulk is reduced and the previous adjustment is no longer valid. Similarly, the referencing technique is not valid for experiments involving heating of TFET or TFEI layer since there is migration of adsorbates into the bulk which disrupts the bulk layer and the formation of GaX species that have a chemical state at a different binding energy value to the surface state. Furthermore differences in surface distributions resulting from etching and migration can result in differential charging.¹⁰ In these cases, three possible solutions are used. 1. The difference between states is discussed and found to be useful in discussing Ga and As formation at high temperatures. 2. Leave the spectra unshifted. 3. Internally reference the spectra to the fluorinated carbon at 293.0 eV due to CF₃.

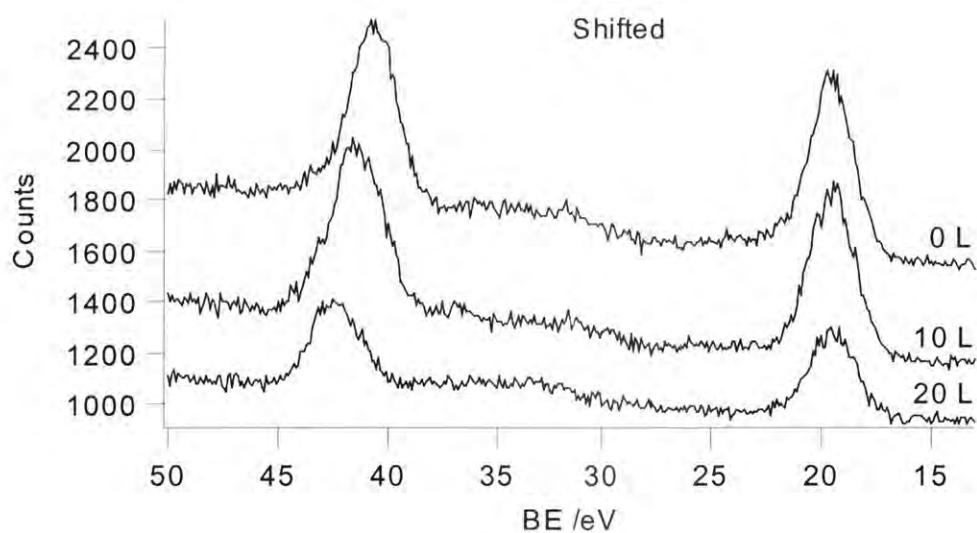
To overcome a lack of a reference peak, the C 1s peak at 293.0 eV due to CF₃¹¹ species was used as the internal standard. Previous studies investigating carbon on GaAs have referenced the C 1s peak to the hydrocarbon contribution at 284.6 eV¹² or 285.0 eV¹³. Although Yang *et al.* have used CF₂ (292.0 eV) as a reference calibrant for CF₂=CF₂ adsorption on Si(100).¹⁴ The hydrocarbon

peak has been found to be potentially unreliable for GaAs surfaces due to interference from substrate Auger peaks.³ Although the peak at 293.0 eV is sufficiently separated from the Auger peaks, F 1s and S 2p or I 3d peaks were used as secondary standards.

This analysis clearly shows the complexity of analysing GaAs using XPS. Where a spectrum has been referenced to either the Ga 3d peak at 19.5 eV or to the C[F] peak at 293.0 eV, it will be coloured blue. If referencing is too ambiguous, the spectrum remains unshifted and be coloured black. Each set of spectra contains a reminder to the reader of this fact. Figure B5 shows the As 3d and Ga 3d XPS region before and after charge correction with the appropriate colour scheme. The same value subtracted from the Ga peak is consistently applied to all peaks in that set of spectra.



a.



b.

Figure B6 The Ga and As 3d XPS regions (a) before and (b) after internally referencing the peaks to Ga 3d (19.5 eV).

The Ga, As, I 3d and S 2p spectra were fitted with peak fitting software subjected to a Shirley background subtraction while a linear subtraction was applied to the C 1s and F 1s spectra. Subsequently, peak synthesis was applied

to all the spectra using the parameters found in Table B1. For both the Ga 3d, As 3d and C 1s photoemission features, a single peak was fitted. For the F 1s, S 2p and I 3d, a minimum number of peaks were fitted using the conditions outlined in Table 5.1.

TABLE B1

Peak fitting parameters for the XPS analysis of the Ga 3d, As 3d, C 1s, F 1s and S 2p regions.

	Peak ratio	S.O.S. ^a	FWHM ^b
Ga 3d	-	-	- ^c
As 3d	-	-	- ^c
C 1s	-	-	- ^c
F 1s	-	-	2.4
S 2p	2p _{3/2} : 2p _{1/2} 2 : 1	1.2	1.4
I 3d	3d _{5/2} : 3d _{3/2} 3 : 2	11.6	2.2

a. S.O.S. – Separation of (spin-orbit) States, **b.** FWHM – Full Width Half Maximum, **c.** The FWHM was fixed for all peaks during peak synthesis except Ga 3d, As 3d, C 1s.

In addition the energy difference between the As and Ga 3d peaks is included for each spectra. The reported difference between As 3d_{5/2} and Ga 3d_{5/2} is 22.0. For a clean surface and using a single peak, it would be expected the difference to be slightly lower than the literature value of 22.0 eV since the surface states are on opposite sides of the bulk peak and shift the overall peaks closer together (*i.e.* 21.2 eV for 0 L of TFET). As GaS and AsS bonds are formed, the As 3d peak shifts away from the Ga 3d peak. This may result in values greater

than 22.0 eV as observed for a coverage of 20 L. This difference is important for thermal studies where there is no unambiguous absolute binding energy scale.

B4 Unshifted XPS Data

The following data is the raw XPS data found in Chapter 5 that has not been corrected for charging effects and the tables of XPS values derived from peak synthesis.

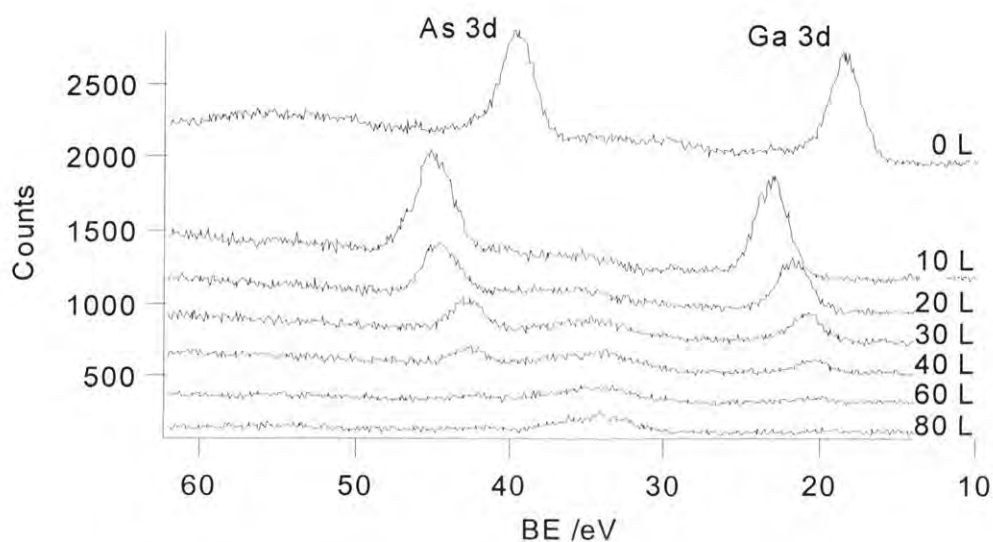


Figure B7 The XPS spectra of the As and Ga 3d regions as a function of TFET exposure on GaAs(100) – (4x1) at 111 K.

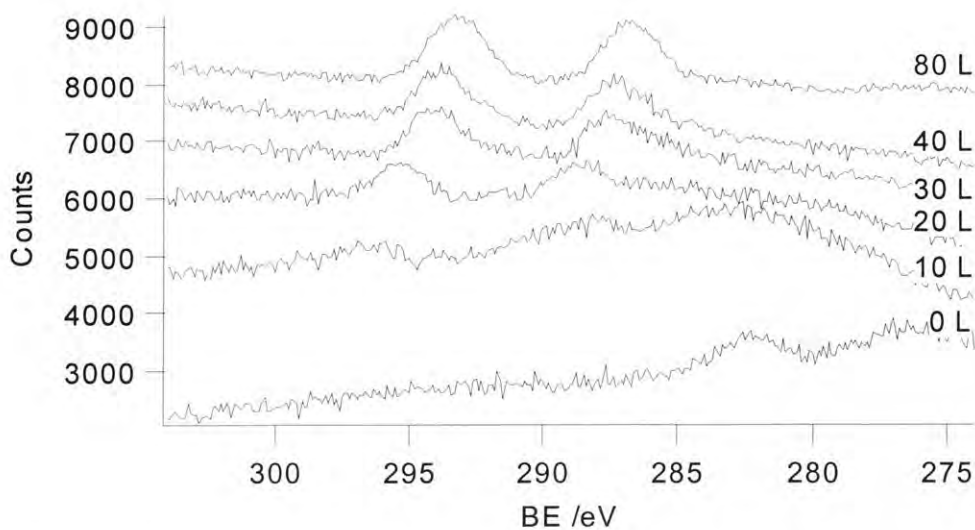


Figure B8 The uptake of TFET on GaAs(100) – (4x1) at 111 K monitored using the C 1s XPS region.

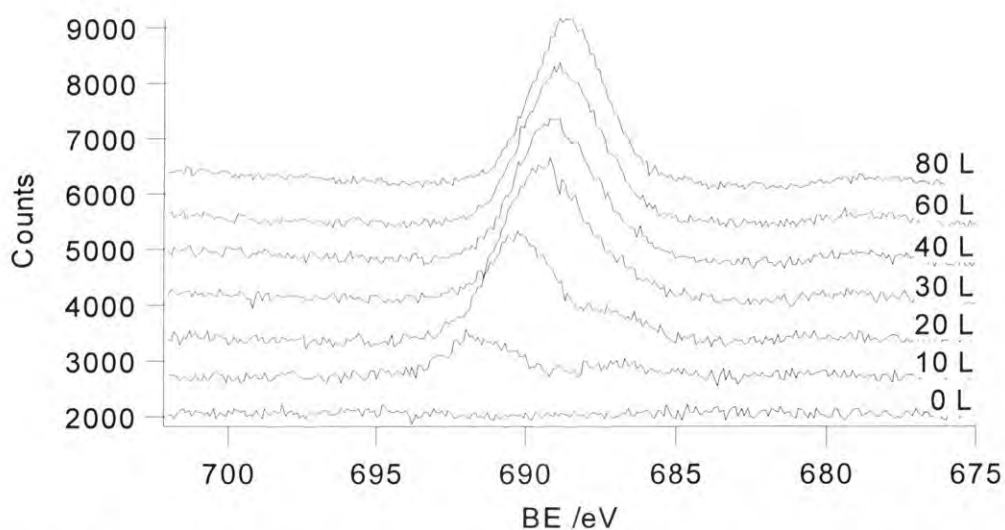


Figure B9 The F 1s XPS region as a function of TFET exposure on GaAs(100) – (4x1) at 111 K.

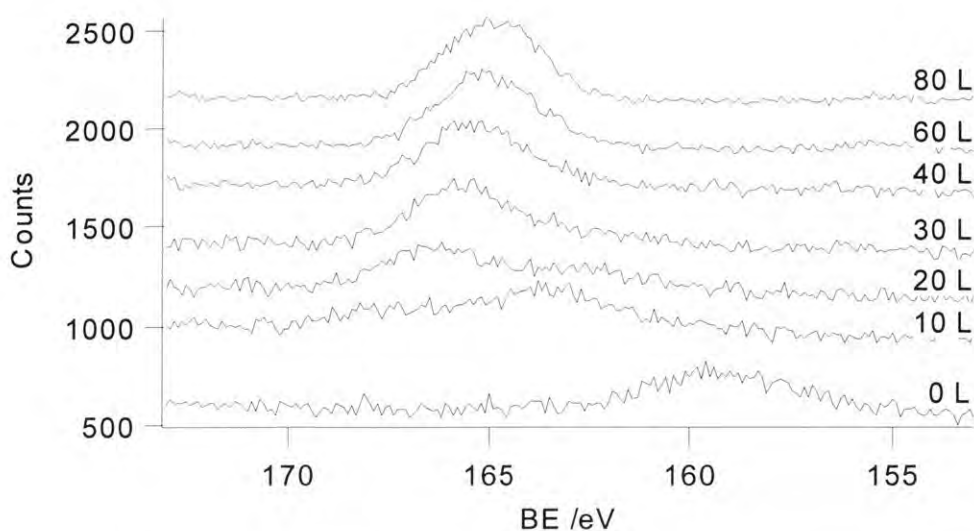


Figure B10 The uptake of TFET on GaAs(100) – (4x1) at 111 K observed using the S 2p XPS region.

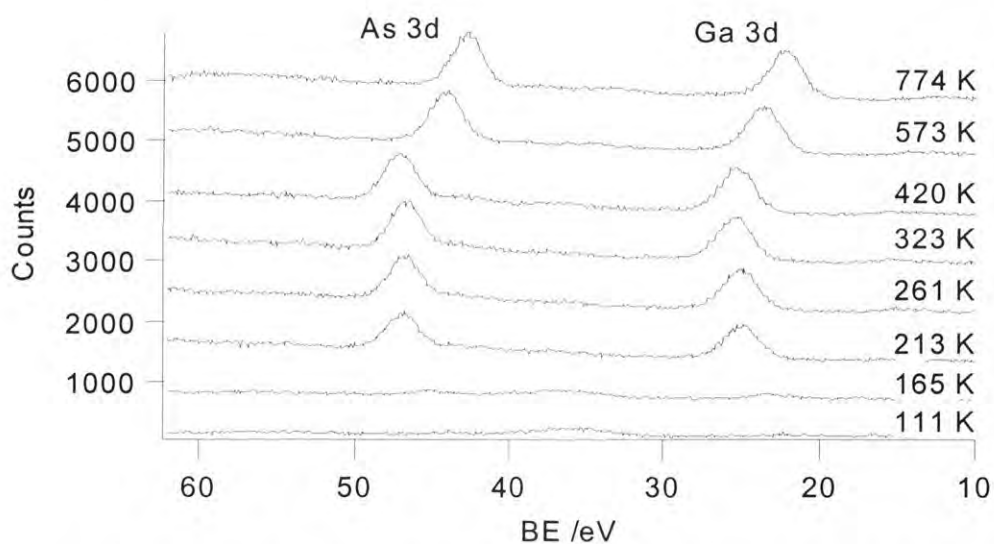


Figure B11 The thermal stability of TFET (100 L at 111 K) on GaAs(100) – (4x1) monitored using the As and Ga 3d XPS region.

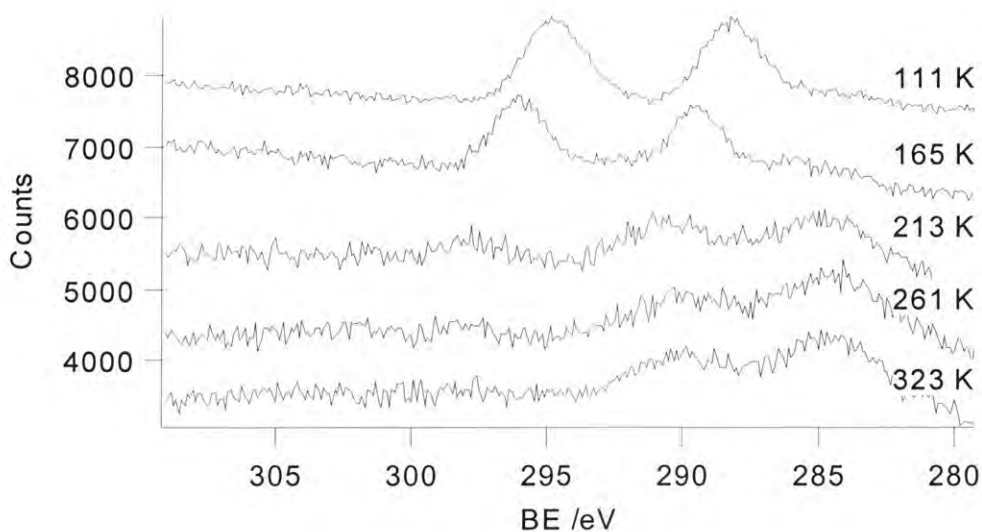


Figure B12 The XPS spectra of the C 1s region observing the thermal stability of TFET layer (100 L at 111 K) on GaAs(100) – (4x1).

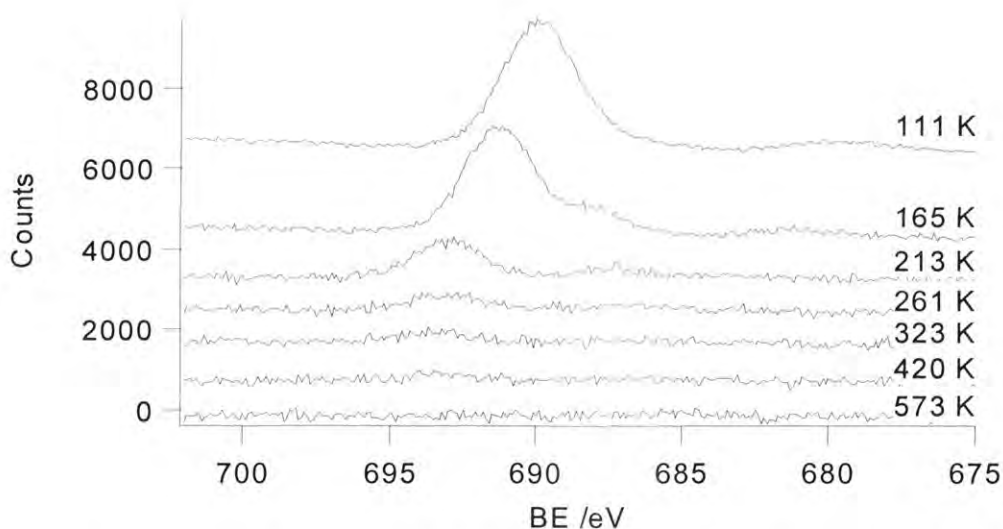


Figure B13 The thermal stability of TFET (100 L at 111 K) on GaAs(100) – (4x1) observed using the F 1s XPS region.

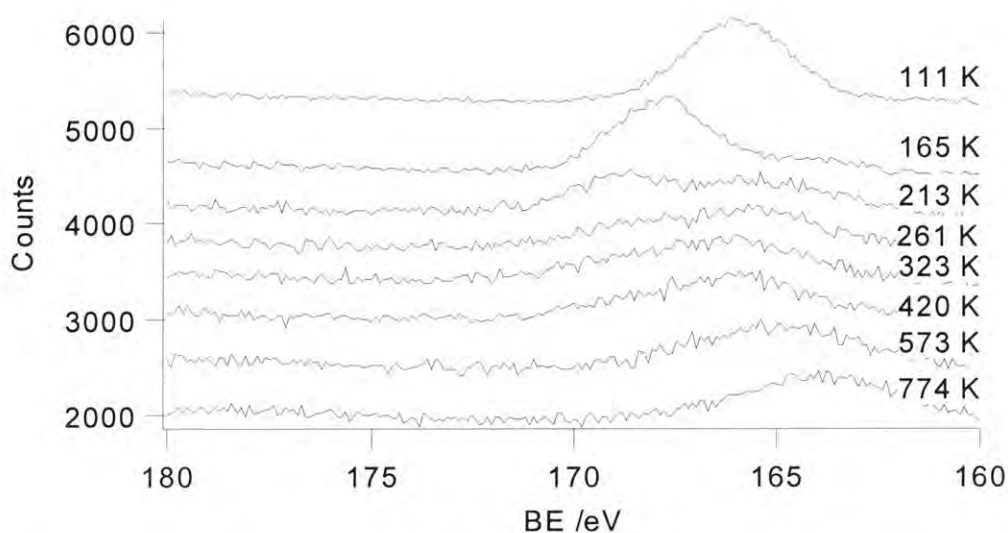


Figure B14 The S 2p XPS region monitoring the thermal stability of TFET layer (100 L at 111 K) on GaAs(100) – (4x1).

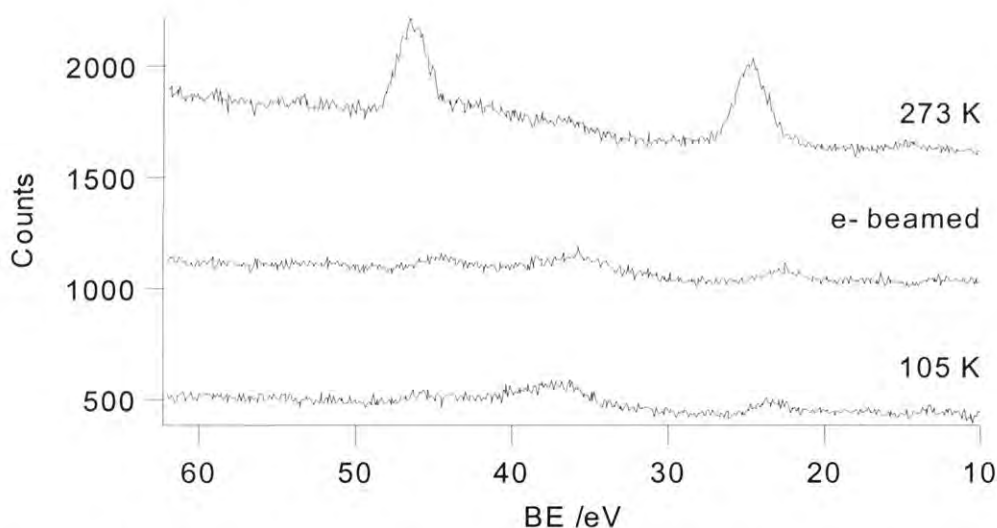


Figure B15 Monitoring of the As and Ga 3d XPS spectra for the thermal stability of TFET (100 L at 105 K) on GaAs(100) – (4x1) after electron irradiation of the surface for 10 minutes.

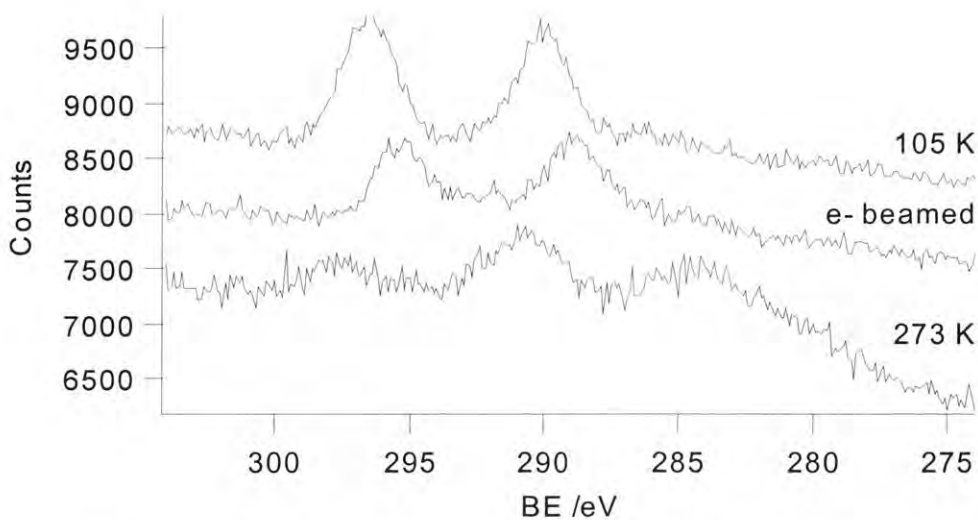


Figure B16 The thermal stability of TFET (100 L at 105 L) on GaAs(100) – (4x1) after electron irradiating the surface for 10 minutes, observed using the C 1s XPS region.

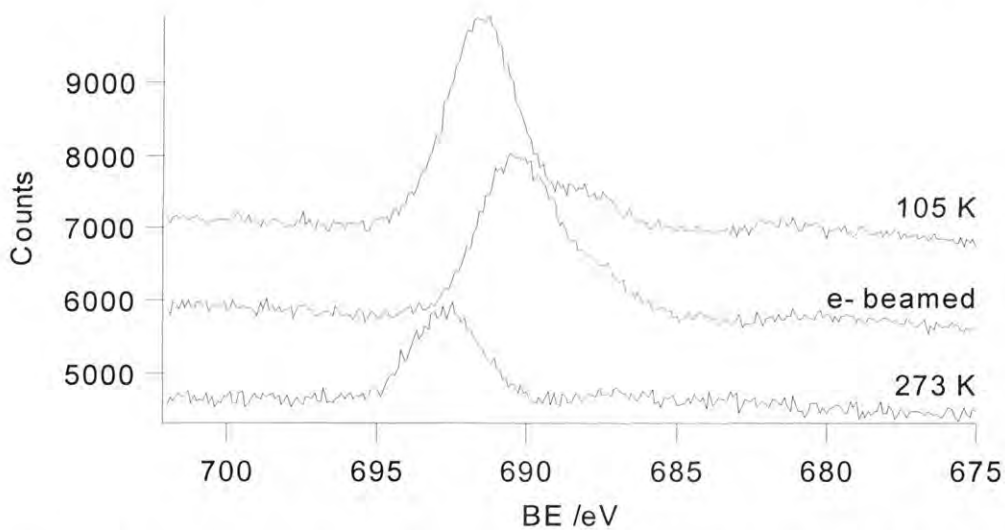


Figure B17 The F 1s XPS spectra monitoring the thermal stability of the TFET layer (100 L at 105 K) on GaAs(100) – (4x1) after electron irradiation for 10 minutes.

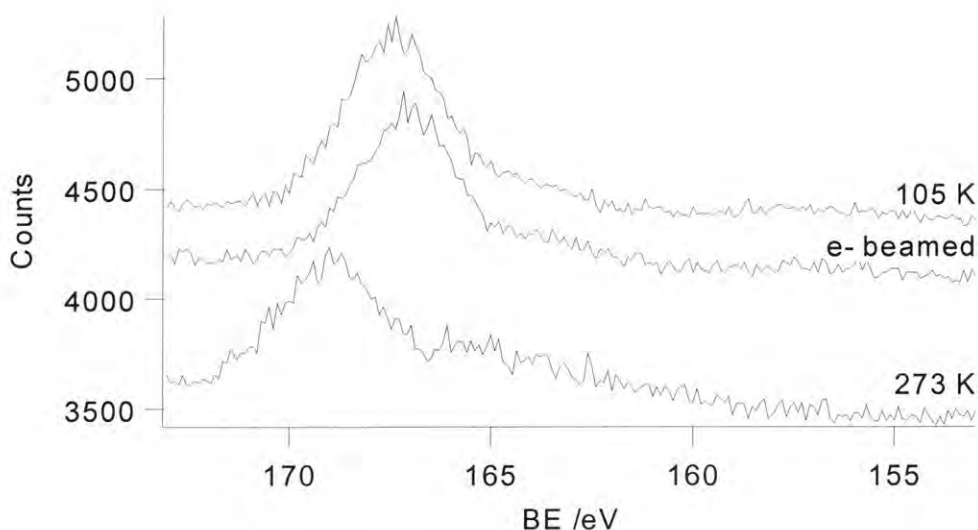


Figure B18 The thermal stability of TFET (100 L at 105 L) on GaAs(100) – (4x1) after electron irradiating the surface for 10 minutes, monitored using the S 2p XPS region.

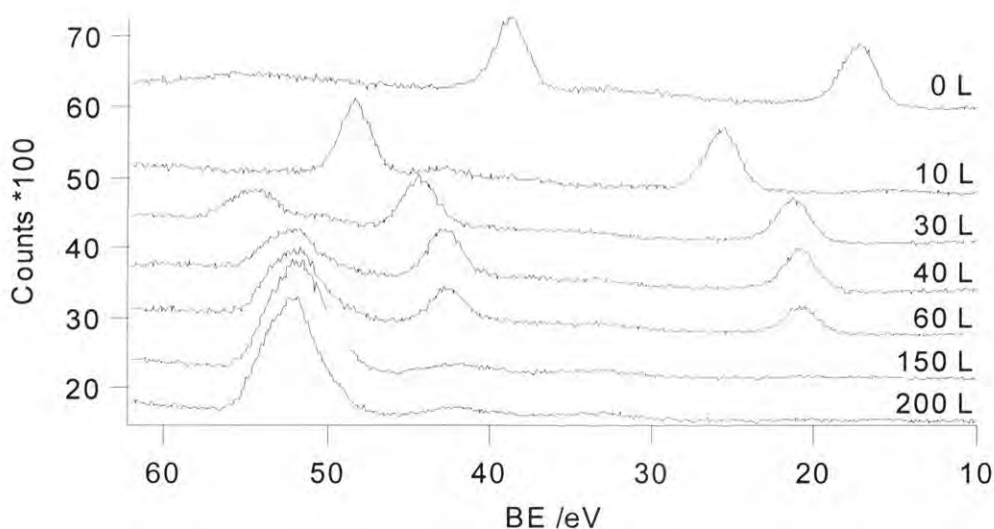


Figure B19 The XPS spectra of the As and Ga 3d regions as a function of TFEI exposure on GaAs(100) – (4x1) at 123 K. Note: The absence of some lines in the I 2p peak. There was a spike that occurred at the missing values. Instead of replacing the points, the points were removed and have no bearing on the results since I 3d peaks showed no such spike and iodide analysis is based on the I 3d rather than the I 2p peaks.

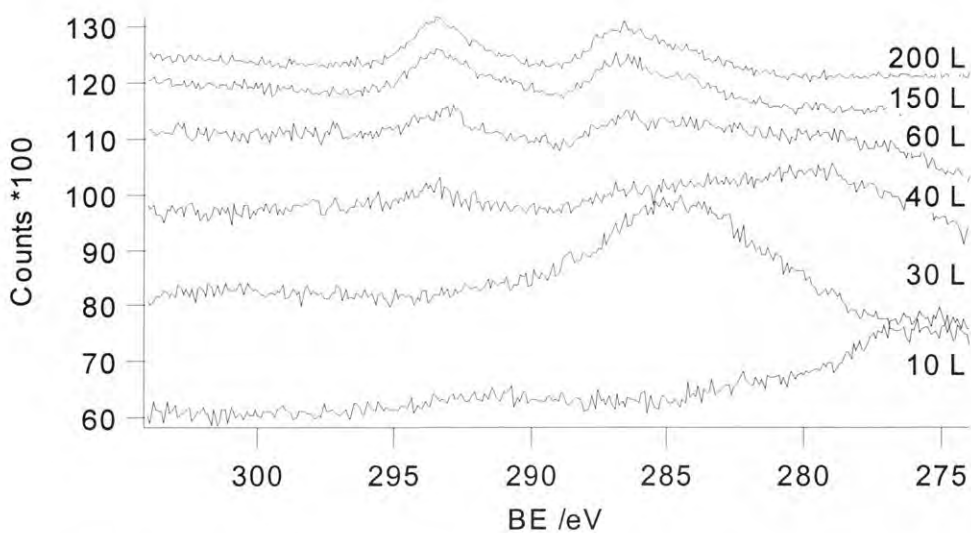


Figure B20 The C 1s XPS region as a function of TFEI exposure on GaAs(100) – (4x1) at 123 K.

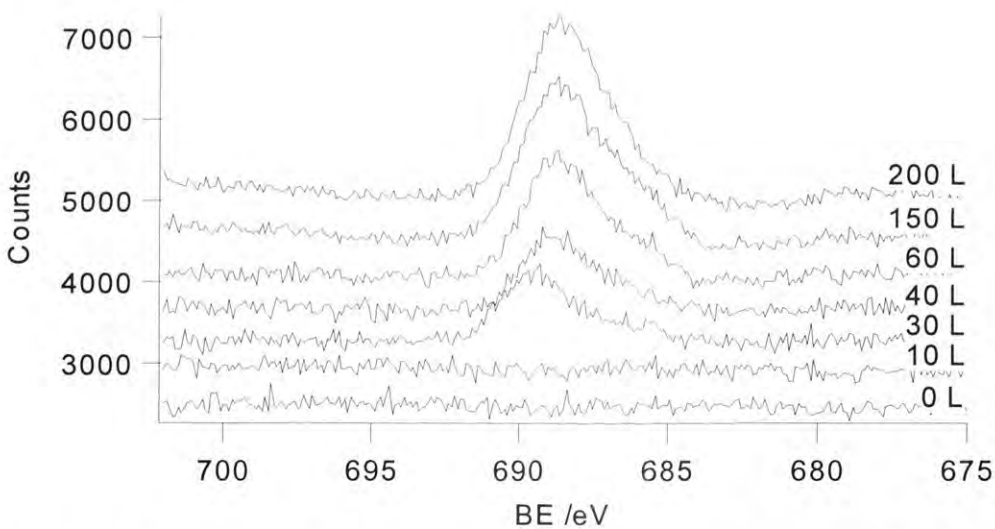


Figure B21 The uptake of TFEI on GaAs(100) – (4x1) monitored using the F 1s XPS region at 123 K.

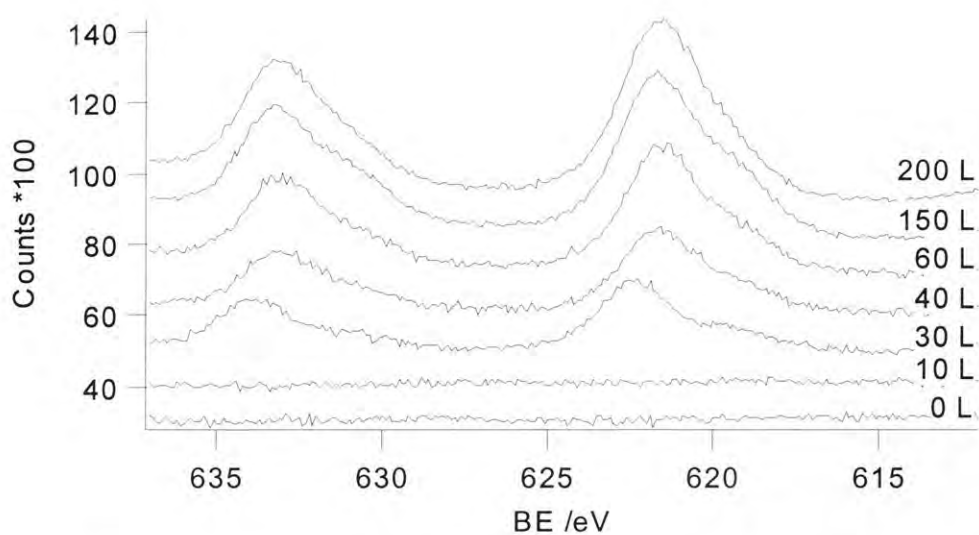


Figure B22 The XPS spectra of the I 3d region as a function of TFEI exposure on GaAs(100) – (4x1) at 123 K.

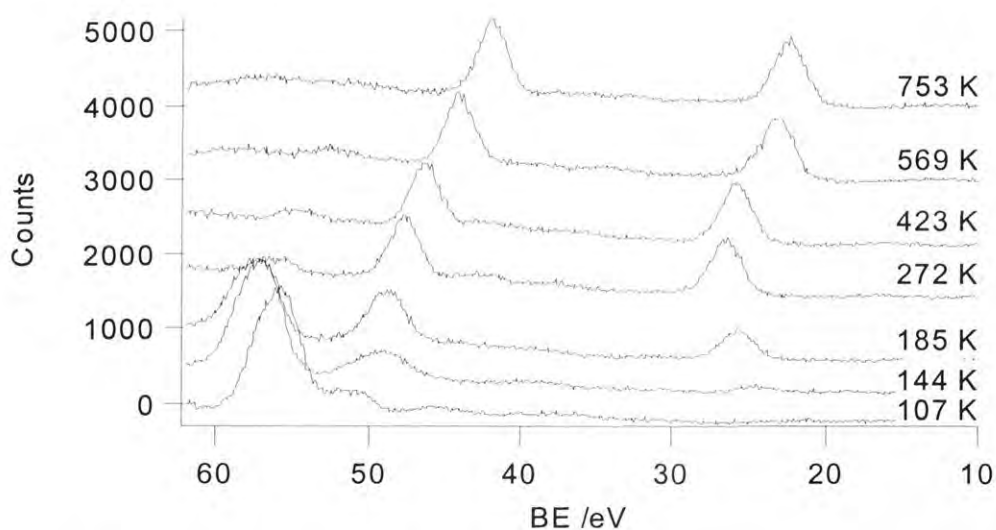


Figure B23 The XPS spectra of the Ga and As 3d regions observing the thermal stability of TFEI (100 L at 107 K) on GaAs(100) – (4x1).

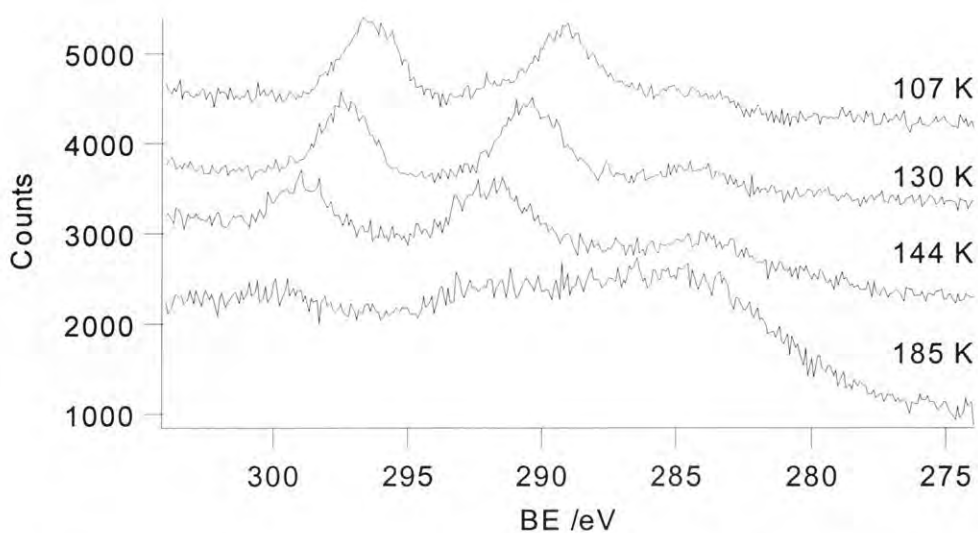


Figure B24 The thermal stability of TFEI (100 L at 107 K) on GaAs(100) – (4x1) observed using the C 1s XPS region.

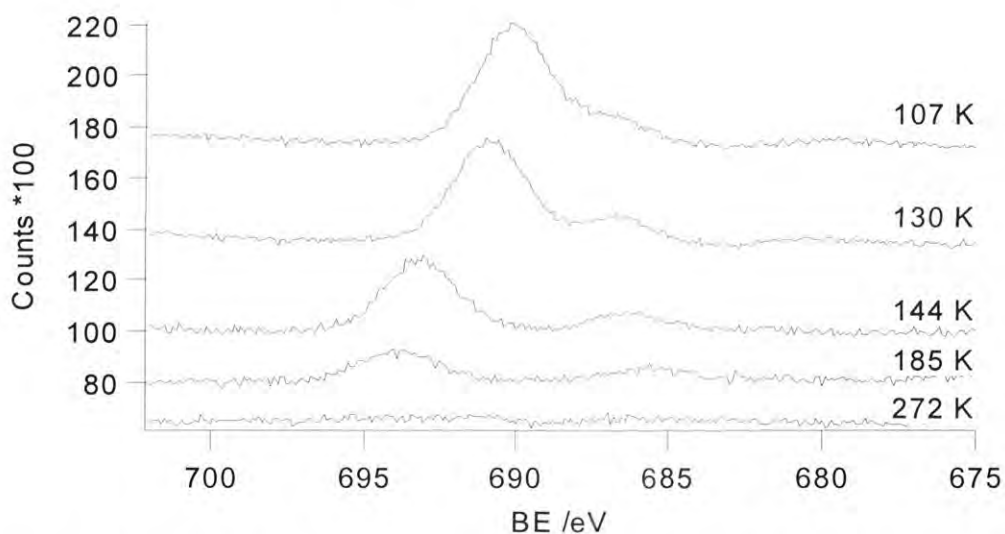


Figure B25 The F 1s XPS spectra monitoring the thermal stability of TFEI (100 L at 107 K) on GaAs(100) – (4x1).

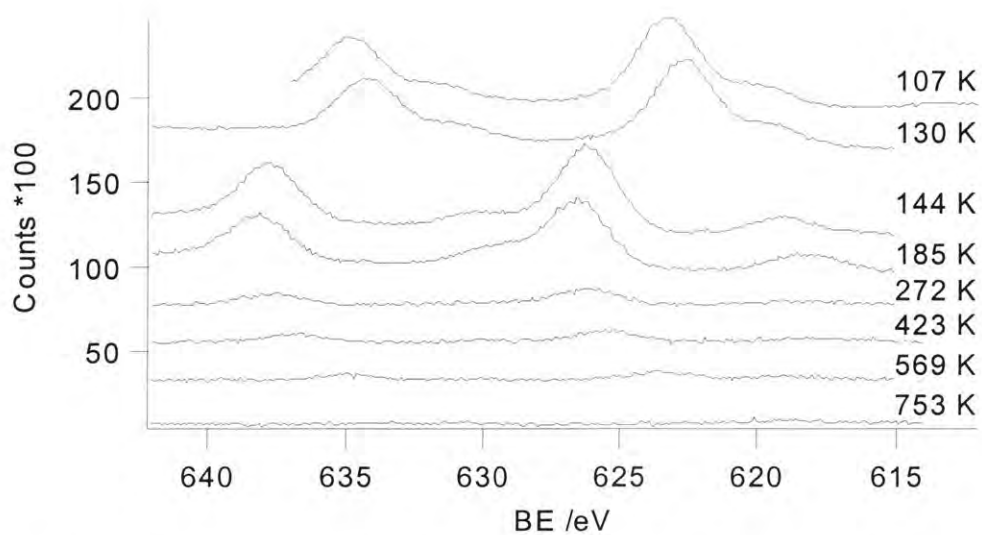


Figure B26 The thermal stability of TFEI (100 L at 107 K) on GaAs(100) – (4x1) monitored using the C 1s XPS region.

TABLE B2

The XPS values for the Ga 3d, As 3d, C 1s, F 1s and S 2p regions as a function of TFET coverage

	Ga 3d	As 3d	Diff.	C 1s		F 1s			S 2p				Ga 3s
0 L													
BE (eV) ^a	19.5	40.7	21.2	-	-	-	-	-	-	-	-	-	160.3
	-	-											-
peak area ^b	2093	2397											1089
FHWM (eV)	1.9	2.2											3.8
10 L													
BE (eV) ^a	19.5	41.4	21.9	-	-	688.3	687.3	683.2	-	163.6	161.8	160.8	159.6
	-	-				-	-	-		164.8	163.0	162.0	-
peak area ^b	1899	2498				2113	796	875		158	40	88	1083
FHWM (eV)	1.9	2.4				2.4	2.4	2.4		1.4	1.4	1.4	3.8
20 L													
BE (eV) ^a	19.5	42.1	22.6	293.2	286.5	688.2	687.3	684.8	164.5	163.7	162.4	160.7	159.6
	-	-		-	-	-	-	-	165.7	164.9	163.6	161.9	-
peak area ^b	966	1157		1498	1391	5568	1497	1048	278	372	139	194	323
FHWM (eV)	1.9	2.1		1.7	1.9	2.4	2.4	2.4	1.4	1.4	1.4	1.4	3.8
30 L													
BE (eV) ^a	19.9	41.7	21.8	293.0	286.5	688.5	686.8	-	164.5	164.1	162.5	160.8	-
	-	-		-	-	-	-		165.7	165.3	163.7	162.0	
peak area ^b	592	657		2350	2352	7610	2056		481	515	220	197	
FHWM (eV)	2.1	2.3		1.8	2.7	2.4	2.4		1.4	1.4	1.4	1.4	
40 L													
BE (eV) ^a	19.8	42.0	22.2	293.0	286.6	688.3	-	-	164.5	163.5	162.4	-	-
	-	-		-	-	-			165.7	164.7	163.6		
peak area ^b	279	343		3234	3069	10215			913	132	170		
FHWM (eV)	1.9	2.3		2.2	3.3	2.4			1.4	1.4	1.4		
60 L													
BE (eV) ^a	20.0	42.1	22.1	293.0	286.5	688.4	-	-	164.5	163.4	-		-
	-	-		-	-	-			165.7	164.6			
peak area ^b	84	90		3495	3132	10483			992	296			
FHWM (eV)	1.9	2.4		2.2	2.6	2.4			1.4	1.4			
80 L													
BE (eV) ^a	-	-		293.0	286.5	688.6	-	-	164.5	163.4	-		-
				-	-	-			165.7	164.6			
peak area ^b				3353	3478	10470			1103	247			
FHWM (eV)				1.9	2.2	2.4			1.4	1.4			

a. The second spin orbit state is included in the cell below if applicable, b. The total area for that state including both spin-orbit states if applicable

TABLE B3

The XPS values for the Ga 3d, As 3d, C 1s, F 1s and I 3d regions as a function of TFEI coverage

	Ga 3d	As 3d	Diff.	C 1s		F 1s			I 3d	
0 L										
BE (eV) ^a	19.5	41.0	21.5	-	-	-	-	-	-	-
	-	-								
peak area ^b	2583	3171								
FHWM (eV)	1.9	2.0								
10 L										
BE (eV) ^a	19.5	42.1	22.6	-	-	-	-	-	-	-
	-	-								
peak area ^b	2479	3236								
FHWM (eV)	1.9	2.1								
30 L										
BE (eV) ^a	19.5	42.6	23.1	-	-	688.3	686.6	684.1	620.5	617.8
	-	-				-	-	-	632.1	629.4
peak area ^b	1761	2294				1997	1496	290	10518	2577
FHWM (eV)	1.9	2.1				2.4	2.4	2.4	2.2	2.2
40 L										
BE (eV) ^a	20.3	42.2	21.9	293.0	-	688.3	686.4	-	621.2	619.6
	-	-		-		-	-		632.8	631.2
peak area ^b	1807	2327		1255		2966	777		10777	3759
FHWM (eV)	2.0	2.3		2.2		2.4	2.4		2.2	2.2
60 L										
BE (eV) ^a	20.6	42.3	21.7	293.0	-	688.5	686.5	-	621.4	619.5
	-	-		-		-	-		633.0	631.1
peak area ^b	1129	1484		1368		2966	1345		16677	5548
FHWM (eV)	2.0	2.1		1.9		2.4	2.4		2.2	2.2
150 L										
BE (eV) ^a	-	-		293.0	286.3	688.4	686.3	-	621.3	619.2
				-	-	-	-		632.9	630.8
peak area ^b				2836	2047	6578	2530		22370	9124
FHWM (eV)				2.5	2.1	2.4	2.4		2.2	2.2
200 L										
BE (eV) ^a	-	-		293.0	286.3	688.3	686.6	-	621.4	619.7
				-	-	-	-		633.0	631.3
peak area ^b				2605	1899	7279	2321		22749	9940
FHWM (eV)				2.2	2.0	2.4	2.4		2.2	2.2

a. The second spin orbit state is included in the cell below if applicable, b. The total area for that state including both spin-orbit states if applicable

B5 References

1. *Eight Peak Index Mass Spectra*, 4th Ed., The Mass Spectrometry Group, (1991), Cambridge, UK
2. NIST Mass Spec Data Center, S.E. Stein, director, "Mass Spectra" in **NIST Chemistry WebBook, NIST Standard Reference Database Number 69**, Eds. P.J. Linstrom and W.G. Mallard, March 2003, National Institute of Standards and Technology, Gaithersburg MD, 20899 (<http://webbook.nist.gov>).
3. C. C. Surdu-Bob, S. O. Saied, J. L. Sullivan, *Appl. Surf. Sci.*, **183**, (2001), 126
4. S. Conrad, D. R. Mullins, Q. –S. Xin, X. –Y. Zhu, *Surf. Sci.*, **382**, (1997), 79
5. G. P. Schwartz, G. J. Gualtieri, G. W. Kammlott, B. Schwartz, *J. Electrochem. Soc.*, **126**, (1979), 1737
6. W. C. Simpson, P. R. Varekamp, D. K. Shuh, J. A. Yarmoff, *J. Vac. Sci. Technol. A*, **13**, (1995), 1709
7. P.R. Varekamp, W. C. Simpson, D. K. Shuh, T. D. Durbin, V. Chakarian, J. A. Yarmoff, *Phys. Rev. B*, **50**, (1994), 14267
8. H. J. Kuhr, W. Ranke, J. Finster, *Surf. Sci.*, **178**, (1986), 171
9. W. C. Simpson, P. R. Varekamp, D. K. Shuh, J. A. Yarmoff, *J. Vac. Sci. Technol. A*, **13**, (1995), 1709
10. T. L. Barr, *J. Vac. Sci. Technol. A*, **7**, (1989), 1677
11. L. R. Williston, I. Bello, W. M. Lau, *J. Vac. Sci. Technol. A*, **11**, (1993), 1242
12. J. L. Sullivan, W. Yu, S. O. Saied, *Appl. Surf. Sci.*, **90**, (1995), 309
13. Y. Mizokawa, H. Iwasaki, R. Nishitani, S. Nakamura, *J. Elec. Spectrosc. Relat. Phenom.*, **14**, (1978), 129
14. G. H. Yang, Y. Zhang, K. G. Neoh, *J. Phys. Chem. B*, **107**, (2003), 2780

APPENDIX C

ANALYSIS OF XPS DATA FOR TiCl_4 ON Pt(111)

The binding energies of the Pt 4f, Ti 2p and Cl 2p XPS peaks were internally referenced to Pt 4f of platinum metal, at 71.0 eV^{1, 2} (Appendix C contains the unmodified spectra). Diffusion of titanium into the platinum surface at high temperatures (840 K) may occur, producing a new surface structure similar to a Pt_3Ti alloy.² In this case, the Pt 4f_{7/2} peak maxima should instead be calibrated to 71.3 eV³ for high temperatures. A 0.3 eV difference is within experimental error and would not affect the assignment of the oxidation states of titanium in these experiments.

Peak synthesis was applied to all peaks. Initially each photoemission feature is subjected to a Shirley background subtraction. No further fitting of the chlorine region was attempted. The Ti 2p and Pt 4f regions were fitted applying the parameters in Table 6.1. A pair of doublets was used for each chemical state, with one state observed for Pt and up to three in the Ti spectra (*i.e.* TiCl_4 , TiCl_3 and TiCl/Ti).

TABLE C1

Peak fitting parameters for XPS analysis of the Pt 4f and Ti 2p regions.

	Peak ratio	S.O.S. ^a	FWHM ^b
Pt 4f	4f _{7/2} : 4f _{5/2} 4 : 3	3.3	1.1
Ti 2p	2p _{3/2} : 2p _{1/2} 2 : 1	5.0	2.3

a. S.O.S. – Separation Of (spin-orbit) States, b. FWHM – Full Width Half Maximum

The following data is the uncalibrated XPS data of the spectra presented in Chapter 6 that have not been referenced to the Pt 4f_{7/2} peak at 71.0 eV.

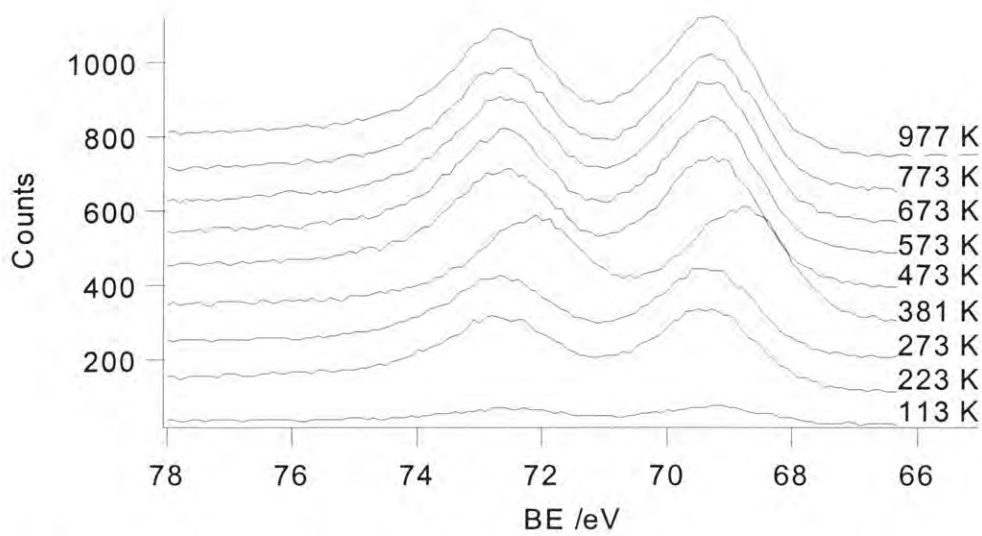


Figure C1 The XPS spectrum of the Pt 4f region as a function of temperature after exposing a Pt(111) surface with titanium tetrachloride (100 L at 113 K).

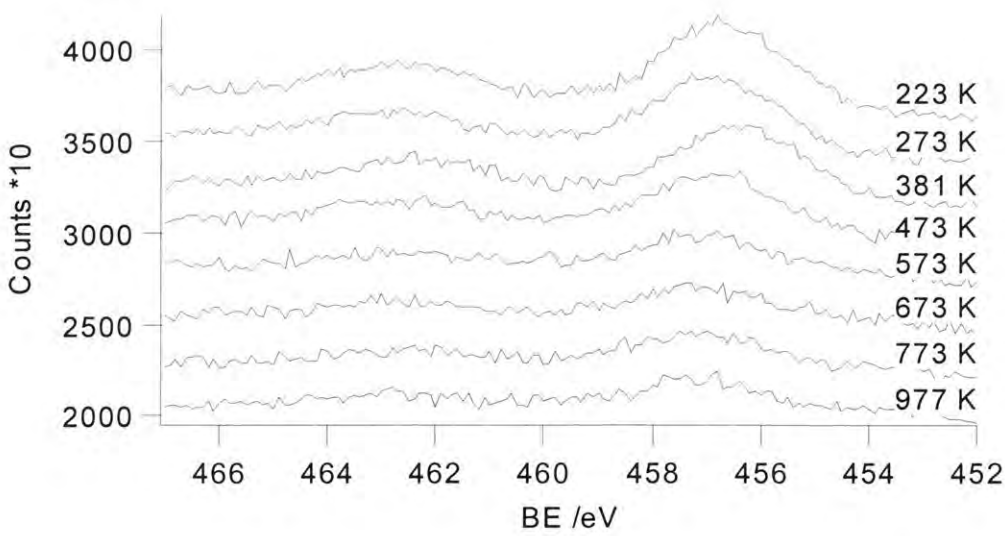


Figure C2 The thermal stability of titanium tetrachloride layer (100 L at 113 K) adsorbed on Pt(111) monitored using the Ti 2p XPS region.

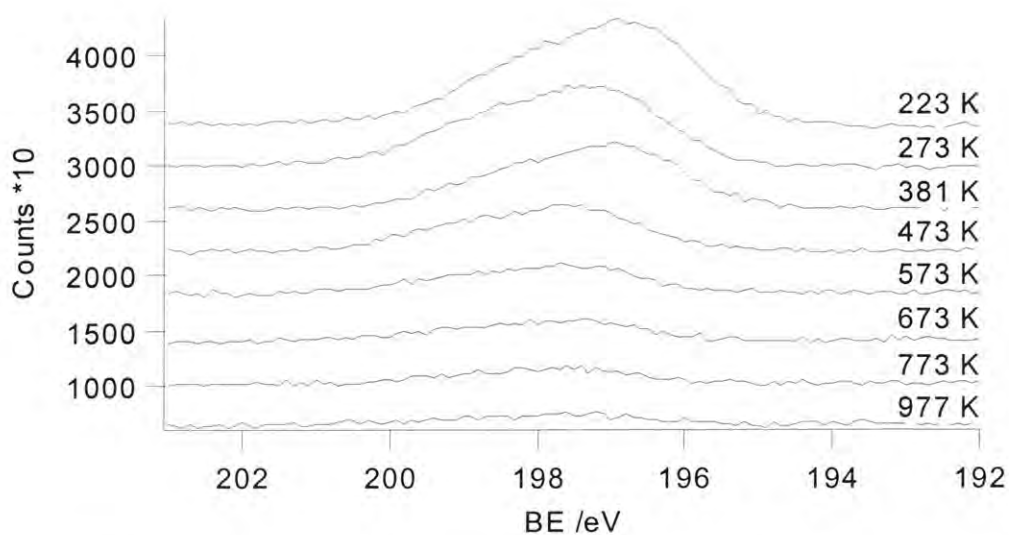


Figure C3 Monitoring of the Cl 2p XPS region as a function of temperature after exposing the Pt(111) surface with titanium tetrachloride (100 L at 113 K).

References

1. T. B. Scoggins, J. M. White, *J. Phys. Chem.*, **103**, (1999), 9963
2. M. C. A. Asensio, M. Kerkar, D. P. Woodruff, A. V. de Carvalho, A. Fernandez, A. R. Gonzalez-Elipe, M. Fernandez-Garcia, J. C. Cornesa, *Surf. Sci.*, **273** (1992), 31
3. A. Dauscher, L. Hilaire, J. C. Spirlet, W. Muller, G. Maire, *Surf. Sci.*, **204**, (1988), 161