Aspects of the Surface Science of Lithium Hydride and Uranium

James P. Tonks MEng

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Department of Mechanical Engineering Sciences
University of Surrey
Guildford
Surrey
GU2 7XH

AWE plc
Aldermaston
Reading
Berkshire
RG7 4PR
Abstract

This thesis contains work on three topics, the commissioning of an integrated surface science instrument, the ageing of LiH and the surface reactivity of U. The integrated system contains a variety of surface science techniques which have been used extensively in the investigations presented here. These techniques are: scanning electron microscopy (SEM), Auger electron spectroscopy (AES), x-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), secondary ion mass spectrometry (SIMS), temperature programmed decomposition (TPD), low energy electron diffraction (LEED) and molecular beam scattering (MBS).

LiH ageing has been split into two regimes, wet and dry ageing. Wet ageing explicitly requires the presence of an external source of H₂O, while dry ageing does not. This work has primarily looked at dry ageing, in which reactions are thermally driven, on both bulk and thin film LiH. Thin films of lithium were deposited in-situ on Ni(100) and were converted to LiH through exposure to H₂ at 1 mbar. Four reactions were found to occur in the dry ageing process. The rate-limiting mechanisms were found to be different in thin films compared to bulk. The rate-limiting mechanism for the decomposition of LiOH was found to be the rate of nucleation in bulk samples, whereas it was the rate of growth of nuclei in thin films. For the solid state reaction (LiH + LiOH → Li₂O + H₂), the same mechanism was found to be rate limiting in both cases (i.e. 3D diffusion). However, the activation energy was determined to be significantly higher in a thin film, thought to be a result of a decrease in defect concentration and the number of grain boundaries in the thin film. The Li₂O layer formed through the solid state reaction exhibited a high defect concentration and poor crystallinity, attributed to the large lattice mismatch between itself and LiH. This was shown to impact on its subsequent reactivity. On exposure of a LiH thin film to H₂O, a chemisorbed H₂O state was observed.

High purity polycrystalline uranium metal sample was prepared in-situ by ambient temperature Ar⁺ sputtering. Annealing of the clean uranium sample caused segregation of UO₂₋ₓ and UOₓCᵧ to the surface, similar to that observed in UO₂ samples. H₂ and H₂O have been shown to dissociatively adsorb onto a uranium metal surface, with the latter causing partial surface oxidation. O₂ exposure caused irreversible surface oxidation of uranium metal, which could be described by a precursor state model whereby adsorption directly onto the surface is more probable than adsorption mediated by a physisorbed second layer. A high purity UO₂ surface was formed by heating the uranium metal in an O₂ atmosphere. The interaction of D₂O with UO₂ at sub-ambient temperatures exhibited the formation of transient ice multilayers. The dynamics of D₂ on the oxide surface suggested the occurrence of trap-desorption, rather than rotationally inelastic scattering.
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I declare that the work in this thesis was carried out in accordance with the Regulations of the University of Surrey. The work is my own, except where explicit reference is made to the contribution of others. The thesis has not been presented to any other University for examination either in the United Kingdom or overseas.

Signed:........................................................

Date:........................................................
## Contents

Abstract ........................................... i

Copyright Notice ................................... ii

Author’s Declaration ................................ iii

Contents ........................................... iv

Nomenclature ....................................... viii

Acknowledgements ................................... xii

1 Introduction ...................................... 1
   1.1 Importance of Surfaces ....................... 1
   1.2 Motivation .................................. 1
   1.3 Objectives .................................. 1
   1.4 Structure .................................. 2

2 Background ....................................... 3
   2.1 Introduction ................................ 3
   2.2 Lithium Hydride .............................. 3
      2.2.1 Metal Hydrides ........................... 3
      2.2.2 Properties ............................... 4
      2.2.3 Applications ............................. 4
      2.2.4 Ageing of Lithium Hydride .............. 5
   2.3 Uranium ..................................... 8
      2.3.1 Properties ............................... 8
      2.3.2 Applications ............................. 8
      2.3.3 Reactions of Uranium with Atmospheric Gases .... 8
   2.4 Conclusions ................................ 11

3 Techniques ....................................... 13
   3.1 Introduction ................................ 13
   3.2 Scanning Electron Microscopy ............... 13
   3.3 X-ray Photoelectron Spectroscopy .......... 14
   3.4 Ultraviolet Photoelectron Spectroscopy .... 18
   3.5 Auger Electron Spectroscopy ............ 18
   3.6 Scanning Auger Microscopy .............. 19
   3.7 Secondary Ion Mass Spectrometry .......... 19
   3.8 Thermal Desorption ......................... 20
      3.8.1 Introduction ............................ 20
      3.8.2 TPD Analysis ............................ 20
CONTENTS

6.2 Lithium ................................................. 85
  6.2.1 Thickness Calibration by LEED ...................... 85
  6.2.2 Thickness Calibration by TPD ...................... 89
  6.2.3 Characterisation .................................. 90
  6.2.4 Growth Mode .................................... 92
6.3 Lithium Hydride ........................................ 94
  6.3.1 Hydriding of Li Films ............................. 94
  6.3.2 Method 1 ....................................... 94
  6.3.3 Method 2 ....................................... 97
  6.3.4 Method 3 ....................................... 99
  6.3.5 Method 4 ....................................... 99
  6.3.6 Method 5 ....................................... 101
  6.3.7 Comparison ..................................... 102
6.4 Lithium Oxide ......................................... 103
  6.4.1 Formation ....................................... 103
  6.4.2 XPS Analysis .................................... 104
  6.4.3 AES Analysis .................................... 104
6.5 Lithium Hydroxide ...................................... 107
  6.5.1 XPS Analysis .................................... 107
  6.5.2 AES Analysis .................................... 109
  6.5.3 TPD Analysis .................................... 111
6.6 Conclusions .......................................... 113

7 Ageing of LiH Thin Films ................................. 114
  7.1 Introduction ....................................... 114
  7.2 Incidental Corrosion of LiH .......................... 114
  7.3 Lithium Hydride Films Exposed to 450 Langmuir of Water ........................................... 116
    7.3.1 Spectroscopic Analysis .......................... 116
    7.3.2 Temperature Programmed Desorption ............. 116
  7.4 Lithium Hydride Films Exposed to 45 Langmuir of Water ........................................... 117
    7.4.1 Spectroscopic Analysis .......................... 117
    7.4.2 Temperature Programmed Desorption ............. 117
  7.5 Activation Energies .................................. 119
    7.5.1 Kissinger Analysis .............................. 119
    7.5.2 Modelling ...................................... 121
  7.6 Summary of Thermal Ageing ........................... 124
  7.7 Conclusions ....................................... 124

8 Uranium .................................................. 126
  8.1 Introduction ....................................... 126
  8.2 Sample Preparation .................................. 126
    8.2.1 Sputtering ..................................... 126
    8.2.2 Annealing ...................................... 131
  8.3 Gas Phase Reactions on Uranium Metal ............... 134
    8.3.1 Hydrogen ....................................... 134
    8.3.2 Water .......................................... 135
    8.3.3 Oxygen ......................................... 137
  8.4 Gas Phase Reactions on Uranium Dioxide .............. 139
    8.4.1 Formation of a Uranium Dioxide Layer .......... 139
    8.4.2 Deuterium ...................................... 141
8.4.3 Water ................................................................. 143
8.5 Conclusions .......................................................... 146

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>9 Conclusions</td>
<td>147</td>
</tr>
<tr>
<td>References</td>
<td>150</td>
</tr>
<tr>
<td>A Reaction Mechanism Models</td>
<td>159</td>
</tr>
<tr>
<td>B Vacuum Schematic of ISSC</td>
<td>160</td>
</tr>
<tr>
<td>C Time of Flight Fitting Script</td>
<td>161</td>
</tr>
<tr>
<td>D Publications</td>
<td>175</td>
</tr>
</tbody>
</table>
# Nomenclature

## Variables

<table>
<thead>
<tr>
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<th>Description</th>
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<tbody>
<tr>
<td>( \alpha )</td>
<td>Reacted fraction</td>
</tr>
<tr>
<td>( \beta )</td>
<td>Heating rate</td>
</tr>
<tr>
<td>( \gamma )</td>
<td>Specific heat capacity ratio</td>
</tr>
<tr>
<td>( \kappa )</td>
<td>Asymmetry parameter</td>
</tr>
<tr>
<td>( \lambda )</td>
<td>Wavelength</td>
</tr>
<tr>
<td>( \lambda_e )</td>
<td>Inelastic mean free path</td>
</tr>
<tr>
<td>( \nu )</td>
<td>Pre-exponential factor</td>
</tr>
<tr>
<td>( \Sigma_a )</td>
<td>Neutron absorption cross-section</td>
</tr>
<tr>
<td>( \Sigma_s )</td>
<td>Neutron scattering cross-section</td>
</tr>
<tr>
<td>( \tau )</td>
<td>Residence time</td>
</tr>
<tr>
<td>( \Theta )</td>
<td>Coverage</td>
</tr>
<tr>
<td>( \theta_1 )</td>
<td>Angle of arc subtended by leading edge of the slit on the molecular beam</td>
</tr>
<tr>
<td>( \theta_2 )</td>
<td>Angle of arc subtended by trailing edge of the slit on the molecular beam</td>
</tr>
<tr>
<td>( \theta_d )</td>
<td>Beam angular divergence</td>
</tr>
<tr>
<td>( \theta_t )</td>
<td>Take off angle</td>
</tr>
<tr>
<td>( \Upsilon )</td>
<td>Local variable used in XPS peak fits, see equation (3.4c)</td>
</tr>
<tr>
<td>( \xi )</td>
<td>Average lethargy gain</td>
</tr>
<tr>
<td>( \zeta )</td>
<td>Ratio of Lorentzian to Gaussian in a Guass/Lorentz peak</td>
</tr>
<tr>
<td>( A )</td>
<td>Area</td>
</tr>
<tr>
<td>( B )</td>
<td>Rotational constant</td>
</tr>
<tr>
<td>( C )</td>
<td>Concentration in atomic % of element ( A )</td>
</tr>
<tr>
<td>( c )</td>
<td>Speed of sound</td>
</tr>
<tr>
<td>( d_f )</td>
<td>Film thickness</td>
</tr>
<tr>
<td>( d_n )</td>
<td>Diameter of nozzle</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
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<tr>
<td>--------</td>
<td>--------------------------------------------------</td>
</tr>
<tr>
<td>$E$</td>
<td>Energy</td>
</tr>
<tr>
<td>$E_a$</td>
<td>Activation energy</td>
</tr>
<tr>
<td>$E_B$</td>
<td>Binding energy</td>
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<td>$E_K$</td>
<td>Kinetic energy</td>
</tr>
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<td>$E_R$</td>
<td>Retardation energy</td>
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<tr>
<td>$E_T$</td>
<td>Thermal energy</td>
</tr>
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<td>$E_i$</td>
<td>Average energy in incident beam</td>
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<tr>
<td>$E_p$</td>
<td>Energy of peak</td>
</tr>
<tr>
<td>$E_s$</td>
<td>Average energy in scattered beam</td>
</tr>
<tr>
<td>$E_{\text{vac}}$</td>
<td>Vacuum level</td>
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<tr>
<td>$F$</td>
<td>Full width half maximum</td>
</tr>
<tr>
<td>$f$</td>
<td>Sensitivity factor</td>
</tr>
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<td>$f_A$</td>
<td>Sensitivity factor of element $A$</td>
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<td>$G$</td>
<td>Critical value for supersonic free jet expansion, see equation (4.1)</td>
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<tr>
<td>$\vec{G}$</td>
<td>Reciprocal lattice vector</td>
</tr>
<tr>
<td>$h\nu$</td>
<td>Photon energy</td>
</tr>
<tr>
<td>$I$</td>
<td>Signal intensity</td>
</tr>
<tr>
<td>$I_\infty$</td>
<td>Peak intensity of clean substrate</td>
</tr>
<tr>
<td>$I_A$</td>
<td>Signal intensity of element $A$</td>
</tr>
<tr>
<td>$I_b$</td>
<td>Signal intensity at background</td>
</tr>
<tr>
<td>$I_p$</td>
<td>Signal intensity at peak</td>
</tr>
<tr>
<td>$I_{p}$</td>
<td>Signal intensity at peak</td>
</tr>
<tr>
<td>$J$</td>
<td>Rotational quantum number</td>
</tr>
<tr>
<td>$K$</td>
<td>Kisliuk parameter</td>
</tr>
<tr>
<td>$k$</td>
<td>HEA constant</td>
</tr>
<tr>
<td>$\vec{k}$</td>
<td>Wave vector</td>
</tr>
<tr>
<td>$\vec{k}_0$</td>
<td>Initial wave vector</td>
</tr>
<tr>
<td>$\vec{k}_{\text{out}}$</td>
<td>Scattered wave vector</td>
</tr>
<tr>
<td>$L_D$</td>
<td>Distance between chopper and mass spectrometer in ISSC</td>
</tr>
<tr>
<td>$M$</td>
<td>Mach number</td>
</tr>
<tr>
<td>$m$</td>
<td>Molecular mass</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>--------</td>
<td>------------------------------------</td>
</tr>
<tr>
<td>( n )</td>
<td>Moles of gas</td>
</tr>
<tr>
<td>( N_f )</td>
<td>Molecular beam flux</td>
</tr>
<tr>
<td>( N_v )</td>
<td>Molecular beam number density</td>
</tr>
<tr>
<td>( P )</td>
<td>Pressure</td>
</tr>
<tr>
<td>( P_0 )</td>
<td>Stagnation pressure</td>
</tr>
<tr>
<td>( P_b )</td>
<td>Background pressure</td>
</tr>
<tr>
<td>( r )</td>
<td>Radius</td>
</tr>
<tr>
<td>( S_0 )</td>
<td>Initial sticking probability</td>
</tr>
<tr>
<td>( T )</td>
<td>Temperature</td>
</tr>
<tr>
<td>( t )</td>
<td>Time</td>
</tr>
<tr>
<td>( T_0 )</td>
<td>Stagnation temperature</td>
</tr>
<tr>
<td>( T_B )</td>
<td>Molecular beam temperature</td>
</tr>
<tr>
<td>( T_N )</td>
<td>Molecular beam nozzle temperature</td>
</tr>
<tr>
<td>( T_S )</td>
<td>Sample temperature</td>
</tr>
<tr>
<td>( T_{max} )</td>
<td>Temperature at which intensity is maximum</td>
</tr>
<tr>
<td>( v )</td>
<td>Velocity</td>
</tr>
<tr>
<td>( V_a )</td>
<td>Accelerating voltage</td>
</tr>
<tr>
<td>( V_d )</td>
<td>Detection volume</td>
</tr>
<tr>
<td>( v_d )</td>
<td>Drift velocity</td>
</tr>
<tr>
<td>( W )</td>
<td>Spectrometer work function</td>
</tr>
<tr>
<td>( w )</td>
<td>Width</td>
</tr>
<tr>
<td>( w_d )</td>
<td>Width of beam at detector</td>
</tr>
<tr>
<td>( w_s )</td>
<td>Width of beam at sample</td>
</tr>
<tr>
<td>( x_M )</td>
<td>Location of Mach disk in relation to nozzle aperture</td>
</tr>
<tr>
<td>( z )</td>
<td>Charge on an ion</td>
</tr>
<tr>
<td>( r_b )</td>
<td>Radius to short beam pulse slit on chopper</td>
</tr>
<tr>
<td>( r_i )</td>
<td>Inner radius of chopper</td>
</tr>
<tr>
<td>( r_o )</td>
<td>Outer radius of chopper</td>
</tr>
<tr>
<td>( r_t )</td>
<td>Radius to timing circuit slit on chopper</td>
</tr>
</tbody>
</table>

**Constants**

\( x \)
NOMENCLATURE

\( e \)  
Electron charge ............................................... \( 1.602 \times 10^{-19} \, \text{C} \)

\( e \)  
Euler’s number ................................................... \( \sim 2.71828 \)

\( h \)  
Planck constant .................................................. \( 6.626 \times 10^{-34} \, \text{J s} \)

\( h \)  
\( \frac{h}{2\pi} \) ......................................................... \( 1.055 \times 10^{-34} \, \text{J s} \)

\( k_B \)  
Boltzmann constant ............................................... \( 1.381 \times 10^{-23} \, \text{J K}^{-1} \)

\( m_e \)  
Mass of an electron .............................................. \( 9.109 \times 10^{-31} \, \text{kg} \)

\( N_A \)  
Avogadro’s number ............................................... \( 6.022 \times 10^{23} \, \text{mol}^{-1} \)

\( R \)  
Molar gas constant ............................................... \( 8.314 \, \text{J K}^{-1} \, \text{mol}^{-1} \)

Functions

\( DS(x) \)  
Doniach-Šunjić peak profile

\( f(\alpha) \)  
Mechanistic function for TPD

\( g(t) \)  
Molecular beam gate function

\( G(x) \)  
Gaussian peak profile

\( GL(x) \)  
Gaussian/Lorentzian sum approximation to Voigt function

\( k(T) \)  
Non mechanistic function for TPD, see equation (3.9b)

\( L(x) \)  
Lorentzian peak profile

\( P_1(t) \)  
Intensity scattered from a clean surface

\( P_2(t) \)  
Intensity scattered from a saturated surface

\( S(t) \)  
Sticking probability

\( v(t) \)  
Molecular beam velocity distribution converted to time domain

Acronyms

\( AC \)  
Alternating current

\( AES \)  
Auger electron spectroscopy

\( ATR \)  
Attenuated total reflection

\( BCC \)  
Body centred cubic

\( BSE \)  
Backscattered electron

\( CAD \)  
Computer aided design

\( DC \)  
Direct current

\( DRIFTS \)  
Diffuse reflectance infrared Fourier transform spectroscopy

\( DRS \)  
Direct recoil spectrometry
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tr>
<td>DU</td>
<td>Depleted uranium</td>
</tr>
<tr>
<td>FAT</td>
<td>Factory acceptance testing</td>
</tr>
<tr>
<td>FCC</td>
<td>Face centred cubic</td>
</tr>
<tr>
<td>FM</td>
<td>Frank-Van der Merwe film growth</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full width half maximum</td>
</tr>
<tr>
<td>HAS</td>
<td>Helium atom scattering</td>
</tr>
<tr>
<td>HSA</td>
<td>Hemispherical sector analyser</td>
</tr>
<tr>
<td>IMFP</td>
<td>Inelastic mean free path</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>ISSC</td>
<td>Inorganic surface science capability</td>
</tr>
<tr>
<td>KE</td>
<td>Kinetic energy</td>
</tr>
<tr>
<td>LEED</td>
<td>Low energy electron diffraction</td>
</tr>
<tr>
<td>MB</td>
<td>Molecular beam</td>
</tr>
<tr>
<td>MBS</td>
<td>Molecular beam scattering</td>
</tr>
<tr>
<td>ML</td>
<td>Monolayer</td>
</tr>
<tr>
<td>PBN</td>
<td>Pyrolytic boron nitride</td>
</tr>
<tr>
<td>PID</td>
<td>Proportional, integral and derivative</td>
</tr>
<tr>
<td>PSU</td>
<td>Power supply unit</td>
</tr>
<tr>
<td>QMS</td>
<td>Quadrupole mass spectrometer</td>
</tr>
<tr>
<td>RBS</td>
<td>Rutherford back-scattering spectroscopy</td>
</tr>
<tr>
<td>RGA</td>
<td>Residual gas analysis</td>
</tr>
<tr>
<td>SAM</td>
<td>Scanning Auger microscopy</td>
</tr>
<tr>
<td>SAT</td>
<td>Site acceptance testing</td>
</tr>
<tr>
<td>SE</td>
<td>Secondary electron</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>SIMS</td>
<td>Secondary ion mass spectrometry</td>
</tr>
<tr>
<td>SK</td>
<td>Stranski-Krastanov film growth</td>
</tr>
<tr>
<td>SM</td>
<td>Simultaneous multilayer film growth</td>
</tr>
<tr>
<td>SP</td>
<td>Sticking probability</td>
</tr>
<tr>
<td>SRG</td>
<td>Spinning rotor gauge</td>
</tr>
<tr>
<td>Acronym</td>
<td>Definition</td>
</tr>
<tr>
<td>---------</td>
<td>------------------------------------------------</td>
</tr>
<tr>
<td>ToF</td>
<td>Time of flight</td>
</tr>
<tr>
<td>TPD</td>
<td>Temperature programmed desorption</td>
</tr>
<tr>
<td>TSP</td>
<td>Titanium sublimation pump</td>
</tr>
<tr>
<td>UHV</td>
<td>Ultra high vacuum</td>
</tr>
<tr>
<td>UI</td>
<td>User interface</td>
</tr>
<tr>
<td>UPS</td>
<td>Ultraviolet photoelectron spectroscopy</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>VW</td>
<td>Volmer-Weber film growth</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
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</table>
Acknowledgements

I would like to thank both my academic and industrial supervisors for their help and support throughout this project; Prof. John Watts, Dr. Mark Baker, Dr. Ewan Galloway and Prof. John Fernie. I would also like to thank my other colleagues at AWE, Dr. Martin King, Mack Johnson, Nick Hill and Sally Davies along with the rest of the old salts and getters team and the new material characterisation team. Dr Gwilherm Kerherve, Scott Lawrence and Dave Bentley from VACGEN Ltd must be acknowledged for the ISSC development work and in service support. AWE and the EPSRC are thanked for the funding which have allowed this project to be completed. Finally the team behind the Industrial Doctorate Centre in Micro and Nano Materials and Technology at the University of Surrey must also be mentioned for their support throughout the project, Prof. Julie Yeomans, Prof. Rob Dorey, Noelle Hartley, Lucie White, Jane Morgan and Debbie Carpenter.
Chapter 1

Introduction

1.1 Importance of Surfaces

The solid surface is of unique importance because it is the point at which a material interacts with the world around it. Therefore a fundamental understanding of the processes occurring between the surface and surrounding gaseous species is of utmost importance in understanding corrosion and material ageing as a whole. This area of research has considerable history in surface science, harking back to the genesis of ultra high vacuum (UHV) technology (c. 1960s). UHV is essential for the study of adsorption on an atomic scale as these pressures increase the time available before the background gases react with the sample surface.

1.2 Motivation

This study was initiated due to a desire to improve the understanding of the early stages of ageing for two important nuclear materials; LiH and U. With respect to their properties and chemistry, these two materials are dissimilar. For example, upon exposure to atmospheric gases, both materials oxidise; however, U forms passivating oxide layers that dramatically reduce further oxidation, whilst LiH does not passivate as the corrosion layers spall from the surface.

Surface science offers an effective tool with which to probe these reactions. For this reason, an integrated UHV system has been commissioned for this project. This system contains a variety of surface sensitive techniques to explore gas-surface interactions, which are described in the forthcoming chapters.

1.3 Objectives

The objectives of this work are to:
1. Install and commission a surface science instrument, known colloquially as the inorganic surface science capability (ISSC).

2. Investigate the early stages of LiH ageing.

3. Further the understanding of the adsorption and reaction of $H_2$ on U and UO$_2$.

4. Further the understanding of the adsorption and reaction of $H_2O$ on U and UO$_2$.

5. Further the understanding of the adsorption and reaction of $O_2$ on U.

1.4 Structure

This thesis is divided into five parts. The first of these is Chapters 2 and 3, which covers the current status of research into the materials of interest (LiH, U) and background on the techniques used within this work. The second part (Chapter 4) is work on the installation and experimental verification of the inorganic surface science capability, this part also includes software development to improve reproducibility and efficiency of work using this equipment. The third part, given in Chapters 5 to 7, compares the decomposition of bulk and thin film LiH corrosion layers. It also contains a study of the formation of thin film Li compounds. The final experimental part assesses the interaction of U and UO$_2$ with $H_2$, $H_2O$ and $O_2$, and is presented in Chapter 8. The thesis is summarised and conclusions drawn in Chapter 9.
Chapter 2

Background

2.1 Introduction

This chapter will first give an overview of hydrides before advancing to the general properties and applications of LiH. It will then give a more detailed background of the current understanding of the ageing of LiH. Following the section on LiH will be a background of U, covering the physical properties and applications. A detailed coverage of the understanding of the chemistry between U and various reactive gases will then be given.

2.2 Lithium Hydride

2.2.1 Metal Hydrides

The majority of elements will form a hydride, with the exception of the noble gases and some noble metals. Hydrides can be categorised dependent upon the prevalent form of bonding; either covalent, metallic or ionic. Electronegativity relative to hydrogen largely determines which category the hydride falls within.

Covalent hydrides are typically formed from the p-block of the periodic table, where the electronegativity of the element is similar to that of hydrogen. Binary covalent hydrides are of the form of discrete molecules and can form a variety of different compositions, for example, B₂H₆, B₄H₁₀, B₅H₉ and B₅H₁₁ are all known to exist. As discrete molecules, Van der Walls’ forces are the only inter-molecular force; therefore the melting point, boiling point and electrical conductivity are generally low. An example of this is GeH₄ which is a gas at room temperature, with a melting point of 107 K and a boiling point of 183 K (Mueller et al., 1968).

Metallic hydrides are formed from transition metals as well as the lanthanides and actinides. These compounds exist as a range of non-stoichiometric compositions, with hydrogen atoms occupying interstitial sites within the host metal lattice. As hydrogen concentration increases, the host metal typically goes through a series of structural changes to accommodate extra atoms. As the primary bonding is of a metallic nature, the hydrogen atoms can be
transported throughout the material by diffusion. These types of hydrides exhibit similar properties to metals, such as high electrical and thermal conductivities; however, unlike metals, they tend to be brittle. This brittleness is caused by the hydrogen inhibiting the plane slippage that would normally occur in response to an applied stress, therefore plastic deformation is not possible. Metallic hydrides lack a molten phase and decompose into its constituent elements at a given temperature (Mueller et al., 1968; Fukai, 2005).

Ionic hydrides are formed by alkali and alkaline earth metals where electrons can easily transfer between the metal and the hydrogen (i.e. M\(^{+}\)H\(^{-}\)). This gives a strong electrostatic force holding the atoms together, which in turn inhibits diffusion transport of hydrogen through the material. Ionic bonds imply charge densities localised on their respective atoms and therefore low electrical conductivity is exhibited. Conductivity is determined by the hopping rate between lattice sites and is therefore related to defect density and activation energy for hopping. These compounds are stoichiometric, form crystalline phases and generally have significantly higher melting points than would be expected for their atomic masses. Ionic hydrides exhibit a molten phase at high temperature rather than the direct decomposition that is observed for metallic hydrides. Although these molten phases exist, hydrogen is preferentially outgassed from the melt and therefore an overpressure of H\(_2\) is required to maintain stoichiometry. LiH falls under this category of hydride (Mueller et al., 1968).

### 2.2.2 Properties

Some of the physical properties of LiH are shown in Table 2.1, these properties were obtained from Kaszubinski (1973) and Staritzky and Walker (1956). At the time of writing the cost of natural LiH was £494/kg from Sigma-Aldrich Co. LLC (2016). The composition of natural Li is 92.5% \(^7\)Li and 7.5% \(^6\)Li (Goodfellow Cambridge Ltd, 2016a).

<table>
<thead>
<tr>
<th>Atomic Mass (amu)</th>
<th>6.9410</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal Structure</td>
<td>Face centred cubic (FCC)</td>
</tr>
<tr>
<td>Lattice Parameter (nm)</td>
<td>0.4083</td>
</tr>
<tr>
<td>Tensile Strength (MPa)</td>
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</tr>
<tr>
<td>Elastic Modulus (GPa)</td>
<td>72.4</td>
</tr>
<tr>
<td>Bulk Modulus (GPa)</td>
<td>45.5</td>
</tr>
<tr>
<td>Density (kg m(^{-3}))</td>
<td>775</td>
</tr>
<tr>
<td>Melting Point (K)</td>
<td>959</td>
</tr>
</tbody>
</table>

### 2.2.3 Applications

LiH has a variety of applications within many different industries. Two key applications which will be reviewed in more detail are its potential as a H\(_2\) storage material (Gislon and Prosini, 2011) and as a low density neutron shield (Welch, 1974).
Hydrogen Storage

The practical utilisation of H$_2$ as a fuel is heavily dependent upon the ability to store it in a lightweight and compact form. The main issue is that the mass ratio of H$_2$ to most metals or alloys gives a low H$_2$ weight capacity, generally this would indicate that a light metal such as Li should be ideal. However there are other requirements which are essential for hydrogen storage such as the ability to release H$_2$ without a need for excessively high temperatures (whilst stable in ambient conditions) and fast absorption and desorption kinetics. These tend to rule out most light metals, such as Li and Na, which form ionic hydrides that are thermally stable to fairly high temperatures (in excess of 573 K) (Banger et al., 2014; Mintz et al., 1980).

A potential solution has been proposed by Gislon and Prosini (2011), which takes advantage of alkali metal hydride hydrolysis (e.g. LiH) as a H$_2$ release mechanism. This makes use of the fact that the reaction between LiH and H$_2$O is facile and generates H$_2$ without any thermal input. The reaction is exothermic which increases the reaction rate without any additional energy input required (Gislon and Prosini, 2011). A major drawback of this is that the reactions are irreversible, as the LiH is converted to LiOH, and therefore it is only possible to use the material once. These reactions are described further in § 2.2.4.

Neutron Shielding

Neutron shielding is the process by which the energy of neutrons is reduced, typically from the range of MeV (tens of millions of K) down to thermal energies of approximately 20 meV (room temperature). The requirements for a good neutron shield are that the material has a high neutron scattering cross-section ($\Sigma_s$) in order to maximise the probability of scattering occurring and a low neutron absorption cross-section ($\Sigma_a$) to minimise the probability of neutron absorption occurring. To do this efficiently the mass should be as close as possible to that of a neutron to efficiently remove energy through collisions. Another parameter to maximise is the average lethargy gain ($\xi$) which is the average fractional amount of energy lost when a neutron collides with a particular atom. An indicator as to the appropriateness of a material to use as a neutron shield is the ratio $\frac{\xi \Sigma_s}{\Sigma_a}$, where a higher value indicates a better material choice.

LiH has a very low density and therefore provides a lower mass for a constant component size which can be key in some applications which are mass sensitive, such as power sources within satellites where it costs tens of thousands of $/kg to launch. Another advantage is that being a solid at ambeint temperature it does not require a containment vessel which would increase the weight for a liquid medium (Kaszubinski, 1973; Welch, 1974).

2.2.4 Ageing of Lithium Hydride

One concern with LiH is that H$_2$ slowly outgasses from the material. This can cause issues for a few reasons, the first is that as the H$_2$ content is reduced, the effectiveness of LiH as a neutron shield is reduced; it also causes issues when being used for long term H$_2$ storage. The ageing and corrosion of LiH can be divided into two main categories: wet-ageing when H$_2$O is involved, and dry-ageing (or thermal ageing) when H$_2$O is not involved in the reaction.
LiH is highly reactive with H$_2$O, resulting in the formation of LiOH and H$_2$ through equation (2.1). However the mechanisms through which this reaction occurs are more complicated than this simple stoichiometric equation indicated. A layer of Li$_2$O has been observed experimentally by Myers (1974) between the LiH and the LiOH; this structure is shown schematically in Figure 2.1.

\[
\text{LiH} + \text{H}_2\text{O} \rightarrow \text{LiOH} + \text{H}_2 \tag{2.1}
\]

![Figure 2.1: Schematic of expected LiH corrosion layers.](image)

This corrosion is believed to occur through the adsorption of H$_2$O onto the LiH surface which reacts to form Li$_2$O, as shown in equation (2.2). H$_2$O will diffuse through the Li$_2$O layer to form further Li$_2$O. This reaction will continue until a thickness defined by the rate of diffusion is obtained, measured to be $\sim$10 nm at ambient conditions (Haertling et al., 2006). H$_2$O will then react with the Li$_2$O at the surface to form LiOH, shown in equation (2.3) (Haertling and Hanrahan Jr, 2007; Phillips and Tanski, 2005).

\[
2\text{LiH} + \text{H}_2\text{O} \rightarrow \text{Li}_2\text{O} + 2\text{H}_2 \tag{2.2}
\]

\[
\text{Li}_2\text{O} + \text{H}_2\text{O} \rightarrow 2\text{LiOH} \tag{2.3}
\]

The reactions described above are competing as equation (2.3) consumes the Li$_2$O produced through equation (2.2). As a result of this, the thickness of the Li$_2$O layer remains constant at the equilibrium thickness of $\sim$10 nm, at ambient temperature and pressure. The diffusion of H$_2$O through the Li$_2$O layer is generally considered to be the rate-limiting mechanism of LiH hydrolysis. This is believed to be the case as scanning electron microscopy (SEM) has shown the LiOH layer to be fractured (Haertling and Hanrahan Jr, 2007; Phillips and Tanski, 2005); therefore it was reasoned that LiOH would not provide any significant limiting effect on the reaction rate.

Infrared (IR) spectroscopy has also been applied to the study of LiH hydrolysis. Smyrl et al. (1983) and Awbery et al. (2008) used diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and observed the O–H stretch at 3675 cm$^{-1}$ upon exposing LiH to H$_2$O, implying the formation of LiOH. A feature associated with LiOH · H$_2$O has also been observed at 3570 cm$^{-1}$ with this technique. The intensity of the O–H absorbance has been monitored to provide kinetic information, for example, it was shown that at 2% relative humidity and room temperature the hydrolysis rate was 0.0474 min$^{-1}$ (Awbery et al., 2008).
DRIFTS can also be used to observe Li$_2$CO$_3$ formation, which is of interest for atmospherically exposed samples (Smyrl et al., 1983). Rutherford back-scattering spectroscopy (RBS) has also been used to assess LiH hydrolysis. It showed an initial rise in O content of the material which then followed a linear trend of lower gradient, from this a diffusion coefficient was measured. At room temperature and ambient pressure this was $4 \times 10^{-7}$ cm$^2$ s$^{-1}$ (Haertling and Hanrahan Jr, 2007).

The possibility that LiOH forms first and then reacts with the LiH at the interface to form Li$_2$O (equation (2.4)) has also been given in literature, however this is less thermodynamically favourable than the oxide first approach discussed above. The heats of reaction for these equations are $-339$ kJ and $-124$ kJ for the two reactions in the oxide first scheme and $-147$ kJ and $-22.9$ kJ for the hydroxide first scheme (Haertling et al., 2006). It has recently been shown that exposing LiH to very small quantities of D$_2$O (0.04% relative humidity) results in Li$_2$O being the only species detectable by X-ray diffraction (XRD) and attenuated total reflection (ATR). At higher D$_2$O pressures, LiOD was observed in addition to Li$_2$O (Guichard et al., 2015).

\[
\text{LiH} + \text{H}_2\text{O} \rightarrow \text{LiOH} + \text{H}_2 \quad (2.4a)
\]
\[
\text{LiH} + \text{LiOH} \rightarrow \text{Li}_2\text{O} + \text{H}_2 \quad (2.4b)
\]

The dry-ageing reactions of LiH have been investigated using thermal desorption techniques (Dinh et al., 2001, 2003, 2005). The desorption products of pure LiH would be expected to consist solely of a single peak of both Li and H$_2$ at the temperature at which LiH decomposes, this is $\sim$900 K under UHV conditions. However, the work by Dinh et al. (2001, 2005) shows that the main temperature programmed desorption (TPD) products are H$_2$ and H$_2$O and appear below a temperature of 700 K. This was believed to be a result of a wet-ageing structure having developed on the LiH following air exposure. The H$_2$O has been attributed to the dehydration of LiOH, shown in equation (2.5).

\[
2\text{LiOH} \rightarrow \text{Li}_2\text{O} + \text{H}_2\text{O} \quad (2.5)
\]

The H$_2$ can not be attributed to the decomposition of LiH as it is present at a much lower temperature than would be expected. This was thought to be a result of some of the H$_2$O reacting with the LiH through the wet-ageing reaction (equation (2.2)). A further potential reaction occurring is that of a solid state reaction between LiH and LiOH which is shown in equation (2.4b). The mechanisms have also been investigated, with H$_2$O having a unimolecular reaction scheme (Dinh et al., 2001) and H$_2$ having a combination of a phase boundary and a diffusion limited reaction schemes (Dinh et al., 2005).

Raman spectroscopy has been used to study the nature of the Li$_2$O layer after heating a H$_2$O exposed LiH sample (i.e. dry ageing). Upon heating, two Raman peaks were observed at 540 cm$^{-1}$ and 565 cm$^{-1}$ in addition to the native Li$_2$O phonon at 515 cm$^{-1}$. These additional peaks were ascribed to Li$_2$O domains that formed to relieve interfacial lattice strain. It was also suggested that these strained Li$_2$O domains allowed for the formation of unstable LiOH phases upon H$_2$O re-exposure (Sifuentes et al., 2013).
2.3 Uranium

2.3.1 Properties

Some of the physical properties of U are shown in Table 2.2, these properties were obtained from Haynes (2012) and Goodfellow Cambridge Ltd (2016b). The price at time of writing was £34 457/kg from Goodfellow Cambridge Ltd (2016c). The crystal structure given in the table is for the α phase, present at room temperature. U has three allotropes with transitions from α to β at 935 K, and β to γ at 1045 K (Bazley, 2004). The β phase is a tetragonal structure with lattice parameters \(a = 0.566\) nm and \(b = c = 1.076\) nm and the γ phase is a body centred cubic (BCC) structure with lattice parameter \(a = 0.352\) nm (Grenthe et al., 2006). The isotopic composition of natural U is 99.275 \% \(^{238}\)U, 0.72 \% \(^{235}\)U and 0.005 \% \(^{234}\)U (Goodfellow Cambridge Ltd, 2016b).

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>Atomic Mass (amu)</td>
<td>238.0289</td>
</tr>
<tr>
<td>Crystal Structure</td>
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</tr>
<tr>
<td>Lattice Parameter (nm)</td>
<td>(a = 0.285, b = 0.495, c = 0.586)</td>
</tr>
<tr>
<td>Tensile Strength (MPa)</td>
<td>580</td>
</tr>
<tr>
<td>Elastic Modulus (GPa)</td>
<td>175.8</td>
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<tr>
<td>Bulk Modulus (GPa)</td>
<td>97.9</td>
</tr>
<tr>
<td>Density (kg m(^{-3}))</td>
<td>19 050</td>
</tr>
<tr>
<td>Melting Point (K)</td>
<td>1408</td>
</tr>
</tbody>
</table>

2.3.2 Applications

The biggest application for U is as a fissile fuel within nuclear power stations, in the form of UO\(_2\) (Shoesmith, 2000; Zinkle and Was, 2013). However other applications exist using depleted uranium (DU) (the concentration of the fissile \(^{235}\)U isotope is reduced), as this is considerably less radioactive it can be used for armour piercing shells and armour for military vehicles due to its high density and relative cost compared to other options such as W (Betti, 2003; Giannardi and Dominici, 2003). There are also civil non nuclear applications, normally taking advantage of its high density, such as, ballast in ships and aircraft counter weights, or for radioactive shielding such as in radiography cameras which typically use a very active γ source (Betti, 2003).

2.3.3 Reactions of Uranium with Atmospheric Gases

Oxygen

The interaction of O\(_2\) with a clean U surface is of importance as in any real situation there will be an oxide film present on the surface. It has therefore been studied in detail. U is highly reactive with O\(_2\) and can form a wide range of oxides stoichiometries (Allen et al., 1982). The application of surface science techniques such as X-ray photoelectron spectroscopy (XPS),
ultraviolet photoelectron spectroscopy (UPS) and Auger electron spectroscopy (AES) have been widely applied to this system (Allen and Wild, 1972, 1974; Veal and Lam, 1974; Ellis, 1976; Allen et al., 1982; McLean et al., 1982; Allen et al., 1988; Swissa et al., 1989; Gouder et al., 1989; Van den Berghe et al., 2001; Bao et al., 2013; Holliday et al., 2013; Tobin and Shuh, 2015).

Swissa et al. (1989) found that the oxide phase appeared in AES after an exposure of 4 L (1 L is equivalent to a dose of $1 \times 10^{-6}$ torr s or $1.33 \times 10^{-6}$ mbar s) was reached, XPS showed a metallic component for both clean and O$_2$ saturated samples which was used to calculate the thickness of the film as 1.5 nm. It was shown that initially isolated islands of incorporated oxygen are formed. Upon increasing O$_2$ exposure, these islands undergo a phase transition into an oxide which spreads over the surface. At the saturation exposure of 20 L, there is a continuous protective oxide film which inhibits further reaction. The kinetic behaviours from both direct recoil spectrometry (DRS) and AES are similar for the entire exposure range (0 L to 10 L), which suggests that the island thickness is maintained throughout this range. An initial sticking probability of 0.2 was also obtained, however the equation for this assumes a surface clustering model rather than three-dimensional islands, taking this into account provides an initial sticking probability close to 1. McLean et al. (1982) showed with XPS that a 40 L O$_2$ exposure resulted in a film comprising of both U and UO$_2$.

Thin layers of U oxide have been deposited on U metal in a partial O$_2$ pressure of $1 \times 10^{-4}$ mbar and shown to consist of stoichiometric and crystalline UO$_2$ (Van den Berghe et al., 2001). The oxide layer can be redistributed into the bulk metal by vacuum annealing at temperatures in excess of 750 K (Swissa et al., 1990; Knowles et al., 2012; Shi et al., 2015).

At higher exposures ($2 \times 10^9$ L), U oxide forms super-stoichiometric phases (UO$_{2+x}$). The binding energy of the U 4f$_{7/2}$ peak is shown to shift from 380.3 eV to 380.6 eV, indicating a change from U$^{4+}$ towards U$^{6+}$. There is also the addition of a shoulder in the O 1s peak at 532.8 eV (Allen et al., 1982). In atmospheric conditions, UO$_2$ will form a surface layer of U$_3$O$_6$ and U$_3$O$_7$ which are crystallographically distinct from UO$_{2+x}$ (McEachern and Taylor, 1998; Polesquen et al., 2007; Siekhaus and Crowhurst, 2010; Holliday et al., 2013). UO$_3$ exists in seven known stable crystalline phases and an amorphous phase (Khilla et al., 1986). However it is more difficult to form than UO$_2$, U$_3$O$_8$ and U$_4$O$_7$. For example, UO$_3$ has been produced from the decomposition of UO$_2$(NO$_3$)$_2$ (uranyl nitrate) in vacuum (Wheeler et al., 1964), heating (NH$_4$)$_2$U$_2$O$_7$ (ammonium diuranate) at 773 K in air (Hoekstra and Siegel, 1961) or the precipitation of UO$_2$(OH)$_2$ (uranium oxyhydroxide) from UO$_2$(CH$_3$COO)$_2$·2H$_2$O (uranyl acetate) solution with base and heating in air to 723 K (Holliday et al., 2013). The UO$_3$ system has also been studied using XPS on four different polymorphs, the binding energies of the U 4f and O 1s were very similar across the polymorphs (Allen and Holmes, 1987). The surface of the UO$_3$ was also found to be reduced following exposure to X-rays in vacuum (Allen and Holmes, 1987). Holliday et al. (2013) obtained XPS and UPS from UO$_3$ and UO$_2$ samples and found the binding energies of these compounds to be in agreement with previous studies. Table 2.3 shows the binding energies of the U 4f$_{7/2}$ peak for a variety of U compounds.

**Water**

It is important to understand the interaction between H$_2$O and U because of the relation between H$_2$O and corrosion processes. There is a common understanding that most transition
Table 2.3: Table showing XPS U 4f7/2 binding energies of U and some of its compounds. Values taken from (Allen and Holmes, 1987; Allen and Stevens, 1988; Ilton and Bagus, 2011)

<table>
<thead>
<tr>
<th>Compound</th>
<th>U Oxidation State</th>
<th>Binding Energy (eV)</th>
<th>Shake-up Offset (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>U</td>
<td>0</td>
<td>377.3</td>
<td>-</td>
</tr>
<tr>
<td>UO2</td>
<td>4+</td>
<td>380.0</td>
<td>6.7</td>
</tr>
<tr>
<td>UO3</td>
<td>6+</td>
<td>381.8</td>
<td>9.6</td>
</tr>
<tr>
<td>UH3</td>
<td>0</td>
<td>378.5</td>
<td>-</td>
</tr>
<tr>
<td>UC</td>
<td>4+</td>
<td>380.0</td>
<td>6.7</td>
</tr>
</tbody>
</table>

Metals will dissociate H2O, either fully and irreversibly (H2 + O) or partially and reversibly (H + OH) (Henderson, 2002). The most common pathway for the irreversible dissociation is for surface oxidation to occur. It is possible to observe both full and partial dissociation, particularly when a metal surface is exposed to a high enough dose of water to generate substantial quantities of surface oxide.

Manner et al. (1999); Shamir et al. (2006); Tiferet et al. (2007b) explored the initial stages of the reaction of H2O and U. Manner et al. (1999) studied the effects of very low exposures of H2O (typically 0 L to 5 L) on metal; this showed that low level OH formation was observed from exposures of ~0.5 L, even at low temperatures (85 K). Shamir et al. (2006) investigated slightly higher coverages (up to 30 L) using DRS and XPS, which showed full dissociation on U at 300 K. It was found that the H+ from the H2 was neutralised by electron transfer from the metal and remained on the surface, while the O2– formed oxide islands that spread across the surface. The interaction of H2O with U changes at low temperature (200 K), here the reaction proceeds by full dissociation until a coverage of ~0.6 ML is reached, beyond which only partial dissociation occurs (Tiferet et al., 2007b). Following a large exposure of U to D2O (2 h, presumably at ambient pressure and temperature), sub-surface UDx has been shown to form (Martin et al., 2016).

Studies on UO2 have produced conflicting results. (Hedhil et al., 2000) used isotopically labelled D218O, to probe its location after interaction with the oxide surface. The results showed the 18O was incorporated into the UO2 surface, implying that D2O fully dissociated upon adsorption. In contrast to this Winer et al. (1987) found that the H2O only dissociates on the metallic surface and not that of the oxide. This was also observed by Idriss (2010), where a single crystal of UO2 showed no H2 desorption in TPD, whereas after sputtering to induce defects, a H2 signal appeared from H2O dosing. Winer et al. (1987) has shown that ice multilayers form on U metal and oxide below ~190 K. Balooch and Hamza (1996) studied the sticking probabilities of H2O with U changes at low temperature (200 K), here the reaction proceeds by full dissociation until a coverage of ~0.6 ML is reached, beyond which only partial dissociation occurs (Tiferet et al., 2007b). Following a large exposure of U to D2O (2 h, presumably at ambient pressure and temperature), sub-surface UDx has been shown to form (Martin et al., 2016).

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Hydrogen

The reaction between U and H2 can be divided into four distinct phases: an induction phase, a growth phase (predominantly of UH3), the bulk reaction and a termination phase (Bazley et al., 2012) The growth and bulk phases have been extensively studied (Bloch and Mintz, 1981, 1990; Cohen et al., 1992; Bazley et al., 2012; Harker et al., 2013; Jones et al., 2013), while the induction phase (i.e. the initial stages of the overall reaction) has
typically been studied indirectly through the delay in the time taken to observe microscopic UH$_3$ crystallites (Bazley et al., 2012). Surface science has been used to elucidate features concerning the induction phase. Previous work regarding the adsorption of H$_2$ on a clean polycrystalline U surface has indicated that there is a single adsorption state (Balooch and Hamza, 1996; Bazley et al., 2008). XPS was insensitive to H$_2$ adsorption and tended to show slight oxidation of the surface due to trace impurities in the gas supply. However XPS was able to identify UH$_3$ albeit at high exposure and temperature (Allen and Stevens, 1988). UH$_3$ has also been generated through sputter deposition. U 4f$_{5/2}$ XPS showed that the electronic structure of UH$_3$ is more similar to U metal than UO$_2$ and therefore is likely to be of a similar oxidation state, as would be expected. The UH$_3$ peak is visibly broader than that of the metal, this is observed for all metal hydride systems as the introduction of hydrogen causes the crystal lattice to expand (Gouder et al., 2004). The initial sticking probability has been estimated using TPD to be $\sim 4 \times 10^{-2}$, this decreases rapidly with increasing hydrogen coverage (Balooch and Hamza, 1996).

It is thought that the initial induction stage of corrosion is limited by the need for H$_2$ to diffuse through an oxide layer until a critical concentration is reached in the metal. This then precipitates into UH$_3$ which has a lower density that that of U metal. This density change causes the oxide layer to buckle and rupture (Bloch and Mintz, 1997), exposing the UH$_3$ to H$_2$ and the growth phase to be entered. As the diffusion constant of H$_2$ through UH$_3$ is higher than U oxide, the reaction rate accelerates; as more of the oxide is damaged the reaction rate continues to increase (Harker, 2006).

As U readily forms oxides, it is important to study the interaction of H$_2$ with an oxide surface. The fact that U can form a multitude of oxide phases (e.g. UO$_2$, U$_3$O$_8$ and UO$_3$) adds to the complexity of this system. It has been shown that U metal will preferentially react with O$_2$ or H$_2$O over H$_2$ to form an oxide, with only 10 ppm of either O$_2$ or H$_2$O required to inhibit hydriding (Allen and Stevens, 1988). Also, traces of 1% H$_2$O have been shown to inhibit the H$_2$ reaction on U metal (Shamir et al., 2006; Tiferet et al., 2007a). The most likely mechanism for this inhibition is by reversible adsorption of H$_2$O molecules onto H$_2$ dissociation sites (Tiferet et al., 2007a). H$_2$ adsorbs onto oxidised U at room temperature and TPD shows that this desorbs between 350 K and 650 K. The sticking probability of H$_2$ onto an oxide surface was estimated from TPD to be $6 \times 10^{-4}$, significantly smaller than that of H$_2$ on U. Splitting the H$_2$ into hydrogen atoms, increases the sticking probability to $\sim 0.7$ (Balooch and Hamza, 1996; Bazley, 2004).

### 2.4 Conclusions

A brief overview of metal hydrides has been presented, followed by a more detailed review of the properties and applications of LiH. The current status of research into the ageing processes of LiH has then been described. This has been divided into two main regimes, wet and dry ageing (i.e. chemical changes to LiH with and without the presence of H$_2$O). Wet ageing has been studied with a variety of techniques, including DRIFTS, RBS, SEM, XRD and ATR. These data have been used to identify corrosion species and calculate empirical rate laws for hydrolysis. Dry ageing has typically been studied with TPD and vibrational spectroscopies (IR and Raman) and has shown that the overall reaction involves the conversion of LiOH to Li$_2$O. The mechanism has been shown to be complex and involves the transport of species across Li$_2$O. However, these techniques lack surface sensitivity and
therefore very little experimental information exists for the early stages of the hydrolysis reaction. Hence a major component of the research presented here is targeted at this area. This will include the use of thin films of LiH and its corrosion products which will be studied using XPS to determine surface composition and TPD to elucidate reaction kinetics. Also presented is a comparative study of bulk LiH hydrolysis with comparisons drawn between this and the aforementioned thin films.

With respect to U, a similar overview of properties and applications has been given. The review of the literature presented here shows that the surface chemistry of U is a much more mature field. For example, XPS and UPS have been widely applied to the interaction of O\textsubscript{2} and H\textsubscript{2}O vapour with U. The data show that both gases cause oxidation of the surface, with the prevalent species formed being UO\textsubscript{2} and UO\textsubscript{2-x}. The adsorption and reaction of H\textsubscript{2} with U has also been explored. It been shown that H\textsubscript{2} adsorbs onto the surface at room temperature, but to form UH\textsubscript{3} requires high temperature and pressure. Sticking probabilities have been measured for O\textsubscript{2}, H\textsubscript{2}O and H\textsubscript{2}, however these have not been used to model adsorption and desorption dynamics. In this work, molecular beam methods have been implemented alongside TPD and XPS to develop the understanding of interactions between these gases and the U surface. Such measurements give information not only on kinetics, but also an indication of the mechanisms involved.
Chapter 3

Techniques

3.1 Introduction

This chapter aims to give an overview of the techniques available on the ISSC. As the majority of the techniques are fairly common and described in detail elsewhere (Van Hove et al., 1986; Woodruff and Delchar, 1994; Watts and Wolstenholme, 2003; Leng, 2013), only a brief introduction will be given to these techniques. More detail will then be given on the molecular beam (MB) based techniques and TPD.

3.2 Scanning Electron Microscopy

SEM is an imaging technique in which an electron beam is rastered across a sample and secondary or backscattered electrons detected. It allows for higher resolution images to be acquired than obtainable through conventional optical microscopy due to the shorter wavelength of electrons in comparison to that of visible light. Resolution in the region of nm are regularly quoted commercially. This technique has a reasonably large depth of field (order of μm at $10^4$ magnification) providing a three dimensional appearance to images. (Leng, 2013)

SEM instruments consist of 4 main sets of components: an electron gun, electromagnetic lenses, scan coils, and an electron detector. The electron gun generates electrons through either thermionic or field emission and then directs them towards the sample as a beam through the use of electromagnetic fields. The electromagnetic lenses focus this beam such that its diameter on the sample surface is on the nm scale. The scan coils move the beam across the sample surface in order to build up an image. The electron detector collects the ejected electrons to generate an intensity corresponding with the current position of the beam upon the surface (Leng, 2013).

As the electron beam passes through the sample there are three effects which can influence the electrons in the beam; the first is that it hits an electron from the sample atoms, the second is that it hits the nucleus of a sample atom, or it is possible for an electron to pass through the sample without any collisions. If the beam collides with an electron from the sample, this electron is ejected from its shell and if it is close enough to the surface it can
escape and be detected (this is a secondary electron (SE)). The depth from which these SEs can escape depend upon the energy of the SE and the atomic number of the material it is escaping from; generally SEs will escape from the top 50 nm of the sample. If the beam is incident on a surface depression, fewer electrons will escape and reach the detector; therefore this creates an image with topographical contrast. When the incident electron collides with a nucleus, it will rebound out of the surface as a backscattered electron (BSE). As a low atomic number element will emit fewer of these backscattered electrons than a higher atomic weight element, it is possible to obtain an image with elemental contrast. The energy of a BSE is normally a large proportion of that of the incident electron and therefore these may escape and be detected from deeper within the sample (Leng, 2013).

There are issues associated with SEM which do not exist with optical microscopy, the first of these is that an electron beam would be absorbed and attenuated in air and therefore the entire system must be under vacuum. Another issue is that as electrons carry an electrical charge, the sample must be able to dissipate this charge, usually requiring that the sample is conductive. There are alternative methods to dissipate this charge build-up, mainly through the application of a conductive coating such as carbon or gold. It is also possible to use a low power ion flood gun.

3.3 X-ray Photoelectron Spectroscopy

XPS is a widely used spectroscopic technique for determination of surface composition and chemistry. The fundamental process behind the technique is the photoelectric effect. In a general experiment, a material is irradiated with X-ray photons which interact with bound electrons in the material. This interaction annihilates the photon and its energy is transferred to the electron. If the energy of the electron is sufficient to overcome the vacuum level ($E_{\text{vac}}$)
it is termed a photoelectron, this process is shown in Figure 3.2. Here a 1s electron of binding energy ($E_B$) has escaped from the material, with a kinetic energy of $E_K$ (Watts and Wolstenholme, 2003; Leng, 2013).

![Figure 3.2: Schematic demonstrating the process by which photoelectrons are formed in XPS.](image)

The kinetic energies and respective intensities of these photoelectrons can then be recorded using a hemispherical sector analyser (HSA) shown in Figure 3.3. The first stage of an analyser is a series of lenses, whose purpose is to increase the amount of photoelectrons accepted into the analyser by allowing photoelectrons emitted at a range of angles into the main hemisphere, rather than just the photoelectrons with a direct path. It also allows the main hemisphere to be located farther from the sample, which allows for other analytical instrumentation. The next stage is to reduce the $E_K$ of the photoelectron; this is achieved using the lenses or by applying a potential difference across grids between the lenses and the hemisphere. This is required as the $E_K$ of the photoelectrons is generally too high to achieve a high resolution, this retardation energy ($E_R$) allows for a higher resolution to be obtained. Within the hemisphere a potential difference of $\Delta V$ is applied, so that the mean path through the analyser will be followed by the photoelectrons for which $E_K$ is equal to that found from equation (3.1a), where $k$ is a constant dependent upon the analyser design, given by equation (3.1b), and $e$ is the charge on the photoelectron. In equation (3.1b), $R_1$ and $R_2$ are the radii of the inner and outer hemispheres respectively. Photoelectrons for which the energy is higher will follow a path with a longer radius and if the energy is lower, the path will be shorter, therefore missing the analyser. However, if the energy is only slightly different from that calculated; then it can be detected through the use of a multi-channel detector (channeltron), this can be used to sum multiple channels of the same energy in order to improve the sensitivity of the analyser (Watts and Wolstenholme, 2003; Leng, 2013).

\[
E_K = ke\Delta V \tag{3.1a}
\]

\[
k = \frac{R_1R_2}{R_1^2 - R_2^2} \tag{3.1b}
\]

XPS spectra are normally plotted with binding energy rather than kinetic energy, this is converted using equation (3.2), where $h\nu$ is the energy of the incident X-ray and $W$ is the work function of the spectrometer.
$E_B = h\nu - E_K - W$ \hspace{1cm} (3.2)

XPS is commonly used for surface analysis as it combines quantifiable analysis with a high surface sensitivity. XPS can probe up to a depth of 10 nm (dependent upon the inelastic mean free path (IMFP) of an electron within an element, as shown in Figure 3.4), and can provide a lateral resolution of 20 \( \mu \)m.

Quantification of XPS requires the peak intensity to be converted to an atomic concentration. There is a variety of factors which must be considered when spectra are being quantified; these are the cross-section for emission for the element and orbital being investigated, the depth from which the electron is emitted, the transmission function of the spectrometer, the detector efficiency and stray magnetic fields. The most common way in which XPS spectra are quantified is to use a sensitivity factor to normalise the peak intensities in such a way as to remove the relative effects of the above factors in relation to other elements. This technique is used to give an atomic percentage by dividing the intensity by the sensitivity factor to normalise it before dividing by the sum of all of the normalised intensities. This is shown in equation (3.3) where \( C_A \) is the concentration in atomic % of element \( A \), \( I_A \) is the intensity of element \( A \), \( f_A \) is the sensitivity factor applied to element \( A \), \( I \) is the signal intensity and \( f \) is the sensitivity factor.

$$C_A = \frac{I_A/f_A}{\sum (I/f)} \times 100\% \hspace{1cm} (3.3)$$

If a feature consists of multiple peaks then it is necessary to peak fit to each individual peak prior to quantification. This is generally achieved using the Voigt function (which is a convolution of a Gaussian with a Lorentzian) as a basis. A Gaussian form is shown in...
equation (3.4a), where $G(x)$ is the Gaussian fit, $\Upsilon$ is defined in equation (3.4c), $E_p$ is the energy of the peak and $F$ is the full width half maximum (FWHM). A Lorentzian form is shown in equation (3.4b), where $L(x)$ is the Lorentzian fit. An analytical form of the Voigt function is not available (Evans, 1991); due to this, two approximations have been adopted, of which equation (3.4d) is used within this work. $GL(x)$ is the sum Voigt approximation, and $\zeta$ is the ratio of Lorentzian to Gaussian. Where this function is used it will be referred to as $GL(x)$. This can be adapted to an asymmetric form by replacing $F$ with $F + \kappa(x - E_p)$, where $\kappa$ is the asymmetry parameter. The other approximation is a more complex product form, which is not displayed (Fairley and Carrick, 2005).

\[
G(x) = 2 \exp(-\Upsilon^2) \tag{3.4a}
\]
\[
L(x) = (1 + \Upsilon^2)^{-1} \tag{3.4b}
\]
\[
\Upsilon = \frac{x - E_p}{F} \tag{3.4c}
\]
\[
GL(x) = (1 - \zeta)G(x) + \zeta L(x) \tag{3.4d}
\]

The Doniach-Šunjić peak profile ($DS(x)$) is also used for some of the peak fitting as it provides an asymmetric peak shape which better models the electronic structure of a metal. Equation (3.5) shows the $DS(x)$ profile in mathematical form (Fairley and Carrick, 2005).

\[
DS(x, \kappa, F, E) = \frac{\cos \left[ \frac{\pi \kappa}{2} + (1 - \kappa) \arctan (\Upsilon) \right]}{(F^2 + (x - E_p)^2)^{(1-\kappa)/2}} \tag{3.5}
\]
3.4 Ultraviolet Photoelectron Spectroscopy

UPS operates with the same principle as XPS, however instead of using X-ray photons to irradiate the material, ultraviolet (UV) photons are used. This technique generally uses the He(I) line which has a $h\nu$ of 21.2 eV or the He(II) line with a $h\nu$ of 40.8 eV, much lower than that of XPS where Al Kα has a $h\nu$ of 1486.7 eV. Unless a monochromater is used, the UV will always consist of both He(I) and He(II), the ratio of which can be controlled through the He pressure. The photon energy limits UPS to obtaining data from the valence band electrons of a material; however He(I) and He(II) emissions have a narrow line width, enabling higher resolution, and a high interaction cross-section at valence energies, giving more intense spectra than would be obtainable with XPS. As a result of these properties it is possible for high resolution UPS spectra to give fine structure of the valence region of a material, providing information on chemical bonding. The resolution of UPS can be exploited to analyse the electronic and vibrational structure of gas phase molecules, which can in turn be used to study the adsorption of molecules on a surface (Woodruff and Delchar, 1994).

3.5 Auger Electron Spectroscopy

In AES an electron beam is used to irradiate the surface instead of photons. The Auger process is shown in Figure 3.5, here an electron from an outer shell fills the gap left by the initial electron, and then another electron is emitted in order to balance the energy. This creates an Auger electron designated $ABC$, in which $A$ is the shell the initial electron was removed from, $B$ is the shell from which the electron filling the hole was demoted from and $C$ is the shell from which the Auger electron was emitted. In the example given in Figure 3.5 this gives a $KL_{2,3}L_{2,3}$ electron. (Watts and Wolstenholme, 2003; Leng, 2013)

![Figure 3.5: Schematic demonstrating the process by which Auger electrons are formed.](image)

AES is used for identification of the surface composition. The depth of analysis for this technique is reduced from the 10 nm of XPS down to 1 nm, with a lateral resolution set by the electron beam (Watts and Wolstenholme, 2003; Leng, 2013).
3.6 Scanning Auger Microscopy

Combining SEM and a HSA allows for scanning Auger microscopy (SAM) to be carried out. This uses the rastering beam from the SEM with the energy analysis of the HSA in order to image with Auger electrons. By selecting multiple energies of interest it is then possible to form an elemental map of the surface. Generally each element will require two energies to be analysed, one for the peak and another to give a background which can be subtracted off. There are multiple methods through which these can be background subtracted, the first is a simple peak \( I_p \) minus background \( I_b \) as shown in equation (3.6) where \( I \) is the final intensity, this removes the background signal from the peak signal before the map is generated, however topographical effects will still be present. This can be corrected by dividing the previous equation by \( I_b \) (equation (3.7)) which will then remove topographical effects from the elemental map. An alternative background correction is given in equation (3.8), this can be used as another equation through which to remove topographical effects, however can overcompensate for variations in backscattering from the substrate on films (Prutton and El Gomati, 2006; Watts and Wolstenholme, 2003).

\[
I = I_p - I_b \tag{3.6}
\]

\[
I = \frac{I_p - I_b}{I_b} \tag{3.7}
\]

\[
I = \frac{I_p - I_b}{I_p + I_b} \tag{3.8}
\]

3.7 Secondary Ion Mass Spectrometry

Secondary ion mass spectrometry (SIMS) uses ions to bombard the surface of a material to generate secondary particles. These secondary particles can include electrons, neutral atoms or molecules and ions. The secondary ions are analysed using a mass spectrometer to provide chemical information. (Leng, 2013)

The mass spectrometer used within this work for SIMS is a quadrupole mass spectrometer (QMS). This type of mass spectrometer uses a quadrupole mass analyser to filter ions based upon their mass to charge ratio \( m/z \). This analyser consists of four parallel metal rods, in which the opposite pairs are electrically connected. An alternating current (AC) field with a direct current (DC) offset is applied across the rods. Only ions with a specific \( m/z \) will pass through the field for a given voltage ratio, with other ions having an unstable trajectory and impacting the rods (de Hoffmann and Stroobant, 2007).

Similar to the spectroscopic techniques mentioned previously, SIMS provides elemental identification of the surface material. It is also possible to raster the ion beam in order to create a map, similar to SAM. There are a few differences between SIMS and the spectroscopic techniques: the first of these is that as SIMS removes material from the surface it can be used to provide information relating to changes in composition with depth. Due to the analysis
of the mass of an ion rather than energy of an electron, it is possible to differentiate between isotopes of an element. SIMS also provides the ability to detect H\(_2\) which is not possible using the electron spectroscopy techniques mentioned previously (Leng, 2013).

### 3.8 Thermal Desorption

#### 3.8.1 Introduction

Thermal desorption consists of two main techniques. Isothermal desorption in which the temperature is held constant for an extended period of time and TPD where the temperature is linearly increased with time. This section will primarily focus upon TPD, however the two techniques have a lot in common. TPD can provide insight into the kinetic and mechanistic desorption reaction parameters, whereas isothermal desorption will generally only yield kinetic information. During these techniques, the sample decomposes with increasing temperature or time. This causes gas to be desorbed which is then analysed using a mass spectrometer. Plotting this mass data against temperature (or time for isothermal) provides a desorption spectrum, of which the peak shape and position provide the mechanistic and kinetic parameters.

#### 3.8.2 TPD Analysis

There are two types of TPD analysis used within this work, the first is modelling of the mass spectrometer output to known kinetic models. The rate of desorption can be defined as in equation (3.9a), where \( \alpha \) is the reacted fraction, \( t \) is the time in seconds, \( k(T) \) is a function which is not dependent upon the mechanism defined as in equation (3.9b), \( f(\alpha) \) is a function describing the mechanism of the reaction. Within equation (3.9b), \( \nu \) is a pre-exponential factor, \( E_a \) is the activation energy in J mol\(^{-1}\), \( T \) is the temperature in K and \( R \) is the molar gas constant in J mol\(^{-1}\). Equation (3.9a) must be converted from time domain to temperature domain in order to compare with TPD data. This is achieved through the substitution of equation (3.9c) into equation (3.9a), where \( \beta \) is the heating rate in K s\(^{-1}\). This gives equation (3.9d) which can be compared to TPD spectra to find both \( E_a \) and the reaction mechanism defined through \( f(\alpha) \) (Dinh et al., 2001).

\[
\frac{d\alpha}{dt} = k(T)f(\alpha) \quad \text{(3.9a)}
\]

\[
k(T) = \nu \exp \left( \frac{-E_a}{RT} \right) \quad \text{(3.9b)}
\]

\[
dt = \frac{dT}{\beta} \quad \text{(3.9c)}
\]

\[
\frac{d\alpha}{dT} = \frac{k(T)f(\alpha)}{\beta} \quad \text{(3.9d)}
\]

It is also possible to integrate across a TPD peak in order to plot \( \alpha \) against \( T \), in which case an integral form of equation (3.9d) is required, given through equation (3.10). An
approximation of this is available, shown in equation (3.11). (Li and Tang, 1999; Dinh et al., 2001)

\[ g(\alpha) = \int_{0}^{\alpha} \frac{d\alpha}{f(\alpha)} \]  
\[ = \frac{1}{\beta} \int_{0}^{T} k(T) dT \]  
\[ = \frac{\nu}{\beta} \int_{0}^{T} \exp \left( \frac{-E_a}{RT} \right) dT \]  
\[ \frac{\nu}{\beta} \int_{0}^{T} \exp \left( \frac{-E_a}{RT} \right) dT \approx \frac{\nu RT^2}{\beta E_a} \exp \left( \frac{-E_a}{RT} \right) \]  
\[ g(\alpha) \approx \frac{k(T)RT^2}{\beta E_a} \]  

Expressions for both \( f(\alpha) \) and \( g(\alpha) \) are readily available in literature (Dinh et al., 2001; Khawam and Flanagan, 2006) and are shown in Appendix A. Using these expressions for \( f(\alpha) \) and \( g(\alpha) \) with equation (3.9d) and equation (3.11b) respectively, allows the model to be fitted to TPD spectra. Comparing the fit of different mechanisms will give the reaction mechanism at work and the \( E_a \) of the reaction (Dinh et al., 2001).

The second method of TPD analysis used within this work is Kissinger analysis. This method for calculation of \( E_a \) is to assign \( T_{\text{max}} \) as the temperature at which the rate of desorption is a maximum. Recognising that this point has a gradient of 0 leads to equation (3.12).

\[ \frac{d}{dT} \left( \frac{d\alpha}{dT} \right) = 0 \]  

It was shown by Kissinger (1957), that an alternative form of equation (3.12) is equation (3.13), where \( C \) is a constant.

\[ \ln \left( \frac{T_{\text{max}}^2}{\beta} \right) = \frac{E_a}{RT_{\text{max}}} + C \]  

Equation (3.13) can be compared to that of a linear equation \((y = mx + c)\), in which \( y \) is equal to \( \ln \left( \frac{T_{\text{max}}^2}{\beta} \right) \) and \( x \) is equal to \( \frac{1}{T_{\text{max}}} \), giving a gradient of \( \frac{E_a}{R} \). As \( R \) is a known constant, \( E_a \) can quickly be determined from a linear graph with multiple values of \( \beta \). The advantage of this over full modelling is the speed at which the \( E_a \) can be found, however no information on the mechanisms can be determined. Kissinger (1957) assumed that \( f(a) = A(1 - a)^n \) in the derivation of equation (3.13), which is not applicable for all reaction mechanisms, most notably diffusion limited processes.
### 3.8.3 Isothermal Analysis

The starting point for analysing isothermal outgassing is the same as that of TPD (equation (3.9a)), this equation is rearranged and integrated to give equation (3.14a). The next step is to calculate the integral (equation (3.14b)), this can then be combined with the known expressions for \( g(\alpha) \) from the table in Appendix A and rearranged for \( \alpha \). This final equation is shown for the \( F1 \) mechanism in equation (3.15) and can be repeated for any reaction mechanism.

\[
\int_{0}^{\alpha} \frac{d\alpha}{f(\alpha)} = \int_{0}^{t} k(T) dt = g(\alpha) \tag{3.14a}
\]

\[
\int_{0}^{t} k(t) dt = k(T) t = g(\alpha) \tag{3.14b}
\]

\[
g(\alpha) = -\ln(1 - \alpha) \tag{3.15a}
\]

\[
k(T) t = -\ln(1 - \alpha) \tag{3.15b}
\]

\[
-k(T) t = \ln(1 - \alpha) \tag{3.15c}
\]

\[
\alpha = 1 - e^{-k(T)t} \tag{3.15d}
\]

Fitting the equation for \( \alpha \) to isothermal outgassing data requires boundaries to be established within the data at points which indicate \( \alpha = 0 \) and \( \alpha = 1 \). \( \alpha = 0 \) can be established by using the point at which the isothermal temperature is reached and making the assumption that at this point no reaction has occurred. While this is not an entirely valid assumption as some reaction is going to occur during the heating process, this can be reduced by heating to the isotherm temperature at as high a rate as possible whilst maintaining thermal control. The reaction is determined to be complete and therefore \( \alpha = 1 \) at the point at which the outgassing rate is negligible in comparison to the background. The data acquired through mass spectrometry can then be integrated between these limits for \( \alpha \) to provide a plot of \( \alpha \) against \( t \), which can then in turn be fitted to mechanistic equations.

The \( E_a \) and \( \nu \) can be determined from the fit by rearranging the equation for \( k(T) \) in equation (3.9b) to be in the form of \( y = mx + c \), as shown in equation (3.16). Here the \( E_a \) is equal to the gradient multiplied by \(-R\), and \( \nu \) is equal to \( e \) to the power of the intercept.

\[
k(T) = \nu \exp \left( \frac{-E_a}{RT} \right) \tag{3.16a}
\]

\[
\ln(k(T)) = \ln \left( \nu \exp \left( \frac{-E_a}{RT} \right) \right) \tag{3.16b}
\]

\[
\ln(k(T)) = \frac{-E_a}{RT} + \ln(\nu) \tag{3.16c}
\]
3.9 Molecular Beam Techniques

3.9.1 Helium Atom Scattering

A helium atom scattering (HAS) experiment uses a He beam to create a diffraction pattern emanating from a single crystallographic direction of the outermost crystal plane. This diffraction pattern occurs by He atoms scattering from the corrugation of the surface electron density (Rieder and Engel, 1980). HAS can be used in order to determine surface order through the intensity of the specular reflection, or the 1D structure of the surface atomic layer using the diffraction pattern. A key property of the beam for this technique is the de Broglie wavelength, in that the wavelength ($\lambda$) must be less than the spacing in order for diffraction to occur. $\lambda$ can be calculated through equation (3.17a), where $h$ is the Planck constant, $m$ is the molecular mass of the gas and $E$ is the energy, which is defined in equation (3.17b) for an atom, where $k_B$ is the Boltzmann constant. Equations (3.17a) and (3.17b) can be combined to give $\lambda$ as equation (3.17c). This equation gives $\lambda$ for He as 73 pm at 298 K, atomic spacing is of the order of 100 pm (Silbey et al., 2005).

$$\lambda = \frac{h}{\sqrt{2mE}} \quad (3.17a)$$

$$E = \frac{3}{2} k_B T \quad (3.17b)$$

$$\lambda = \frac{h}{\sqrt{3mk_B T}} \quad (3.17c)$$

3.9.2 Sticking Probability

There are a few different methods with which to acquire a sticking probability (SP) using a MB, which typically uses a reactive gas seeded into an inert MB. The first of these is the King-Wells method (King and Wells, 1972); this technique is based upon equation (3.18), where $S(t)$ is the sticking probability, $P_1(t)$ is the intensity scattered from a clean surface and $P_2(t)$ is the intensity scattered from a saturated surface. $P_2(t)$ here is measured through the pressure rise within the chamber when a shutter is blocking the MB from the sample surface, and $P_1(t)$ is recorded from the pressure drop with time after the sample is exposed to the MB. The main issue with this is that the variation in the pumping speed of the chamber wall must be considered. A background measurement of the pressure of the random gas in the chamber must also be taken prior to the experiment.

$$S(t) = \frac{P_2(t) - P_1(t)}{P_2(t)} = 1 - \frac{P_1(t)}{P_2(t)} \quad (3.18)$$

The second method, and the one used within this work is the modified King-Wells method (Takaoka and Kusunoki, 1998); this method uses equation (3.18) as a base, however the method of recording the pressures is different. In this technique, $P_1(t)$ is measured using a QMS to record the mass intensity of the seeded reactive gas before the scattered MB can collide with the wall, thus removing any dependence of time on variations in pumping
speed of the chamber wall. Once the QMS signal reaches a saturation point, the MB is blocked by a shutter, and then the initial experiment is repeated in order to record $P_2(t)$, which is independent of $t$ if the sample surface is brought fully to saturation. The modified King-Wells method is typically carried out with the sample at 45° to the MB, and the QMS normal to the sample surface. A schematic of the geometry of a SP experiment carried out using the modified King-Wells method is shown in Figure 3.6.

Figure 3.6: Schematic of a sticking probability experiment carried out using the modified King-Wells method.

These methods only provide information regarding how much of the reactive gas sticks to the surface, a further analysis technique (the Kisliuk method (Kisliuk, 1957)) can be employed to provide information on how it is sticking. This model assumes that the atom will initially enter a precursor state which is weakly bound to the surface and therefore highly mobile and able to diffuse considerable distances across the surface to find an empty adsorption site. These precursor states (indicated by the superscript of $p$) can be either intrinsic, an unoccupied surface site, or extrinsic, on top of adatoms (Weiss and Ranke, 2002). Kisliuk (1957) assumed that there is a certain probability of adsorption from the gas phase into either of the precursor states, desorption out of either of the precursor states, migration between precursor states, direct chemisorption and chemisorption from the intrinsic state, these probabilities can be used to define an equation. This equation is shown in equation (3.19a) where $\Theta$ is the coverage, $S_0$ is the initial sticking probability, $K$ is the Kisliuk parameter (defined in equation (3.19b)) and $p$ is the probability of an atom sticking in a specified state, where the superscript defines the precursor state and the subscript defines the final state. This $K$ value gives an indication of the adsorption dynamics; $K < 1$ shows that adatoms in extrinsic sites are more likely to diffuse and find an intrinsic site prior to desorbing, whereas the opposite is true when $K > 1$. The special case of $K = 1$ indicates Langmuir adsorption, where atoms will always stick on unoccupied intrinsic sites and will always desorb from an extrinsic site without any mobility. The effect of varying $K$ values on the shape of the sticking probability curve is shown in Figure 3.7. (Kisliuk, 1957; Weiss and Ranke, 2002)

\[
S(\Theta) = \frac{S_0(1 - \Theta)}{1 + \Theta(K - 1)} \quad (3.19a)
\]

\[
K = \frac{p_{ee}^d}{p_{en}^d + p_{dn}^d} \quad (3.19b)
\]
3.10 Low Energy Electron Diffraction

Low energy electron diffraction (LEED) uses an electron beam with energies typically $< 300$ eV in order to obtain a diffraction pattern of the surface layers. This can be used in order to obtain information regarding the 2D crystal structure along the surface plane, for the top 1 nm to 3 nm of material. The symmetry of the diffraction pattern gives the surface unit cell, however to get a full structural determination it is necessary to analyse the spot intensities across a variety of beam energies and then compare to calculations, known as LEED-IV.

The diffraction pattern is formed through the use of four concentric grids and displayed on a fluorescent screen, shown in Figure 3.8. The first grid is connected to earth to provide a field-free region between the grids and the sample, this minimises any electrostatic deflection.
of the diffracted electrons before they reach the grids and screen. The second and third grids are sometimes reduced to a single grid and have a varying negative potential applied to provide a suppressing field to remove inelastically scattered electrons, which contribute to the background of the pattern. The fourth grid is connected to earth to reduce effects of the high voltage required by the screen (typically 6 kV) from interfering with the suppressor grids.

In order for strong diffraction to occur, the Bragg condition (equation (3.20a)) must be satisfied, where \( \vec{k}_{\text{out}} \) is the scattered wave vector, \( \vec{k}_{0} \) is the initial wave vector and \( \vec{G} \) is the reciprocal lattice vector. The magnitude of \( \vec{k} \) can be calculated from equation (3.20b) where \( m_{e} \) is the mass of an electron, \( E \) is the energy in eV and \( \hbar \) is \( h/2\pi \). This can be illustrated graphically through the Ewald circle as shown in Figure 3.9. Where the Ewald circle crosses a reciprocal lattice rod, equation (3.20a) is true and therefore a diffraction spot will appear. The radius of the circle is equal to \( |\vec{k}_{0}| \) and is therefore proportional to the energy of the electron beam, meaning that a higher energy beam will excite higher order diffraction spots (Van Hove et al., 1986).

\[
\vec{k}_{\text{out}} - \vec{k}_{0} = \vec{G} \quad (3.20a) \\
|\vec{k}| = \frac{\sqrt{2m_{e}E}}{\hbar} \quad (3.20b)
\]

Figure 3.9: The Ewald sphere as it applies to LEED.


3.11 Conclusions

This chapter has presented an overview of the techniques which are used within this work. These techniques can provide a large amount of information concerning the surface structure and composition of a sample, with SEM providing topographical information and XPS, UPS, AES and SIMS contributing to chemical information. These can also be combined to give SAM, providing data on any changes in composition across the surface. LEED and HAS can be used to determine the surface crystallography of a well ordered sample surface. The other techniques described here provide information on reactions, with TPD giving kinetic and mechanistic information and SP providing data on the adsorption of reactive gases onto the surface. A comparison of the techniques presented within this chapter is given in Table 3.1.

Table 3.1: A comparison of the techniques used within this work.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Input</th>
<th>Output</th>
<th>Depth of Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>SEM</td>
<td>Electrons</td>
<td>Image</td>
<td>50 nm</td>
</tr>
<tr>
<td>XPS</td>
<td>X-rays</td>
<td>Spectrum</td>
<td>10 nm</td>
</tr>
<tr>
<td>UPS</td>
<td>Ultraviolet</td>
<td>Spectrum</td>
<td>10 nm</td>
</tr>
<tr>
<td>AES</td>
<td>Electrons</td>
<td>Spectrum</td>
<td>1 nm</td>
</tr>
<tr>
<td>SAM</td>
<td>Electrons</td>
<td>Image</td>
<td>1 nm</td>
</tr>
<tr>
<td>SIMS</td>
<td>Ions</td>
<td>Spectrum or Image</td>
<td>Time dependent</td>
</tr>
<tr>
<td>TPD</td>
<td>Thermal Energy</td>
<td>Spectrum</td>
<td>Sample dependent</td>
</tr>
<tr>
<td>HAS</td>
<td>He Atomic Beam</td>
<td>Diffraction Pattern</td>
<td>1 atomic layer</td>
</tr>
<tr>
<td>SP</td>
<td>Seeded He Beam</td>
<td>Probability</td>
<td>Sample dependent nm-μm</td>
</tr>
<tr>
<td>LEED</td>
<td>Electrons</td>
<td>Diffraction Pattern</td>
<td>1 nm</td>
</tr>
</tbody>
</table>
Chapter 4

Inorganic Surface Science Capability

4.1 Introduction

The ISSC is a new UHV system procured by AWE which has been designed and constructed by VG Scienta Ltd (now VACGEN Ltd). It has been developed in order to provide a research capability combining a variety of standard surface analysis techniques along with some more complex techniques into a single vacuum system. This allows multiple techniques to be carried out on samples which are highly air-sensitive without any atmospheric contamination. There is also a capability to transfer samples directly from inert glove box conditions into the system through the use of a vacuum suitcase, thereby eliminating a further potential source of atmospheric exposure.

The system is equipped with various sample preparation techniques such as vapour deposition, gas dosing and an Ar⁺ sputter gun. As these are all available in a single system \textit{in-situ} they can be used together in order to provide a clean thin film sample, or independently in order to carry out controlled experiments on bulk samples. The system is equipped with a variety of analytical techniques;

- Helium atom scattering
- Sticking probability
- X-ray photoelectron spectroscopy
- Auger electron spectroscopy
- Ultraviolet photoelectron spectroscopy
- Secondary ion mass spectrometry
- Low energy electron diffraction
- Scanning electron microscopy
- Temperature programmed desorption

It is envisaged that this instrument will be used to characterise the ageing and corrosion of air-sensitive materials through the use of controlled gas dosing with TPD and MB. This is expected to consist of the surface analysis of bulk material along with thin films generated \textit{in-situ}. TPD can be used with these samples to gain a greater mechanistic understanding of the effects that gases are having upon the material and SP experiments performed to improve
the understanding of how these gases react with a particular surface. The surface sensitive spectroscopy techniques can then show any changes in composition from these reactions.

A computer aided design (CAD) model of the ISSC is shown in Figure 4.1, this is labelled with the four main chambers of the system. A full vacuum schematic is presented in Appendix B. The sample holder is a VACGEN XL25. This provides connections for heating and thermocouples which are transferred between chambers along with the sample holder. A brief introduction to each of these chambers will now be given.

4.1.1 Loading Chamber

The loading chamber is the first chamber that a sample encounters upon entering the ISSC. This chamber is equipped with a fast entry air lock in order to allow sample entry within a relatively short space of time without exposing the main body of the instrument to pressures above $10^{-6}$ mbar. There is also a vacuum suitcase which attaches to the air lock, allowing a sample to be prepared under inert conditions in a glove box and then transferred into the ISSC without any atmospheric exposure, shown in Figure 4.2.

This chamber is fitted with the capability to:

- Clean samples with an Ar$^+$ ion gun (Omicron ISE 5).
- Gas dose with:
  - CO$_2$
  - H$_2$O
  - O$_2$
- $\text{H}_2$
  - Dose with atomic hydrogen using a gas cracker (Mantis MGC-75).
  - Physical vapour deposition using an electron beam deposition system (Mantis Quad-EV).

The gas dosing system allows for fundamental surface studies of the interaction of the various gases with a substrate; whereas the gas cracker produces highly reactive gas radicals, should the substrate be inert to the elemental gas. The sample manipulator has thermocouple and heating connections to allow sample heating, using proportional, integral and derivative (PID) control, up to 1200 K as well as liquid nitrogen cooling which allows the manipulator to reach 173 K. This chamber is shown in Figure 4.3.
4.1.2 Scattering Chamber

The main function of the scattering chamber is to carry out TPD and molecular beam experiments. TPD is carried out using a stage with the capability to both heat and cool samples (similar to that within the loading chamber) on a 6-axis manipulator. A novel QMS manipulation system is housed within a differentially pumped chamber with both radial and angular movement allowing for configuration to the requirements of both TPD and molecular beam experiments. This system is described further in § 4.1.5. This chamber also has a LEED optic (Omicron SPECTALEED) fitted in order to carry out LEED experiments, as well as a second QMS (Hiden SIM300) and ion gun (Hiden IG20) in order to perform SIMS. Figure 4.4 shows a CAD model of this chamber with the key analytical components labelled.

![CAD model of the scattering chamber with the key components labelled.](image)

4.1.3 Analysis Chamber

The analysis chamber provides a variety of complimentary surface analytical techniques, which include SEM, XPS, UPS, AES and SAM. The equipment fitted for these techniques are an Al and Mg twin anode X-ray source (Omicron DAR400), a He UV discharge lamp (Focus HIS13), a 12 kV electron gun (Staib EK-12-M), a secondary electron detector (Omicron) and a HSA (Omicron EA125). There is also a charge neutraliser (Omicron CN10) to allow the analysis of insulating samples. This chamber uses an ion pump, a Ti sublimation pump (TSP) and vibration dampening feet in order to provide UHV pressures with minimal vibrations that would interfere with the high spatial resolution analytical techniques (SEM, AES), it is also constructed from mu-metal to reduce the effect of any magnetic fields. This chamber is again fitted with the ability to heat and cool samples between 173 K and 773 K. Figure 4.5 shows an image of this chamber.

4.1.4 Molecular Beam Chamber

The MB used within this work is generated from a free-jet source. This process uses a high pressure gas passing through a small aperture (within the ISSC this aperture is 40 ± 5 µm) in
a converging nozzle into a low pressure background in order to accelerate the gas to supersonic velocities. The ISSC uses a Gottingen type design, in which the pressure within the nozzle is lower than other designs (for example a Campargue design), however the pumping speed is higher within the chamber to provide the required pressure difference. This expansion is shown as a schematic in Figure 4.6, where $M$ indicates the Mach Number, $P_0$ is the pressure inside the nozzle or stagnation pressure, $T_0$ is the temperature inside the nozzle, or stagnation temperature and $P_b$ is the background pressure (Miller, 1988; Adamson and Nicholls, 1959).

In order to accelerate the gas to supersonic speeds it is required that $M$ is equal to 1 at the nozzle exit, which requires that the ratio $P_0/P_b$ is equal to a critical value ($G$) the definition of which is shown in equation (4.1), where $\gamma$ is the ratio of the specific heat capacities. $G$ is $<2.1$ for all gases. If the ratio is lower than $G$, then the gas will not expand and will have a pressure of $\sim P_b$ after exiting the nozzle. However when this critical value is met, the gas will be at $M = 1$ at the nozzle exit and will expand to a pressure of $P_0/G$. As this pressure exceeds $P_b$ the flow is underexpanded and therefore requires further expansion in order to meet the boundary condition defined by $P_b$ (Miller, 1988).
\[ G \equiv \left( \frac{\gamma + 1}{2} \right)^{\frac{1}{\gamma - 1}} \]  

(4.1)

The MB cannot sense any boundary conditions imposed downstream as it is travelling at supersonic velocities and information propagates at the speed of sound; however it must still meet these conditions. This dilemma is resolved through the formation of shock waves, which are very thin regions with large property changes. These provide a mechanism through which the direction or velocity of a supersonic flow can be instantaneously changed in order to move toward the imposed boundary conditions. Once the flow has decelerated to \( M < 1 \), it can adapt to boundary conditions as a standard subsonic flow. With reference to Figure 4.6, the flow exits the nozzle into the zone of silence, where the flow is isentropic and properties are fully independent of \( P_b \) due to the supersonic flow. This region is bounded by two shock waves, a barrel shock around the edges of the expansion and a Mach disk perpendicular to the flow direction. The reflected shock is formed through an interaction between the barrel shock and the Mach disk. It is possible to calculate the position of the Mach disk shock wave through equation (4.2), where \( x_M \) is the position of the Mach disk in relation to the nozzle aperture and \( d_n \) is the diameter of the nozzle (Grant, 2010).

\[ x_M = 0.67d_n\sqrt{\frac{P_0}{P_b}} \]  

(4.2)

For the system used within this work with typical operating pressures of \( P_0 = 4500 \text{ mbar} \) and \( P_b = 10^{-6} \text{ mbar} \), the distance between the nozzle and the Mach disk is 1798 mm. This value is of importance as the MB is extracted from the zone of silence through the use of a skimmer, and so the distance given by equation (4.2) gives an absolute maximum distance between the nozzle and skimmer; although in practise, it should be significantly closer in order to allow for pressure variations and to reduce effects of particles being reflected off the wall behind the skimmer. It is necessary to extract a beam from this region as the Mach disk provides a very large velocity gradient, dropping \( M \) from a value \( \gg 1 \) to \( < 1 \) and the region between the barrel shock and the jet boundary (boundary of area at which \( M > 1 \)) is nonisentropic; therefore neither of these areas are appropriate for a MB (Miller, 1988).

The next component of the MB generation system equipped on the ISSC is a rotating disk, or chopper. This is used in order to generate a chopped beam, as required for some MB based techniques. Within the ISSC it is designed to be able to provide two different types of chopped beam, a short pulse equating to \( \sim 1.5\% \) of the full cycle and a 50\% duty cycle. A LED timing system is fitted to indicate the start of a chopped pulse, allowing for the time of flight (ToF) of the beam to be determined with highly time sensitive mass spectrometry. The chopper design is shown in Figure 4.7 where \( r_o \) is the outer radius (50.0 ± 0.3 mm), \( r_i \) is the inner radius which is used for the 50\% cycle (46.0 ± 0.3 mm), \( r_b \) is the radius to the slit for short beam pulse (35.5 ± 0.3 mm) and \( r_t \) is the radius to the slit for the timing circuit (22.7 ± 0.3 mm). The finite width of the slot means that the detected signal is a convolution of the intrinsic velocity distribution of the gas molecules with a gating function defined by the geometry of the slot and velocity of the disk. The derivation of the gating function for the ISSC can be found in § 4.2.8 (Gentry, 1988).

The final component of the MB generation system is a collimator (which can be changed between a variety of sizes), used to increase the directional alignment of the beam particles and to reduce the diameter of the beam. There is however a compromise to the increased
spatial resolution obtained through the use of a smaller collimator, in that the intensity of the signal obtained will be reduced. A plan view of the MB chamber is presented in Figure 4.8.

Figure 4.8: Plan view of the molecular beam chamber showing the components involved in the generation of the molecular beam. (a) is the nozzle, (b) is the skimmer, (c) is the chopper, (d) is the collimator, (e) is the LED timing circuit and (f) is a diffusion pump.

4.1.5 Quadrupole Mass Spectrometer System

HAS, SP and TPD are complementary techniques for studying interactions at a solid-gas interface. However these three techniques all require significantly different geometry; HAS requires a narrow QMS entrance aperture and a reasonably long working distance (typically >0.5 m) to provide the required angular resolution. For SP, a working distance which can provide moderate angular resolution (approximately 5°) is required with a large QMS entrance aperture to maximise signal. In contrast, TPD generally requires a working distance as short as possible (typically 1 mm) and a large QMS entrance aperture in order to maximise the detected signal against the background pressures. While instruments that can carry out both have been previously produced, they have used a mass spectrometer fixed at a working distance for TPD and therefore the angular resolution has been reduced to
∼4° (Campbell et al., 1981). The QMS chamber design on the ISSC (shown in Figure 4.9) allows for the system to be configured for both high signal TPD and high resolution HAS through movement in both radial and angular directions.

Figure 4.9: Labelled photograph of the mass spectrometer chamber within the scattering chamber. Red arrows indicate the axes of motion available to the mass spectrometer.

The entire QMS system is mounted on a goniometer and sealed from the scattering chamber at the point of rotation. The motion of the goniometer is driven by an externally mounted stepper motor, this gives a rotational range of ∼200° limited solely by the location of the instrumentation for SIMS and LEED within the scattering chamber. The number of steps per degree (1948) was calibrated across a movement of 180° giving a theoretical step resolution of the motor of 0.0005°, realistically this is reduced by tolerances in the gears but can be considered as <0.01°. The bellows mounted upon the goniometer allow for the QMS to be moved along the radial direction through the use of a further stepper motor attached to a screwdriver on a feed through; this screwdriver drives a linear translator attached to the bellows. The range of motion in this direction is 0 mm to 237 mm. The QMS is covered by a rotatable housing containing a variety of aperture sizes (1 mm, 2 mm, 3 mm and 5 mm). This allows for the size of the aperture to be changed using a screwdriver mounted internally on a feed through. This system design allows the choice between signal intensity and angular resolution. At a working distance of 237 mm and with an aperture of 1 mm the angular resolution should be ∼0.24°, greatly improved over previous systems allowing for both TPD and HAS (Campbell et al., 1981).

4.2 Commissioning of the ISSC

4.2.1 Introduction

This section will cover the work carried out in order to commission the ISSC. This will primarily cover work carried out in site acceptance testing (SAT), however any major differences between SAT and factory acceptance testing (FAT) will also be presented.
4.2.2 Scanning Electron Microscopy

Testing

The only specification relating to the SEM during testing was that the resolution is less than 500 nm in both x and y directions. This was tested using a copper grid, in which the size of each of the grids is known to be 12.5 µm. This was imaged using the SEM and the pixel intensities were analysed along the grid axis using a calculation between 16% and 84% to obtain the resolution. The result of this for the x direction was 516.4 nm and is shown in Figure 4.10 for FAT; the resolution in the y direction at this stage of testing was 341.1 nm. While this did not meet specification in the x direction, it was believed at the time that vibrations from other equipment in the factory were having a detrimental effect upon the attainable resolution. When this test was repeated at AWE for the SAT, the resolution did improve to 374 nm and 273 nm for x and y respectively, thereby meeting the specification in both directions.

![Figure 4.10: Pixel intensities across copper mesh in x direction for FAT. Used for resolution test, specification of 500 nm.](image)

An image was obtained in both SE and BSE modes using a polycrystalline U sample and the Mo sample clip. These are shown in Figure 4.11.

Calibration

The SEM software packaged with the ISSC gives a scale bar as ‘20% of raster’, however the only indication of raster size is a scan width voltage rather than a distance. This scale bar also does not appear when an image is exported out of the SEM software. In order to form a correlation between these two values, the same grid used to test the SEM resolution was imaged at a variety of scan widths. The number of pixels across a grid was then obtained, thus giving a ratio of µm to pixels. The width of the image in pixels can be multiplied by this ratio in order to obtain an image width in µm. This calculated image width was then plotted against the scan width for all of the images, shown in Figure 4.12. A linear fit was applied to this data to obtain a direct conversion between the scan width voltage and
Figure 4.11: Two SEM images of the same area of a Mo sample clip (bottom left) on a polycrystalline U sample (top right). (a) Secondary electron mode. (b) Backscattered electron mode.
the actual raster size, found to be that the raster size is 0.94 times the scan width. This
calibration can then be used with image modification software in order to add a scale bar to
the micrograph.

![Image Width vs Scan Width](image.png)

Figure 4.12: Plot of calculated image width against the given scan width. Black squares
show the acquired data and the red line is a linear fit.

4.2.3 Spectroscopic Techniques

X-Ray Photoelectron Spectroscopy

The XPS system was tested using an Ag(100) sample that had been cleaned under UHV
conditions using an Ar⁺ sputter gun. A survey spectrum was acquired from this sample
using a Mg Kα x-ray source and then compared to a reference spectrum supplied by the
manufacturer. The spectrum was expected to show;

- No adventitious C.
  - This would be removed during the sputter cleaning.
- High secondary electron background at high $E_B$.
  - This is typical of XPS due to the occurrence of multiple scattering events.
- Distinct peaks at the correct binding energies for Ag.
- No cross-talk between the Mg Kα and Al Kα.

The survey spectrum taken for this test is shown in Figure 4.13. This survey fulfils the
requirements as there is only trace levels of the C 1s peak at 285 eV. There is also a high
background at high $E_B$. The main silver peak (Ag 3d₅/₂) is clearly present within the spectra
at 367 eV, along with all of the other Ag peaks within the experimental range (Moulder et al.,
There is a large amount of oxygen contamination within the sample which is shown by the high intensity of the O 1s peak, this could be reduced with further sputtering of the sample.

The next test was to confirm that the FWHM matched the specified line width from the analysis conditions. This was checked using high resolution scans of the Ag 3d$_{5/2}$, again using the Mg Kα x-ray source. The data obtained during the SAT is shown in Figure 4.14. Here the separation between the Ag 3d$_{3/2}$ and the Ag 3d$_{5/2}$ is 6 eV as expected, and the area ratio is 3:2 also as expected. The separation and area ratio values are also valid for the Kα$_{3,4}$ peaks.
Ultraviolet Photoelectron Spectroscopy

Similarly to XPS, the UPS was tested using an Ag(100) sample at room temperature, for which a survey scan from $-1\text{ eV}$ to 20 eV was taken and compared to literature (Garfunkel et al., 1985). The data from this test is shown in Figure 4.15 and was comparable to the expected results, taking into account broadening of the peaks due to the temperature not being close to 0 K, with the main feature being the Ag 4d band between 7 eV and 3.5 eV.

![Figure 4.15: UPS spectrum of the valence region of a Ag sample for SAT.](image)

The next test was to determine the resolution of the UPS. This is found by analysing the Fermi edge for the energy between 90% and 10% intensity, the value given in the equipment manual and therefore the target to achieve was 140 meV. The main issue with this technique is that a small change in the judgement of where the 100% and 0% intensities are located can cause a large change in the resolution found. Figure 4.16 shows the data acquired for this test, black dashed lines have been added at 0 meV and $-140\text{ meV}$ in order to indicated the resolution specified, and red dashed lines indicated the intensities calculated as 90 and 10%, 24 570 $\text{c s}^{-1}$ and 5130 $\text{c s}^{-1}$ respectively. The difference in energy between these two positions is clearly larger than the 140 meV specification, it can be calculated as 248 meV. However there are a variety of factors which will broaden this resolution, such as background counts from the UV source, sample contamination and the sample being at room temperature rather than the ideal 0 K. Due to these factors, the UPS apparatus was deemed to meet specification with external factors causing a broadening of the resolution.
Figure 4.16: UPS spectrum of the Fermi edge using a Ag sample for SAT. The red dashed lines show the intensities determined to be 10% and 90% and the difference between the black dashed lines is the target of 140 meV.

**Auger Electron Spectroscopy**

The same Ag(100) sample was again used for commissioning of the AES. The only required test for this system was to confirm that the signal satisfied the specification of $120 \text{kc s}^{-1} \text{nA}^{-1}$; as the HSA has shown with both XPS and UPS to be performing to specification. Figure 4.17 shows the spectrum acquired using AES for this test, acquired with a drain current measured as 300 nA. The Ag $M_{5/2}N_{4.5}N_{4.5}$ has an intensity of $43200 \text{kc s}^{-1}$, with the recorded drain current this gave a signal of $144 \text{kc s}^{-1} \text{nA}^{-1}$, clearly meeting the specification. However when the background level of $31800 \text{kc s}^{-1}$ is taken into consideration, the signal drops to $38 \text{kc s}^{-1} \text{nA}^{-1}$, clearly below the $120 \text{kc s}^{-1} \text{nA}^{-1}$ specification. Given that there is a strong peak definition with this intensity, the signal is considered ample to pass testing. Even though the sample had been cleaned, the C $K_{LL}$ is still present at 261 eV, indicating that either the amount of time sputtering the sample is insufficient or the UHV chamber is not clean enough for the sample to be left for more than a few hours.
Figure 4.17: AES spectrum of Ag carried out for SAT.

**Scanning Auger Microscopy**

SAM was tested using a U sample and the Mo clip used to attach samples to the sample holder. This requires two energies for each pixel of the final image: one at the peak energy and one for the background. A point scan was carried out with AES to determine the energies to be used, which were 74.3 eV and 125 eV for U and 187.8 eV and 200 eV for Mo for the peak and background respectively. These energies were then recorded across an area which included the edge of the clip, this should show a sharp change between the U of the sample and the Mo of the clip. The elemental map obtained from this test is shown in Figure 4.18 along with an SEM image of the area. The intensity used in the map was determined using \((I_p - I_b)/I_b\) signal correction to remove topographical effects.
Figure 4.18: Images showing the testing of the SAM. (a) SEM image in location of SAM map. (b) SAM map with U in red and Mo in green.
4.2.4 Secondary Ion Mass Spectrometry

Prior to testing the SIMS, it was required to use a phosphorescent sample (P43 - Gd$_2$O$_2$S:Tb) to carry out an initial alignment of the sample holder with the ion beam. The phosphorescent material glowed under the ion beam, allowing for an initial visual alignment. The next stage was to further align the sample with both the ion beam and the QMS, this was carried out by changing the rotation of the sample in order to maximise the signal.

The SIMS could then be tested using a LiF crystal. The data from the test is shown in Figure 4.19, with the signal detected with the QMS in positive mode shown in black and the signal detected while in residual gas analysis (RGA) or neutral mode is shown in red. The data shows clear peaks in the positive spectrum for both $^6$Li$^+$ and $^7$Li$^+$ at a ratio of 1 : 9 while the ratio of natural Li is 2 : 23 (Holden, 2012), within the error of the measurement. However, the negative ions could not be recorded as the sample was charging under the ion beam, and therefore the negative ions were not emitted.

![Figure 4.19: SIMS spectra of LiF. Positive ions are shown in black and neutral atoms are shown in red. Negative ions could not be collected due to sample charging.](image)

In order to ensure that the QMS was fully working, a conducting sample of AgO (i.e. the Ag(100) sample with its native oxide layer) was also used, with the O peaks expected to be visible within the negative spectrum. This data is shown in Figure 4.20, with the negative ions shown in blue. The expected isotopic ratio between $^{107}$Ag$^+$ and $^{109}$Ag$^+$ is 13 : 12 (Holden, 2012) and the ratio within the data collected is 11 : 9, similarly to that of Li above, this small amount of variation can be expected. The negative ion spectrum primarily shows O$^-$ and F$^-$, the O$^-$ is expected from the sample of AgO, and F is a common contamination on Ag. Also present is a small amount of O$_2^-$, formed by the recombination of O, and HO$^-$ potentially from the presence of some surface hydroxide or from the combination of O$^-$ and H within the UHV chamber.
4.2.5 Low Energy Electron Diffraction

The LEED apparatus was tested using the Ag(100) sample used previously. The LEED pattern taken at an energy of 142 eV is shown in Figure 4.21. The image shown is sharp and there are no prominent overlayers visible, such as could be expected if the UHV was not of a high quality, causing the adsorption of CO, O₂ or CO₂. The pattern matches the pattern that can be expected for a clean Ag(100) surface and therefore can be assigned as the Ag(100) surface.

Figure 4.21: The LEED pattern of a sputter cleaned Ag(100) surface taken with a beam energy of 142 eV. Labelled with the Miller indices of the diffraction spots and the lattice parameters of the surface reciprocal mesh.
4.2.6 Temperature Programmed Desorption

Testing of the TPD equipment consisted of two main stages, the first was to test the heating capability with a blank sample holder. This was carried out at three different target heating rates, 0.001 K s\(^{-1}\), 0.1 K s\(^{-1}\) and 1 K s\(^{-1}\). The temperature for these tests was recorded against time and then fitted with a linear fit in order to determine the actual heating rate. The data acquired for 0.1 K s\(^{-1}\) and 1 K s\(^{-1}\) are shown in Figure 4.22, with the parameters of the linear fit for each shown in Table 4.1. The fits show that at all ramp rates tested, the heating rate is very precise and easy to control as the R\(^2\) value is 1.000, indicating that the line fits to every single data point. The gradients are also close to the desired heating rate, with the only rate which does not follow the exact rate requested being the 1 K s\(^{-1}\) where it is still very close at 0.99 K s\(^{-1}\). The specification states that the minimum heating rate is 0.0001 K s\(^{-1}\), however this was not obtainable as the PID controller rounds anything below 0.001 K s\(^{-1}\) to 0. This has been deemed as acceptable as 0.001 K s\(^{-1}\) provides an accurate and satisfactory heating rate, and over a typical temperature range for LiH (300 K to 800 K) will last ~140 h. This test shows that the hardware can control the heating to a satisfactory level to heat samples in a linear manner at a range of heating rates.

![Figure 4.22: Plot of temperature against time for two blank TPDs to confirm the heating rate. The target rates were 0.1 K s\(^{-1}\) and 1 K s\(^{-1}\).](image)
Table 4.1: Table of the fitted gradients from Figure 4.22, used to confirm the heating rates in TPD. Errors given are one standard error.

<table>
<thead>
<tr>
<th>Gradient (m)</th>
<th>0.001 K s(^{-1})</th>
<th>0.1 K s(^{-1})</th>
<th>1 K s(^{-1})</th>
</tr>
</thead>
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<tr>
<td>Gradient (m)</td>
<td>0.001</td>
<td>0.1</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>±3.25 \times 10^{-9}</td>
<td>±2.43 \times 10^{-8}</td>
<td>±4.09 \times 10^{-4}</td>
</tr>
</tbody>
</table>

The second test was to carry out a TPD on LiH and compare to the results from TPDs carried out using the dedicated TPD rig (this work is presented in § 5.2). The main peak is expected to be present at \(\sim 600\) K within both the H\(_2\) and the H\(_2\)O traces, it is also expected that an exponential increase will be present in the Li and H\(_2\) traces from \(\sim 650\) K. This requires the sample to be aligned with the selected aperture on the QMS hat and then the QMS moved towards the sample holder until at a working distance of \(< 0.5\) mm. The ability to move the QMS to this required working distance was first carried out as a proof of concept with a blank sample holder, a photograph of this is shown in Figure 4.23.

Data acquired using the TPD capability of the ISSC for LiH is shown in Figure 4.24. The data shows the two main expected structures previously mentioned, the peak at \(\sim 500\) K in the H\(_2\)O trace has also been seen within the work presented in § 5.2. However the peak in both H\(_2\) and H\(_2\)O at \(\sim 630\) K has not been found previously, this could be due to either a variation within the sample holder or from the superior experimental resolution available on the ISSC in comparison to the dedicated TPD rig described in § 5.2. The sinusoidal effect visible below 550 K in the H\(_2\) trace is due to power fluctuations from the PID controller as the ramp rate was being obtained, caused by the temperature initially lagging behind where it was expected to be. This can easily be resolved by adjusting the PID parameters for the sample, which can automatically be carried out by the controller by providing a known amount of power and analysing the temperature response.
4.2.7 Calibration of Mass Spectrometer

The QMS used for TPD and MB based experiments was calibrated to pressure using a certified spinning rotor gauge (SRG). This could not be carried out directly as the SRG only operates at pressures higher than $10^{-6}$ mbar, while the QMS can not be used above this pressure without risking damage to the electron multiplier. A calibration was achieved by using an ion gauge as a middle step; the ion gauge was calibrated to the SRG and then the QMS was calibrated to the ion gauge. Figure 4.25a shows the calibration of ion gauge to SRG and Figure 4.25b shows the calibration between the QMS and the ion gauge for He. The final calibrations are shown in Table 4.2 for He, CO$_2$, O$_2$ and H$_2$; the H$_2$O signal has not been calibrated as the pressures required would be too large for a UHV system and baking would then be necessary.

Table 4.2: Table showing the QMS pressure calibration for He, CO$_2$, O$_2$ and H$_2$.

<table>
<thead>
<tr>
<th>Gas Species</th>
<th>Calibration (mbar s c$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>$(1.86 \pm 0.05) \times 10^{-13}$</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>$(8.88 \pm 0.05) \times 10^{-13}$</td>
</tr>
<tr>
<td>O$_2$</td>
<td>$(1.94 \pm 0.01) \times 10^{-12}$</td>
</tr>
<tr>
<td>H$_2$</td>
<td>$(5.88 \pm 0.06) \times 10^{-14}$</td>
</tr>
</tbody>
</table>
CHAPTER 4. INORGANIC SURFACE SCIENCE CAPABILITY

(a) Calibration between ion gauge and spinning rotor gauge.

\[ y = 5.89x + 2.47 \times 10^{-5} \]

(b) Calibration between mass spectrometer and spinning rotor gauge, using the calibration with the ion gauge.

\[ y = 1.87 \times 10^{-13}x - 3.58 \times 10^{-8} \]

Figure 4.25: Calibration of the mass spectrometer intensity to pressure for He
4.2.8 Molecular Beam

Velocity Characterisation

The beam velocity (or drift velocity \(v_d\)) was tested by acquiring ToF spectra using a He MB and the QMS to record the He signal. This data was recorded with the QMS at full linear extent for both 0° and 180° positions; this gives a known distance between the points of 475.0 ± 0.7 mm. This known distance allows \(v_d\) to be calculated from the time offset between the peaks in the two spectra. A theoretical value can also be calculated for \(v_d\) by considering that the only source of \(E_K\) available is thermal energy (\(E_T\)), and therefore must be equal. The equations for \(E_K\) and \(E_T\) are given in equations (4.3a) and (4.3b) respectively. Making these equations equal and \(v\) equal to \(v_d\) gives a theoretical \(v_d\) through equation (4.3c).

\[
E_K = \frac{1}{2}mv^2 \quad (4.3a)
\]
\[
E_T = \frac{\gamma}{\gamma - 1}RT \quad (4.3b)
\]
\[
v_d = \sqrt{\frac{2\gamma RT_N}{(\gamma - 1)m}} \quad (4.3c)
\]

The spectra obtained for a beam with a nozzle temperature (\(T_N\)) of 298 K and the beam pulsing at a speed of 400 Hz are shown in Figure 4.26 for both positions. The time of arrival of the peak and associated error for both points is shown in Table 4.3. These points were determined by fitting a Lorentzian curve to the peak using MATLAB® (2014) (see Appendix C for the code). The \(v_d\) was calculated by dividing the change in arrival time of the two points by the distance between them; this gives a \(v_d\) of 1758 m s\(^{-1}\). This was also carried out with the nozzle at 500 K, again with the QMS in both of the positions previously mentioned.

<table>
<thead>
<tr>
<th>Position (°)</th>
<th>Time (s)</th>
<th>Error (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.4 × 10(^{-4})</td>
<td>±2 × 10(^{-5})</td>
</tr>
<tr>
<td>180</td>
<td>5.1 × 10(^{-4})</td>
<td>±2 × 10(^{-5})</td>
</tr>
</tbody>
</table>

On initial testing the predicted MB velocity for a known temperature varied from the actual velocity observed. The discrepancy implies a potential issue with thermocouple contact on the nozzle, which is plausible as the thermocouple is mounted in reasonably close proximity to the heating element around the nozzle and therefore may read a higher temperature than that of the nozzle. This has since been adjusted and Table 4.4 shows the final values of the beam velocity at both ambient and elevated temperatures. These are both within reasonable error of the value predicted from theory and so the velocity of the MB was determined to meet the required specification.

The \(v_d\) found above can be divided by the local speed of sound in order to calculate the Mach number of the beam, where the local speed of sound in the beam can be calculated from equation (4.4);


Figure 4.26: ToF molecular beam spectra showing the normalised He intensity, with the QMS at 0° (black) and 180° (red).

\[ c = \sqrt{\frac{\gamma RT_B}{m}} \]  

(4.4)

where \( c \) is the local speed of sound, \( \gamma \) is the specific heat ratio for the gas, \( R \) is the molar gas constant, \( T_B \) is the beam temperature. For He, \( \gamma \) is 5/3 and \( m \) is 0.004 kg mol\(^{-1}\).

There is an effect upon the velocity distribution of the beam caused by the chopper. This effect is in the form of a convolution as shown in equation (4.5), where \( \text{signal} \) is the detected signal by the QMS, \( v(t) \) is the intrinsic Maxwell-Boltzmann velocity distribution of the beam converted to time domain and \( g(t) \) is the effect of the chopper also known as the gate function.

\[ \text{signal} = v(t) \otimes g(t) = \int_0^t v(t - \tau) g(\tau) d\tau \]  

(4.5)

The chopper consists of two rectangular slits on a rotating disk; this movement of a rectangular slit across the circular MB was modelled using the equation for the area of a segment, given in equation (4.6). Where \( A \) is the area of the segment, \( r \) is the radius of the beam and \( \theta \) is the angle of the segment defined by the intersection of the beam and the slit.

<table>
<thead>
<tr>
<th>Nozzle Temperature (K)</th>
<th>Theoretical Velocity (m s(^{-1}))</th>
<th>ToF Velocity (m s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>1754</td>
<td>1758</td>
</tr>
<tr>
<td>500</td>
<td>2340</td>
<td>2350</td>
</tr>
</tbody>
</table>
It was assumed that the radial motion of the slit could be approximated to a linear movement across the beam diameter in order to simplify the model. This was considered to be a reasonable assumption considering the short distances concerned. Equation (4.7) shows the piecewise function that has been derived as defining $g(t)$. Where $V$ is the linear velocity of the slit, $w$ is the width of the slit and the subscripts on the $\theta$'s are defined as $x = 1$ is the leading edge of the slit and $x = 2$ is the trailing edge of the slit, as shown in the schematic shown in Figure 4.27. The shape of $g(t)$ is shown in Figure 4.28 with two different sized beams.

$$g(t) = \begin{cases} 
\frac{r^2}{2} (\theta_1 - \theta_2 - \sin \theta_1 + \sin \theta_2) & \text{for } 0 \leq t < \frac{r}{V} \\
\frac{\pi r^2}{2} - \frac{r^2}{2} (\theta_1 + \theta_2 - \sin \theta_1 - \sin \theta_2) & \text{for } \frac{r}{V} \leq t < \frac{w + r}{V} \\
\frac{r^2}{2} (\theta_2 - \theta_1 - \sin \theta_2 + \sin \theta_1) & \text{for } \frac{w + r}{V} \leq t < \frac{w + 2r}{V} \\
0 & \text{otherwise}
\end{cases}$$  
(4.7)
Figure 4.28: Graphical representation of the model of $g(t)$. The upper image shows a beam with a diameter half the width of the slit; the lower image shows a beam with a diameter double the width of the slit. The time and intensity scales vary between the two images, however they have been made to appear the same to ease comparison of shape. A smaller beam will result in a shorter and less intense pulse.
This convolution was carried out in MATLAB® (2014) (Appendix C) and fitted to data using a manual fit to find $T_B$ and then an iterative fit with decreasing steps in order to find $M$. The best fit for a beam pulsed at 400 Hz with a $T_N$ of 298 K is shown in Figure 4.29, using a $T_B$ of 2.5 K. Using this value in equation (4.8) gives $M$ of 19, this gives an improvement to other MB systems within the literature such as those used by Cardillo et al. (1978) of 10 and Miyake and Yamamoto (1993) of 12.

![Fitted and normalised ToF profile with a 400 Hz pulse and 298 K nozzle temperature and the QMS in the 180° position. Beam temperature giving this fit is 2.5 K.](image)

**Figure 4.29**: Fitted and normalised ToF profile with a 400 Hz pulse and 298 K nozzle temperature and the QMS in the 180° position. Beam temperature giving this fit is 2.5 K.

**Seeded Beams**

When using reactive gases it is common practice to seed the beam with a small percentage of the reactive gas into a inert MB (He within the ISSC). This has the benefit of accelerating the heavier reactive gas up to the higher velocity MB. Calculating $v_d$ for O$_2$, CO$_2$, and H$_2$ on the ISSC results in Table 4.5. H$_2$O was not used during this calculation as it was not possible to generate high enough pressures to seed the beam with enough moisture to create a range of seed concentrations. $P_0$ was 4.5 bar when He was present, while the 100% beams were run at the following pressures: CO$_2$ - 3.5 bar, O$_2$ - 3 bar and H$_2$ - 2.8 bar.

**Beam Intensity**

The beam intensity and flux are both important parameters for scattering experiments. It is essential to have a high beam flux as the scattered molecules detected by the QMS are normally no more than 2% of the incident beam (Farias and Rieder, 1998). The intensity of the beam is defined by the number density ($N_v$) which is the number of atoms per unit volume. $N_v$ of the MB was measured by using the QMS pressure calibration from § 4.2.7. $N_v$ can then be estimated using the ideal gas law as given in equation (4.9), where $N_a$ is Avogadro’s number, $n$ is the number of moles of gas, $V_d$ is the detection volume, $P$ is the pressure in Pa, $R$ is the molar gas constant and $T_N$ is the nozzle temperature.
Table 4.5: $v_d$ for O$_2$, CO$_2$ and H$_2$ at a range of concentrations.

<table>
<thead>
<tr>
<th>Species</th>
<th>Concentration (%)</th>
<th>$v_d$ (m s$^{-1}$)</th>
<th>$v_d/v_d$(He)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>5</td>
<td>1580</td>
<td>0.90</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>1270</td>
<td>0.72</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>1043</td>
<td>0.59</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>869</td>
<td>0.49</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>688</td>
<td>0.39</td>
</tr>
<tr>
<td>O$_2$</td>
<td>5</td>
<td>1548</td>
<td>0.88</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>1440</td>
<td>0.82</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>1112</td>
<td>0.63</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>908</td>
<td>0.52</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>753</td>
<td>0.43</td>
</tr>
<tr>
<td>H$_2$</td>
<td>5</td>
<td>1788</td>
<td>1.02</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>1850</td>
<td>1.05</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>1951</td>
<td>1.11</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>2147</td>
<td>1.22</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>2693</td>
<td>1.53</td>
</tr>
</tbody>
</table>

The MB flux ($N_f$) is the number of atoms impinging on a unit area per unit time, this is equivalent to $N_v$ multiplied by $v_d$. The recorded QMS pressures and the resulting $N_v$ and $N_f$ values using all of the available collimating apertures are presented in Table 4.6.

Table 4.6: Beam $P$, $N_v$ and $N_f$ at varying collimating apertures.

<table>
<thead>
<tr>
<th>Collimator (mm)</th>
<th>$P$ (mbar)</th>
<th>$N_v$ (cm$^{-3}$)</th>
<th>$N_f$ (cm$^{-2}$s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Open</td>
<td>$4.2 \times 10^{-6}$</td>
<td>$1.0 \times 10^{23}$</td>
<td>$1.8 \times 10^{16}$</td>
</tr>
<tr>
<td>4</td>
<td>$3.8 \times 10^{-6}$</td>
<td>$9.3 \times 10^{22}$</td>
<td>$1.6 \times 10^{16}$</td>
</tr>
<tr>
<td>2</td>
<td>$3.4 \times 10^{-6}$</td>
<td>$8.2 \times 10^{22}$</td>
<td>$1.4 \times 10^{16}$</td>
</tr>
<tr>
<td>1.5</td>
<td>$2.8 \times 10^{-6}$</td>
<td>$6.9 \times 10^{22}$</td>
<td>$1.2 \times 10^{16}$</td>
</tr>
<tr>
<td>1</td>
<td>$1.7 \times 10^{-6}$</td>
<td>$4.2 \times 10^{22}$</td>
<td>$7.4 \times 10^{15}$</td>
</tr>
<tr>
<td>0.5</td>
<td>$5.1 \times 10^{-6}$</td>
<td>$1.2 \times 10^{22}$</td>
<td>$0.2 \times 10^{15}$</td>
</tr>
<tr>
<td>0.2</td>
<td>$1.2 \times 10^{-7}$</td>
<td>$2.8 \times 10^{21}$</td>
<td>$5.0 \times 10^{14}$</td>
</tr>
</tbody>
</table>

Angular Divergence

Another important parameter of the MB for scattering experiments is the angular divergence ($\theta_d$) as this defines the size of the beam at any given point and defines a limit to the achievable angular resolution of a scattering experiment. The divergence of the MB on the ISSC was determined by using the QMS at two known distances from the collimator ((216 ± 1) mm and (716 ± 1) mm) to measure the width of the beam for each of the collimator diameters available. The farther of the distances used is equivalent to the distance the beam will travel to reach the QMS in a scattering experiment. Using these known distances, it is possible to use the beam divergence to calculate the size of the beam at the sample and...
the detector. A smaller collimator gives a better resolution as the beam is smaller, however
the beam intensity reduces. The best compromise between these two factors for scattering
experiments was the 1 mm collimating aperture which provided a beam diameter of 6.3 mm
at the point of detection, while still providing a readily detectable signal. Table 4.7 shows
$\theta_d$, angular resolution, the width of the beam at the detector ($w_d$) and the width of the beam
at the sample ($w_s$) for all of the collimating apertures.

Table 4.7: Determination of beam divergence.

<table>
<thead>
<tr>
<th>$d_c$</th>
<th>$\theta_d$ (°)</th>
<th>$w_d$ (mm)</th>
<th>$w_s$ (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>1.22</td>
<td>15.27</td>
<td>13.94</td>
</tr>
<tr>
<td>2</td>
<td>0.80</td>
<td>10.08</td>
<td>8.56</td>
</tr>
<tr>
<td>1.5</td>
<td>0.61</td>
<td>7.60</td>
<td>6.44</td>
</tr>
<tr>
<td>1</td>
<td>0.50</td>
<td>6.30</td>
<td>5.10</td>
</tr>
<tr>
<td>0.5</td>
<td>0.34</td>
<td>4.26</td>
<td>3.27</td>
</tr>
<tr>
<td>0.2</td>
<td>0.30</td>
<td>3.77</td>
<td>2.66</td>
</tr>
</tbody>
</table>

Molecular Beam Scattering

Molecular beam scattering (MBS) was tested during SAT using a He beam on a Cu(111)
single crystal. As this is a metallic crystal, only the specular reflection was expected to be
visible with no diffraction (Farias and Rieder, 1998). The largest collimator was used within
the beam generation chamber in order to maximise the size of the beam on the sample,
thereby improving the ability to align the sample with the beam. The largest aperture
available on the QMS was also used as this will maximise the signal at the detector. The
sample was placed within the beam path at an arbitrary angle of 59°, therefore a specular
reflection is expected at 118°. A 4.5 bar He beam was then impinged at a temperature of
298 K, this temperature equates to a beam energy of 64 meV. The sample temperature ($T_S$)
was at ambient temperature and $T_B$ was 6 K. The QMS was then set to record He while
moving from 0° to 180° using the software that will be described in § 4.3.4. This allowed the
intensity of the He signal to be automatically recorded against the angle of the QMS.

Figure 4.30 shows the data focussed around the specular reflection at 118°. A Lorentz curve
was fitted to the peak in order to determine the FWHM, and found to be 10° from this fit.
This can be reduced by using smaller apertures on the QMS or collimator. This was repeated
using a Ni(100) crystal with a 1 mm collimating aperture, this is shown in Figure 4.31 and
gives a FWHM of 1.7°. FWHM values of 0.65° and 0.44° have been given in previous studies
(de Miguel et al., 2002; Graham et al., 1992), however these are making use of cooled beams
and high pressure nozzles; both of these improve the resolution but are not possible with the
ISSC.
Figure 4.30: Specular reflection of a He beam on Cu(111) with an incident angle of 59°. The data is shown in black with a Lorentz fit in red.

Figure 4.31: Specular reflection of a He beam on Ni(100) with an incident angle of 47°. The data is shown in black with a Lorentz fit in red.
Sticking Probability

The ability to perform a SP experiment was tested using O\textsubscript{2} on Ni(100). This work has been documented in previous literature (Stuckless \textit{et al.}, 1997); this allows for the resulting test data to be compared to previous work for accuracy.

The experiment was carried out on a sputter-annealed Ni(100) single crystal, verified as clean and structurally ordered using XPS and LEED. The sample was placed in the beam path at an incidence angle of 47.5° with the QMS normal to the sample surface. The QMS was moved to a position as close as possible to the sample without interfering with the beam. This was achieved by watching the mass intensity whilst moving the QMS towards the sample until the intensity started to reduce; this was found to be 4.2 cm from the chamber centre.

The experiment was recorded in accordance with the modified King-Wells method (see § 3.9.2), with \( P_1(t) \) being recorded from a clean sample surface. This was followed by the use of a flag to occlude the MB from the surface of the sample, this provided a background level between the collection of \( P_1(t) \) and \( P_2(t) \). Finally the flag is removed and \( P_2(t) \) is recorded from the saturated surface to give an intensity for a sticking probability of 0. A background was taken before and after the experiment using the flag to ensure there was no change in beam characteristics or background pressure during the dosing.

The data from this test is shown in Figure 4.32 for the collection of \( P_1(t) \), showing both the He and O\textsubscript{2} mass traces against time for a beam consisting of 15\% O\textsubscript{2} in He. There is a clear increase in the amount of O\textsubscript{2} being detected over time, indicating that more is being scattered and therefore less is sticking. However the background after the experiment has changed significantly from before. This is indicating that the composition of the beam was not stable at 15\% O\textsubscript{2}, an investigation into this found that the beam was not mixing instantly due to a difference in the flow volume between the He and the O\textsubscript{2} supplies. This was confirmed by recording a direct beam of 15\% O\textsubscript{2} in He, and the same effect was shown as in Figure 4.32. Due to this all future SP experiments allowed 30 min for beam stabilisation before opening the valve to the scattering chamber.

A further attempt was made, using both a stabilisation time of 30 min and a reduced O\textsubscript{2} concentration of 2\% in He. The results of this test are shown in Figure 4.33, with the time scale trimmed so that \( t = 0 \) indicates the start of the experiment. Section 1 within this data is the acquisition of \( P_1(t) \), section 2 is when the flag was inserted and section 3 is the acquisition of \( P_2(t) \). Section 1 shows an increase in the O\textsubscript{2} signal, with section 3 showing that \( P_2(t) \) has no real dependence on time; this is as expected for a SP experiment using the modified King Wells method.

This data can then be converted into \( S(t) \) using equation (3.18) with \( P_2(t) \) as a constant. Figure 4.34 shows \( S(t) \) for 2\% O\textsubscript{2} in He on Ni(100), with \( S(t) = 70\% \) at \( t = 0 \) s and \( S(t) = 0\% \) at \( t \approx 400 \) s. This correlates well with the work carried out by Stuckless \textit{et al.} (1997), showing that SP experiments can be performed successfully on the ISSC.
Figure 4.32: Sticking probability experiment with 4.5 bar beam of 15\% O\textsubscript{2} in He. The He trace is in black and the O\textsubscript{2} trace is in red. The removal and insertion of the flag are visible within the He trace as an instantaneous change in intensity.

Figure 4.33: Sticking probability experiment with 4.5 bar beam of 2\% O\textsubscript{2} in He, with a 30 min stabilisation time. The He trace is in black and the O\textsubscript{2} trace is in red. Section 1 is the collection of \( P_1(t) \), section 2 is the time between the data collection when the flag was inserted and section 3 is the collection of \( P_2(t) \).
4.3 Software Modifications to the ISSC

4.3.1 Introduction

The ISSC is equipped with a variety of experimental modules, each with their own software. For many applications this is not a problem, however some techniques require using multiple pieces of equipment simultaneously and recording and correlating data from all of them. While this is possible by using timestamps and manually merging the data, it is more efficient to use custom software in order to collect all of the data within a single file. LabVIEW™ (2013) has been used in order to provide the software solutions to the above. Using LabVIEW™ (2013) it was also possible to create software in order to control the sample manipulators such that samples can be placed into repeatable analytical positions.

4.3.2 Stage Control

The sample manipulators on the scattering and analysis chambers and the movement of the internal QMS are all controlled by stepper motors. However the initial system could only be controlled by a manual axis stepper called a ‘jog box’ or through a text based command system. Both of these methods have problems, with the ‘jog box’ there is inherent user error as the axis must be lined up by eye, it is also only possible to move one axis at a time. Whereas the command based system requires knowledge of the commands in order to move the motors, as well as remembering the required position. While it is possible to move multiple axis at once with the command system, each axis command must be entered individually. In order to reduce the chance of damage from misaligned manipulators during transfers and to improve the speed with which commands can be entered, software has been developed based around the text based system, which can store the locations and enter multiple commands simultaneously.

Figure 4.34: Sticking Probability of $O_2$ on Ni(100).
The user interface (UI) of this software is displayed in Figure 4.35 and consists of two tabs. The first tab is the user side of the software; in this tab the manipulator is selected, followed by the required position. This allows for the sample or QMS to be moved to a repeatable position. This tab also contains a manual mode in which the relevant axis can be selected and moved in either steps or the relevant axis unit. The second tab is the administrator side of the software; from here it is possible to change each saved position. This is particularly important after a bake as the motors are likely to be reattached to the manipulator in a slightly different position. Along the right hand side of the UI is a readout of the current position of each motor in both steps and axis units. This also contains boxes that display if the limit switches have been tripped or if the motor is currently in motion.

![Figure 4.35: Image of the user interface for the stage control software. Some of the motors on the Analysis chamber were disconnected to show limit switch indicator.](image)

**4.3.3 Temperature Programmed Desorption**

TPD requires the recording of both temperature and mass spectrometry data. The ISSC does not contain any direct way to record the temperature, making it even more essential to develop software to integrate both sets of data. The software that was developed initially uploads the spectral peaks \((m/z)\) of interest to the QMS and the desired final temperature, ramp rate and PID control values for the sample to the PID hardware. During an experiment, the QMS reading for all of the masses will be taken, along with the current temperature, desired current temperature and the % of power being provided from the PID.

The UI of this software is shown in Figure 4.36. The majority of the screen is used to display the recorded data in real time. One graph displays the TPD plot of mass intensity against temperature, and another graph is used to monitor the PID by plotting the current temperature, desired current temperature and power against time. The top left of the UI is used for set-up and control, with inputs available for all the required values, and start and stop buttons for controlling the hardware. The final part of the UI is the lower left corner, in which the current values from the PID are displayed, along with outputs displaying the elapsed and remaining time.
4.3.4 Molecular Beam Scattering

A MBS experiment requires a QMS reading at multiple angles with small steps between each angle. This can be carried out manually by taking a mass intensity and then moving the QMS rotation by a small angle; however this is very slow and time consuming. An alternative is to use custom software in order to control both automatically. The software designed for this allows two options, one is to run the QMS rotation continuously and collect data as the rotation is carried out, which can be used to give a quick survey scan. The other option is to move the QMS by a set amount of degrees and then dwell for a set amount of time in order to collect higher resolution data.

The UI for the MBS software is shown in Figure 4.37. The right hand side is taken up by a plot of mass intensity against angle. Along the left hand side of the UI are the various required inputs. The first of these is the selection of gases to be recorded; this will always include He, however also allows for the detection of a seeded gas when required through a drop-down menu. The next box is an output of the current angle. Next are the step size in degrees and the dwell time in ms, which are only applicable when running in the stepping mode rather than survey. The final set of boxes are the start and end angles for running the experiment, along with a toggle to choose whether the QMS will return to the start angle at the end of the experiment.

4.3.5 Deposition

Metal depositions were initially defined by the electron beam power and the time for which the shutter is open. However this was found to give an inconsistent film thickness over time, as the temperature of the source (e.g. Li) is unmonitored. For this reason an alternative method was required using the detected drain current, by integrating with respect to time, a flux integral can be acquired in nA s; this should be proportional to the film thickness. A program was developed to record this and provide an integrated flux, representative of
the amount of material deposited, which can be calculated in real-time, during a deposition. This has the benefit of more control, as well as saving the acquired data in order to provide a record of each deposition.

The UI for this software is shown in Figure 4.38, where the majority of the screen space is used to plot the drain current against time. Along the right hand side of the interface are the controls to start and stop the software as well as to initiate the connection to the picoammeter used to detect the drain current. There are also inputs to set the background current before the deposition source flag is opened (this reduces the effect of electrical noise), as well as a button to reset the calculated flux to zero. The flux detected is displayed in A along with the calculated flux integral in nAs, which is also mirrored onto a separate magnified window to enable the value to be read by an operator working at the instrument.
Figure 4.38: Image of the user interface for the deposition monitoring software.
Chapter 5

Ageing of Bulk LiH

5.1 Introduction

This section will present the work carried out on the ageing of bulk LiH samples using TPD, isothermal desorption and SEM. This work was carried out in a separate instrument whilst awaiting delivery and commissioning of the ISSC. This instrument will first be described, followed by the sample preparation carried out and then the experimental results.

5.2 Dedicated TPD Apparatus

5.2.1 Introduction

Prior to delivery of the ISSC, a dedicated UHV system for TPD was constructed (henceforth called the dedicated TPD rig). This system was limited to bulk material rather than thin films synthesised in situ. It was also not possible to prevent atmospheric exposure during the loading process as the entire system had to be vented in order to place a sample into the holder. Therefore, exposure was not as controllable as it was in any experiment carried out using the ISSC. However, even with these drawbacks, the dedicated TPD rig allowed for TPD data to be acquired before the ISSC was delivered and commissioned. It was also more convenient for bulk samples as the speed at which samples could be tested and replaced was significantly faster than it would have been through the ISSC loading and transfer system.

5.2.2 Equipment

The dedicated TPD rig consists of a QMS (MKS Microvision Plus) with a mass range of 0 amu to 200 amu and a custom built sample holder within a small UHV chamber pumped by two turbomolecular pumps (Oerlikon Leybold TURBOVAC SL 80) with a pumping speed of 65 L s\(^{-1}\) and two scroll pumps (Oerlikon Leybold SCROLLVAC SC15 D) with a pumping speed of 3.6 L s\(^{-1}\), in order to achieve a base pressure in the region of 10\(^{-9}\) mbar. A photograph of the system can be seen in Figure 5.1 with the main components labelled, the
scroll pumps are outside of the shot. The space between the sample holder and the QMS is approximately 20 mm, ideally this working distance would be shorter, however this was not possible within the constraints of the hardware that was available.

The sample holder consisted of two pieces of Mo foil, mechanically fastened by folding the edges to create a pocket. This sample holder had Ta wires and a K-type thermocouple spot welded to the surface of the sample holder and attached to feedthroughs in order to provide thermal control. A photograph of the sample holder can be seen attached to a feed-through flange (used to mount the sample holder inside of the UHV system) in Figure 5.2. The thermocouple was connected to a PC to provide the capability to record the temperature against time for cross reference with the mass spectrometry data, and the Ta heating wires were connected to a power supply unit (PSU) manually controlled to provide a linear temperature ramp. This design provides advantages and disadvantages in relation to that used with the ISSC. A key disadvantage is that as the sample holder must be vented to load a sample, it is not possible to remove atmospheric contamination. However, as the design used here has less connections between the thermocouple and the point at which it is measured, the temperature is likely to be more accurate. There is also less chance of thermal gradients across the sample as the heating surface is in contact with both sides of the sample, whereas on the ISSC it is only in contact with one edge.

![Turbopump Mass spectrometer Sample holder Pressure gauge](image)

Figure 5.1: Photograph of the dedicated TPD rig with the main components labelled.
5.3 Sample Preparation

All sample preparation steps were carried out under Ar in a positive pressure Ar glovebox (Saffron Alpha) with a maximum concentration of both O$_2$ and H$_2$O of 2 ppm monitored by built in analysers. LiH samples were received as a powder which had been compressed into cylinders of diameter 20 mm. These cylinders were then cut using a low speed diamond saw to disks of \(\sim2\) mm thickness and were then broken up into irregular shapes of approximately 5 mm \(\times\) 5 mm \(\times\) 2 mm. These shapes were polished using 1200 grit SiC paper to remove any corrosion layers formed from previous air exposures. They were then loaded into a vial filled with Ar to allow for transfer to instrumentation with minimal air exposure. The process of loading the samples onto a sample holder and pumping down to vacuum conditions gave an air exposure of approximately 5 min.

5.4 Temperature Programmed Desorption

5.4.1 Overview

TPD was carried out on LiH samples as described in § 5.3 at ramp rates of 0.25 K s\(^{-1}\), 0.5 K s\(^{-1}\), 1 K s\(^{-1}\), 2 K s\(^{-1}\) and 3 K s\(^{-1}\) from 300 K to 825 K. The ongoing reactions are monitored through measurement of the species outgassed during the heating. The species monitored here were \(m/z\) of 2 (H$_2$), 7 (Li) and 18 (H$_2$O). A typical mass spectrometer output
is shown in Figure 5.3 for H₂, Li and H₂O. The H₂O trace shows only one main feature; a peak at ~600 K which can be attributed to the decomposition of LiOH (equation (5.1)).

The H₂ trace shows three main features, the first is the solid state reaction between LiH and LiOH (equation (5.2)) at ~550 K, labelled as (2) on Figure 5.3. The second feature in the H₂ trace is a clear peak at ~600 K (3), this has been attributed to the hydrolysis reaction of LiH (equation (5.3)) due to its concurrent appearance with the outgassing of H₂O from equation (5.1) (1). Some of this H₂O is believed to react with the LiH rather than escaping into the vacuum to be detected by the QMS. The final feature is that of the sublimation of LiH (equation (5.4)) which commences at ~600 K (4); this is also visible as the only feature within the Li trace from ~750 K. It is not surprising that H₂ is evolved before Li as it has a lower boiling point than Li and therefore is likely to desorb earlier.

\[
2 \text{LiOH} \rightarrow \text{Li}_2\text{O} + \text{H}_2 \quad (5.1)
\]

\[
\text{LiH} + \text{LiOH} \rightarrow \text{Li}_2\text{O} + \text{H}_2 \quad (5.2)
\]

\[
\text{LiH} + \text{H}_2\text{O} \rightarrow \text{LiOH} + \text{H}_2 \quad (5.3)
\]

\[
2 \text{LiH} \rightarrow 2 \text{Li} + \text{H}_2 \quad (5.4)
\]

### 5.4.2 Determination of Activation Energy

The \( E_a \) of each of the reactions has been initially determined using Kissinger analysis (see § 3.8.2) in order to provide a starting point for explicit modelling of the peak structure. This
is however only possible for the reactions described in equations (5.1) and (5.3) as it is not possible to determine a specific peak temperature for the other reactions (equations (5.2) and (5.4)).

The $\text{H}_2\text{O}$ mass spectrometer output ($m/z = 18$) is shown in Figure 5.4 at ramp rates of $0.25 \text{K s}^{-1}$, $0.5 \text{K s}^{-1}$, $1 \text{K s}^{-1}$, $2 \text{K s}^{-1}$ and $3 \text{K s}^{-1}$. These all show a clear peak relating to the LiOH decomposition reaction (equation (5.1)), this peak has been normalised such that the intensity of the peak is 1 at all ramp rates to ease comparison. These peak positions can be used with the relevant ramp rates to create a Kissinger plot for the decomposition of LiOH as shown in Figure 5.5. The gradient of this plot is $11200 \pm 800$, giving an $E_a$ of $93 \pm 7 \text{kJ mol}^{-1}$.

![Figure 5.4: Trace of $\text{H}_2\text{O}$ for the TPD of LiH at a variety of ramp rates. The intensity is normalised to 1 for each peak.](image)

The same process can be applied to the hydrolysis reaction of LiH within the $\text{H}_2$ mass spectrometer trace ($m/z = 2$), shown in Figure 5.6 for heating rates of $0.25 \text{K s}^{-1}$, $0.5 \text{K s}^{-1}$, $1 \text{K s}^{-1}$, $2 \text{K s}^{-1}$ and $3 \text{K s}^{-1}$. The gradient of the Kissinger plot (Figure 5.7 plot is $10600 \pm 1200$, giving an $E_a$ of $88 \pm 10 \text{kJ mol}^{-1}$ for the hydrolysis of LiH.

![Figure 5.4: Trace of $\text{H}_2\text{O}$ for the TPD of LiH at a variety of ramp rates. The intensity is normalised to 1 for each peak.](image)
CHAPTER 5. AGEING OF BULK LIH

Figure 5.5: Plot of $\ln\left(\frac{T_{\text{max}}^2}{\beta}\right)$ against $T_{\text{max}}^{-1}$ from TPD peaks of the decomposition of LiOH.

Figure 5.6: Trace of $H_2$ for the TPD of LiH at a variety of ramp rates. The intensity is normalised to 1 for each peak.
5.4.3 Modelling

It is also possible to carry out explicit modelling to determine the rate limiting mechanisms within these reactions, using the mechanistic equations presented in Appendix A. The H$_2$O trace is shown in Figure 5.8 with a variety of mechanisms fitted to the peak for the decomposition of LiOH at a ramp rate of 0.25 K s$^{-1}$, the best fit is provided by the $F1$ mechanism (shown in red) which is where the rate of nucleation is the rate-limiting mechanism of the reaction. The parameters of this fit are an $E_a$ of 96 ± 4 kJ mol$^{-1}$ and a $\nu$ of $2.3 \pm 0.2 \times 10^7$ s$^{-1}$. The $D3$ (3D diffusion limited) (shown in dark blue) mechanism also fits reasonably well, however, this is unlikely to be the limiting mechanism as the LiOH is the outermost layer of the tri-layer structure of LiH and therefore there is limited potential for diffusion to be rate-limiting. The $E_a$ obtained from the $D3$ fit is 194.0 ± 0.2 kJ mol$^{-1}$ which is very high and unlikely to be proceeding at these temperatures. The high $E_a$ for $D3$ and the value of $\sim$93 kJ mol$^{-1}$ from both literature and the previous Kissinger analysis suggest that $F1$ is likely to be the correct choice here.

The H$_2$ trace is shown in Figure 5.9 with the best fits for each peak shown; these are a $D3$ for the solid state reaction of LiH with LiOH, $F1$ for the hydrolysis of LiH and a non mechanistic exponential curve for the sublimation of LiH. The fitting parameters for the solid state reaction are an $E_a$ of 63.9 ± 0.2 kJ mol$^{-1}$ and $\nu$ of 2000 ± 100 s$^{-1}$. The parameters for the hydrolysis reaction are an $E_a$ of 90.5 ± 0.3 kJ mol$^{-1}$ and $\nu$ of $4.6 \pm 0.3 \times 10^5$ s$^{-1}$; this $E_a$ for the LiH hydrolysis is not a true value as the limiting mechanism is the supply of H$_2$O from decomposition of LiOH rather than a reaction mechanism.

The fits for all of the reactions can be integrated such that the start of the peak indicates $\alpha = 0$ and the end is $\alpha = 1$. This provides a plot which shows the reacted fraction for each reaction with temperature for a given $\beta$. This plot is shown in Figure 5.10 for $\beta$ of 0.25 K s$^{-1}$. 

![Figure 5.7: Plot of ln($T_{max}^2/\beta$) against $T_{max}^{-1}$ from TPD peaks of the hydrolysis of LiH.](image-url)
Figure 5.8: Trace of $\text{H}_2\text{O}$ for the TPD of LiH at 0.25 K s$^{-1}$. Data is shown by the dashed line and mechanistic fits are shown by solid lines.

Figure 5.9: Trace of $\text{H}_2$ for the TPD of LiH at 0.25 K s$^{-1}$. Data is shown by the dashed line and mechanistic fits are shown by solid lines.
Figure 5.10: Reacted fractions of the reactions occurring during the TPD of LiH for a ramp rate of 0.25 K s\(^{-1}\). (1) is the decomposition of LiOH (equation (5.1)), (2) is the hydrolysis of LiH (equation (5.3)) and (3) is the solid state reaction between LiOH and LiH (equation (5.2)).

### 5.4.4 TPD of Thermally Treated Sample

To ascertain the surface composition of the samples following heating to 830 K, a second TPD was performed without any further exposure to air. The mass spectrometer traces for both H\(_2\)O and H\(_2\) are shown in Figure 5.11 with the original TPD for this sample shown for comparison. The H\(_2\)O trace shows no signal other than background, indicating that LiOH is not present within the sample as there is no evidence of its decomposition. This is further confirmed with the H\(_2\) trace where only the LiH decomposition is present; the hydrolysis of LiH does not occur without H\(_2\)O generated through decomposition of LiOH and the solid state reaction requires LiOH.

### 5.4.5 Re-exposed Sample

It would be expected that a LiH sample which has been heated to 825 K and then re-exposed to air would regenerate the LiOH layer through equation (5.5). Figure 5.12 shows the TPD trace from a sample re-exposed to air after heating along with that of a standard sample. The H\(_2\)O trace shows that the general shape of the LiOH decomposition has returned albeit in a slightly different position and with increased broadness. This change is likely to be the result of an increase in the disorder of the LiOH layer. The increase in the disorder may be a result of the change in surface morphology shown by SEM (presented in § 5.7), where the surface after heating is blistered and cracked. Another possibility would be chemical differences between the initial LiOH and the LiOH generated after baking. It has been shown by Sifuentes et al. (2013) that there is a decrease in crystallinity (and therefore an increased width of the TPD peak) for a LiOH layer generated from Li\(_2\)O following heating in comparison to a reference LiOH sample.
\[
\text{Li}_2\text{O} + \text{H}_2\text{O} \rightarrow 2\text{LiOH}
\] (5.5)

The H\textsubscript{2} trace shows a similar change to the hydrolysis of LiH peak as to that of the decomposition of LiOH. This is to be expected due to the link between these two reactions whereby the hydrolysis requires the H\textsubscript{2}O outgassed from the decomposition. The H\textsubscript{2} trace also shows a large reduction in the solid state reaction, again a reduction in LiOH could explain some of this; however such a large reduction is more likely to be explained by a thicker Li\textsubscript{2}O layer at the start, resulting in less diffusion across this layer. Another potential explanation for the reduced \textit{D3} structure is that there is H\textsubscript{2} trapped within the pores of the sample, and this represents the majority of this peak (Banger \textit{et al.}, 2014). This inventory would not re-generate during the re-exposure to air and therefore the peak would not reappear.
5.5 Isothermal Desorption

5.5.1 Water Outgassing

Isothermal desorption was also carried out to provide verification and refinement of the $E_a$ values determined through TPD. The isotherms were carried out at temperatures of 378 K, 450 K, 463 K, 488 K and 500 K.

The $\text{H}_2\text{O}$ TPD peak structure showed only a single rate limiting mechanism, this was the $F1$ mechanism associated with the decomposition of LiOH. Figure 5.13 shows the mass spectrometer trace for $\text{H}_2\text{O}$ at an isothermal temperature of 378 K. This figure shows a rapid decrease in outgassing rate within the first 2000 s followed by a slight plateau before steadily decreasing until the end of the reaction. The mass spectrometer trace has been converted to $\alpha$ as shown in Figure 5.14 and fitted to the equation for a $F1$ mechanism. This fit gives a $k(T)$ of $6.66 \pm 0.01 \times 10^{-5}$ s$^{-1}$.

Also presented are the mass spectrometer trace (Figure 5.15) and the kinetics plot (Figure 5.16) for the 488 K isotherm. The mass spectrometer trace shows a few unexpected features at around 50 s and 200 s where the intensity peaks. This is likely to be caused by small fluctuations in the power required to hold the sample at 488 K due to changes in the thermal properties of the sample and holder. However other than these unexpected peaks, the trace is behaving as would be expected, with the reaction completing significantly faster than that of the 378 K (1200 s in comparison to 55 000 s). The $F1$ fit shown in Figure 5.16 has a $k(T)$ of $4.86 \pm 0.03 \times 10^{-3}$ s$^{-1}$. 

Figure 5.12: Mass spectrometer trace of $\text{H}_2\text{O}$ (red) and $\text{H}_2$ (black) of a LiH sample, at a rate of 0.25 K s$^{-1}$. The solid line indicates a standard sample and the dashed line is a sample which has been previously heated to 825 K and then exposed to a further 5 min of air.
Figure 5.13: Isothermal trace of $\text{H}_2\text{O}$ from a LiH sample at 378 K.

Figure 5.14: Plot of $\alpha$ against time and the mechanistic $F1$ fit for $\text{H}_2\text{O}$ outgassing from a LiH sample at 378 K.
This fitting has been carried out on all of the isotherms and the $k(T)$ values for these are presented in Table 5.1. These values for $k(T)$ can be used to determine the $E_a$ through the use of an Arrhenius plot of ln($k(T)$) against $T^{-1}$. This is shown in Figure 5.17; the gradient of $-8100 \pm 1000$ equates to an $E_a$ of $68 \pm 8 \text{kJ mol}^{-1}$ and an intercept of $11.8 \pm 2.2$ equating to a $\nu$ of $1.35 \times 10^5 \text{s}^{-1}$ with the standard error giving a maximum value of $1.2 \times 10^6 \text{s}^{-1}$ and a minimum of $1.5 \times 10^4 \text{s}^{-1}$ to a 68% confidence.
Table 5.1: Table showing $k(T)$ values for the isothermal outgassing of H$_2$O from LiH.

<table>
<thead>
<tr>
<th>Temperature K</th>
<th>$k(T)$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>378</td>
<td>$(6.66 \pm 0.01) \times 10^{-5}$</td>
</tr>
<tr>
<td>450</td>
<td>$(2.07 \pm 0.02) \times 10^{-3}$</td>
</tr>
<tr>
<td>463</td>
<td>$(2.25 \pm 0.02) \times 10^{-3}$</td>
</tr>
<tr>
<td>488</td>
<td>$(4.86 \pm 0.03) \times 10^{-3}$</td>
</tr>
<tr>
<td>500</td>
<td>$(2.19 \pm 0.05) \times 10^{-2}$</td>
</tr>
</tbody>
</table>

Figure 5.17: Arrhenius plot of $\ln(k(T))$ against $T^{-1}$ for the H$_2$O isothermal outgassing of LiH. The gradient of the fit is $-8135 \pm 1000$ and the intercept is $12 \pm 2$.

In comparison with the values obtained from TPD for $E_a$ and $\nu$ of $96 \pm 4$ kJ mol$^{-1}$ and $2.3 \pm 0.2 \times 10^7$ s$^{-1}$ respectively, there is clearly a large difference between TPD and isothermal results, with both values being outside of standard error. This error is large enough to be unlikely to be caused by the error induced by the choice of location for the points at which $\alpha = 0$ and $\alpha = 1$, though this could contribute some of the error. There could also be adsorbed H$_2$O within the corrosion layers which constantly diffuse towards the surface with either a low or no $E_a$, with a varying thickness of the corrosion layer across the surface this could have a varying apparent $E_a$ as the H$_2$O would take longer to diffuse with a thicker layer. A variation in Li$_2$O layer thickness has been observed by Haertling and Hanrahan Jr (2007) using Rutherford backscattering.

5.5.2 Hydrogen Outgassing

Isothermal analysis of the H$_2$ outgassing is more complex that that of the H$_2$O. The primary reason for this is that there are multiple reactions causing the H$_2$ to be outgassed, and with isothermal analysis it is not possible to differentiate between multiple reactions occurring simultaneously. However at the temperatures used, the TPD shows that the $D3$ mechanism related to the solid state reaction is the majority source of H$_2$ by a considerable margin. Therefore fitting a $D3$ mechanism to the isothermal curves should give a reasonable approximation of the true fit.
The mass spectrometer trace for $\text{H}_2$ at an isothermal temperature of 378 K is shown in Figure 5.18. The $\alpha$ plot is shown in Figure 5.19 and has been fitted to the equation for a $D3$ mechanism. This fit gives a $k(T)$ of $1.07 \pm 0.01 \times 10^{-5} \text{s}^{-1}$.

![Figure 5.18: Isothermal trace of $\text{H}_2$ from a LiH sample at 378 K.](image)

![Figure 5.19: Plot of $\alpha$ against time and the mechanistic $D3$ fit for $\text{H}_2$ outgassing from a LiH sample at 378 K.](image)

Also presented are the mass spectrometer trace (Figure 5.20) and the $\alpha$ plot (Figure 5.21) for the 488 K isotherm. The $D3$ fit shown in Figure 5.21 has a $k(T)$ of $1.30 \pm 0.01 \times 10^{-4} \text{s}^{-1}$.
As with the H$_2$O, this fitting has been carried out on all of the isotherms and the $k(T)$ values for these are presented in Table 5.2. The Arrhenius plot for H$_2$ is shown in Figure 5.22. It has a gradient of $-4480 \pm 1000$ which equates to an $E_a$ of $37 \pm 8$ kJ mol$^{-1}$ and the intercept of $0.33 \pm 2.00$ equates to a $\nu$ of $1.39$ s$^{-1}$ with the standard error giving a maximum value of $10.28$ s$^{-1}$ and a minimum of $0.19$ s$^{-1}$ to a 68% confidence. The values found from the TPD for the $D3$ reaction were and $E_a$ of $63.9 \pm 0.2$ kJ mol$^{-1}$ and a $\nu$ of $2000 \pm 100$ s$^{-1}$.

Similarly to the H$_2$O, the isothermal values are outside the errors of those found through TPD; however while the same sources of potential errors exist (adsorbed H$_2$ or H$^+$ rather than H$_2$O), there are other possible sources of error with the H$_2$ data. The first of these is that there is multiple simultaneous reactions underway, with $D3$ and $F1$ mechanisms having rate-limiting effects. While it is not possible to distinguish between these two mechanisms
with isothermal analysis, it may not have been an appropriate assumption that it could be accurately fitted with just one. A further source of error could be from changes in the morphology of the surface with temperature, the formation of cracks and blisters as LiOH and LiH are converted to Li$_2$O for example (as seen in § 5.7). While it would be expected that changes in morphology would also affect TPD experiments, this affect may not be visible due to the relatively high rate at which the TPD is carried out.

Table 5.2: Table showing $k(T)$ values for the isothermal outgassing of H$_2$ from LiH.

<table>
<thead>
<tr>
<th>Temperature K</th>
<th>$k(T)$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>378</td>
<td>(1.07 ± 0.01) × 10$^{-9}$</td>
</tr>
<tr>
<td>450</td>
<td>(6.12 ± 0.01) × 10$^{-5}$</td>
</tr>
<tr>
<td>463</td>
<td>(5.62 ± 0.01) × 10$^{-5}$</td>
</tr>
<tr>
<td>488</td>
<td>(1.30 ± 0.01) × 10$^{-4}$</td>
</tr>
<tr>
<td>500</td>
<td>(8.8 ± 0.2) × 10$^{-4}$</td>
</tr>
</tbody>
</table>

Figure 5.22: Arrhenius plot of ln($k(T)$) against $T^{-1}$ for the isothermal outgassing of H$_2$ from LiH. The gradient of the fit is $-4480 \pm 1000$ and the intercept is $0.33 \pm 2.00$.

### 5.6 Summary of Thermal Desorption

A summary of the $E_a$ found for the reactions are given in Table 5.3. This table shows a comparison between the $E_a$ results found through Kissinger analysis and modelling of the TPD peak, modelling of the isothermal desorption and results from Dinh et al. (2005) in kJ mol$^{-1}$. 
Table 5.3: Table showing $E_a$ in kJ mol$^{-1}$ for reactions present within the thermal desorption of LiH using different methods of analysis, with a comparison to results from Dinh et al. (2005).

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Kissinger</th>
<th>Modelling</th>
<th>Isothermal</th>
<th>Literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Decomposition of LiOH</td>
<td>93 ± 7</td>
<td>96 ± 4</td>
<td>68 ± 8</td>
<td>93.3</td>
</tr>
<tr>
<td>Solid state reaction</td>
<td>N/A</td>
<td>63.9 ± 0.2</td>
<td>37 ± 8</td>
<td>69.9</td>
</tr>
<tr>
<td>Hydrolysis of LiH</td>
<td>88 ± 10</td>
<td>90.5 ± 0.3</td>
<td>N/A</td>
<td>93.3</td>
</tr>
</tbody>
</table>

## 5.7 Scanning Electron Microscopy

To visualise the effect of heating upon the surface morphology of LiH samples, SEM was used to image the surface using a Hitachi TM-3000 with an accelerating voltage ($V_a$) of 15 kV. This was used over the SEM fitted to the ISSC for a variety of reasons. The main reason was that LiH is an insulator and therefore charges under an electron beam, the TM-3000 was able to compensate for this more effectively through the use of lower current imaging, whereas the ISSC required a charge neutraliser to offset charging – low current imaging was not achieved using the ISSC SEM. Another advantage of the TM-3000 was that as it is a dedicated tabletop SEM, the internal geometry has been optimised for SEM and is more user friendly than the ISSC. There are also disadvantages to the TM-3000, primarily that the instrument runs at high vacuum rather than UHV and requires the sample to be transferred ex-situ, providing an increased level of contamination.

Figure 5.23 shows low magnification micrographs of a LiH sample before (Figure 5.23a) and after (Figure 5.23b) heating to 830 K. Prior to heating, the samples show a rough surface consistent with the mechanical polishing process and no evidence of any other forms of surface damage. Following heating to 830 K, the micrograph shows blisters occurring on the surface (indicated by white circles in Figure 5.23b). These blisters are thought to occur due to the release of H$_2$O and H$_2$ from the corrosion layers generating a pressure build up that causes blisters as pressure relief mechanism. Another option is that the blisters are caused by spallation of LiOH due to the significant difference in density and lattice parameter between LiOH and Li$_2$O; spallation is also commonly observed in LiH hydrolysis (Phillips and Tanski, 2005). These blisters provide a potential route for further corrosion to occur due to an increase in the surface area available for reaction.
Figure 5.23: SEM micrographs of a LiH sample before (a) and after (b) heating to 830 K. The white circles indicate blisters which have spalled from the surface.
5.8 Conclusions

Four main reactions have been identified concerning the ageing of LiH using TPD; the decomposition of LiOH, a solid state reaction between LiOH and LiH, the hydrolysis of LiH and the sublimation and decomposition of LiH. Initial estimates of the activation energies have been determined using Kissinger analysis and then further refined by modelling reaction mechanisms to the TPD traces for $H_2$ and $H_2O$. The most likely reaction mechanisms have also been identified as $F1$ for the decomposition of LiOH and $D3$ for the solid state reaction. The activation energies which have been determined are consistent with those which have been previously published by Dinh et al. (2005).

Isothermal desorption of LiH samples was also attempted to verify and refine the energies determined from TPD, however large inconsistencies were found between the values. These are likely to be caused from a variety of causes; human error in selection of start and end points, layer thickness effects, multiple mechanisms competing and changes in surface morphology. The layer thickness has been shown to vary by Haertling and Hanrahan Jr (2007) and SEM was used to investigate any changes in the morphology; this found that after baking blisters appeared in the surface of the LiH.
Chapter 6

Formation of Lithium Based Thin Films

6.1 Introduction

This chapter will investigate the methods by which atomically clean films of Li and its compounds can be grown. These films provide a variety of advantages over bulk samples such as the elimination of charging effects, improved control over corrosion layer growth as the films are grown in-situ, a reduction in thermal gradients across the sample and a decreased risk of damage to the QMS through signal saturation.

The first part of this is to deposit a clean Li film which can then form the other compounds through controlled reaction with gaseous species. This film was calibrated for both thickness and cleanliness, using LEED, TPD, XPS and AES. The next step is to form films of LiH, Li₂O and LiOH. This has been attempted using H₂, H₂O and O₂ and the resulting film compositions determined using XPS and AES.

6.2 Lithium

6.2.1 Thickness Calibration by LEED

In order to create films of LiH, Li₂O and LiOH, a Li film of controlled thickness must first be deposited. The first step in providing a Li film is to deposit a known flux of Li atoms using an e⁻ beam deposition source onto the surface, this can then be calibrated to an apparent coverage on the Ni(100) crystal. The Li was deposited from a Mo crucible within a pyrolytic boron nitride (PBN) liner. The thickness of a Li film on Ni(100), can be determined from the overlayer structure observable by LEED. This structure can be used to give the coverage of the Li film by comparing observed patterns with apparent monolayer (ML) coverages from previous work (Jiang et al., 1997a,b). The pattern for a clean Ni(100) crystal is shown in Figure 6.1 for a beam energy of 74 eV; the red square shown in this figure indicates the unit cell of the Ni(100) crystal.
CHAPTER 6. FORMATION OF LITHIUM BASED THIN FILMS

Figure 6.1: LEED pattern of a clean Ni(100) single crystal, with a beam energy of 74 eV. The red square indicates the unit cell of the crystal.

Figure 6.2: (a) LEED pattern of a 9.8 nA s flux of Li on Ni(100), showing a $(2 \times 2)$ overlayer. The red square shows the Ni unit cell and the green square shows the Li unit cell. (b) shows the $(2 \times 2)$ structure as a schematic of the surface with the white circles as the Ni and the green circles as the Li overlayer lattice points.

Once this pattern had been obtained, depositions of Li can be carried out, using the deposition software described in § 4.3.5 to calculate a flux in units of nA s. This flux can then be calibrated to a coverage using the overlayer structure determined by LEED and known coverages from Jiang et al. (1997a). The lowest coverage is for a deposition flux of 9.8 nA s, for which the LEED pattern is shown in Figure 6.2a. This pattern shows an overlayer structure of $(2 \times 2)$ ([6 $\sqrt{2}$ 2]), shown schematically in Figure 6.2b, which equates to a coverage of $\sim0.25$ ML; this makes the assumption that the basis of the structure is a single atom per lattice point at low coverages. This would imply that 39.2 nA s would equate to a single ML of Li, assuming linear growth.

Within the range of 20 nA s to 25 nA s the LEED shows a number of complex patterns with small changes in the flux. For a flux of 22.1 nA s (Figure 6.3a), the overlayer structure is shown to have a lattice of $c(6\sqrt{2} \times 2\sqrt{2})R45^\circ$ ([14 $\sqrt{8}$ 6 $\sqrt{8}$]); this lattice structure is shown in Figure 6.3b. This must have a complex basis, as a single atom per lattice point would result in a lower coverage than that of the 9.8 nA s film. The basis cannot be determined through standard LEED. This requires analysis of the I-V profiles of each diffraction spot, known as LEED-IV, which is not currently possible with the ISSC. However work by Jiang et al. (1997a) on a series of similar lattices ($c(n\sqrt{2} \times 2\sqrt{2})R45^\circ$ with $n = 2, 3, 5$) using LEEDIV gave a coverage of 0.6 ML. The calibration from the 9.8 nA s film would give a coverage of 0.56 ML, which would appear to be a reasonable value. Jiang et al. (1997a) also suggests
that the LEED pattern is only visible at elevated temperature; the pattern in Figure 6.3a
was only visible at temperatures higher than \( \sim 400 \text{K} \); below this temperature the pattern
was that of a diffuse \((1 \times 1)\) overlayer.

Figure 6.3: (a) LEED pattern of a 22.1 nA s flux of Li on Ni(100), showing a \(c(6\sqrt{2} \times 2\sqrt{2})R45^\circ\) overlayer. The red square shows the Ni unit cell and the green square shows the
Li unit cell. (b) shows the \(c(6\sqrt{2} \times 2\sqrt{2})R45^\circ\) structure as a schematic of the surface with
the white circles as the Ni and the green circles as the Li overlayer lattice points.

A flux of 25 nA s generates the LEED pattern shown in Figure 6.4a, with a \((5 \times 5)\) \([5 \times 5]\) overlayer structure as shown in Figure 6.4b. The coverage for this should be 0.64 ML using
the earlier calibration. Jiang et al. (1997b) showed a \((5 \times 5)\) coverage of Li on Ni(100) with
a complex multilayer system, with an effective coverage of 0.68 ML. Given the accuracy of
LEED for determining the thickness of a film (where a pattern does not correspond with
a single coverage, but a range of coverages where that structure is most common) this
calibration appears to be consistent with previous work.

The final deposition used as part of the calibration is for a deposition flux of 47.1 nA s,
a coverage of 1.2 ML using the calibration. Ideally this would be exactly 1 ML, however
this was not possible within experimental constraints. The LEED pattern for this 47.1 nA s
deposition is shown in Figure 6.5a, and shows a \((1 \times 1)\) overlayer (Figure 6.5b). The pattern
is diffuse, indicating that there is a degree of disorder within the film; this is potentially a result of the way in which films grow, anything greater than a ML may create islands or other three dimensional structures on the surface rather than growing in the same manner as the initial layer. It could also be diffuse as the pattern may be from, or have a contribution from, the underlying Ni(100) rather than from the Li, the Li is then causing an attenuation and broadening of the signal.

Figure 6.5: (a) LEED pattern of a 47.1 nA s flux of Li on Ni(100), showing a (1 × 1) overlayer. The red square shows the Ni unit cell and the green square shows the Li unit cell. (b) shows the (1 × 1) structure as a schematic of the surface with the white circles as the Ni and the green circles as the Li overlayer lattice points.

Figure 6.6: He reflectance at specular angle from clean Ni(100). The angle of incidence was 97.5°.

The disorder within this structure was investigated with HAS as this technique is sensitive to surface order, such that slight variations in height within the top surface layer will cause large amounts of attenuation within the scattered beam. The most intensely scattered beam, particularly with metals, is the specular reflection. A comparison between the specular reflection of 0.25 ML and 1.2 ML and the clean Ni(100) crystal is shown in Figure 6.6. This figure shows that the Li film is either highly disordered or three dimensional as the intensity
CHAPTER 6. FORMATION OF LITHIUM BASED THIN FILMS

of the specular reflection has halved with a 0.25 ML film and completely attenuated by the 1.2 ML film. The lack of any specular reflection is indicative of the (1 × 1) pattern of Figure 6.5 originating from the Ni(100), with Li forming a disordered overlayer.

6.2.2 Thickness Calibration by TPD

There are two desorption peaks within TPD associated with Li metal in a film on Ni (Engbæk et al., 2006). The first of these is the multilayer structure (Li on Li) at ∼550 K, and the other is a monolayer structure (Li on Ni) at ∼850 K. This can also be used to obtain a thickness using the ratio between the areas of these two peaks.

A TPD spectra of a deposition of 100 nA s (2.55 ML using the LEED calibration) is shown in Figure 6.7. This shows two peaks which can be attributed to the multilayer and monolayer structures at 640 K and 850 K respectively. 640 K is higher than the 550 K reported by Engbæk et al. (2006) for multilayer desorption. However, that work was carried out using Ni(111) as the substrate, whereas this work uses Ni(100). The Ni(111) surface is close packed which is known to be less reactive than the slightly more open Ni(100) surface. It is therefore plausible that the interaction with Li follows this trend, which would imply that the $E_a$ for desorption would be lower from the Ni(111) surface.

Fitting a Gaussian curve to the two peaks in Figure 6.7 provides the area of each peak, and therefore the ratio of multilayers to monolayers. The numbers provided by these fits are an area of 27 676 K c s$^{-1}$ for the multilayer desorption and 9293 K c s$^{-1}$ for the monolayer desorption. This gives a ratio of 2.98 multilayers per monolayer, therefore a total of 3.98 layers of Li on the surface of the Ni(100) using a TPD thickness calibration. The flux per monolayer from this thickness is 25.1 nA s ML$^{-1}$. This calibration is significantly lower than that found using LEED (39.2 nA s ML$^{-1}$); however when using TPD, Li which is on the sample holder will also be detected which could cause an increase in the apparent multilayer desorption and therefore make it appear as if there are more layers of Li on the Ni surface than are actually present. The sample holder does not cause issues with the LEED calibration as the area of analysis is significantly smaller, of the order of 1 mm$^2$. Thus the calibration using LEED has been used for the future determination of thickness.
6.2.3 Characterisation

XPS and AES have been used to confirm film composition. The low cross-section of Li meant that this required a film with a high thickness in order to maximise the ability of XPS to detect the Li 1s peak. Even with a high thickness, the Li 1s peak was not visible within the XPS spectrum presented in Figure 6.8, with only Ni, Mo, oxygen and carbon present. If the Mo is ignored as the sample holder and not part of the sample, then quantification yields a sample surface composition of 97 at% Ni, 2 at% oxygen and 1 at% carbon. As TPD has shown that Li is present, the XPS can be used to indicate a clean film with minimal oxygen and carbon contamination.

Figure 6.8: XPS survey spectrum of a Li film on Ni(100). Li is not visible due to the low cross-section and close proximity of Ni 3p.
The kinetic energy (KE) of Li \( KLL \) is 50 eV, whereas it is 1434 eV for Li 1s. This difference in KE gives a reduced analysis depth when using AES in comparison to XPS. The smaller depth of analysis means that AES is more likely to detect the Li film, as it will consist of a larger proportion of the depth of analysis in comparison to XPS. A survey spectrum is shown in Figure 6.9, and Figure 6.10 shows the same survey focused on the low KE region, from 30 eV to 80 eV. The survey spectrum shows the expected Ni peaks at 60 eV, 710 eV, 776 eV and 848 eV, a small amount of carbon at 267 eV and some Mo contamination at around 170 eV. The final peak present within the AES survey spectrum presented in Figures 6.9 and 6.10 is the Li \( KLL \) peak, showing that Li is present on the surface, and as the energy of the peak is at 52 eV; this is consistent with the \( E_K \) of metallic Li, as oxides have been shown to exhibit peaks at 33 eV and 42 eV (Clausing \textit{et al.}, 1973; Madden and Houston, 1977; Mallinson \textit{et al.}, 2013).

![Figure 6.9: AES survey spectrum of a Li film on Ni(100).](Figure 6.9)

![Figure 6.10: AES spectrum of a Li film on Ni(100) in the range of 30 eV to 80 eV.](Figure 6.10)
6.2.4 Growth Mode

There are four common routes through which thin films can grow; these are Volmer-Weber (VW), Stranski-Krastanov (SK), Frank-Van der Merwe (FM) and simultaneous multilayer (SM), all of which assume that the film material has sufficient mobility at the deposition temperature so that the growth is not kinetically limited. VW growth consists of the formation of islands of material, without a full film being formed; SK growth is similar to VW, however an atomically smooth and uniform monolayer forms prior to the growth of islands. In FM growth, the deposited atoms grow layer-by-layer, forming complete a monolayer before the next layer starts to form. SM growth forms stacks of atoms, where the deposited material sticks where it lands. These growth modes are shown schematically in Figure 6.11 (Wulfsberg et al., 2016).

Figure 6.11: Schematics of the four common thermodynamic growth routes for thin films. Grey is substrate material and green is film. (a) is Volmer-Weber growth, (b) is Stranski-Krastanov growth, (c) is Frank-Van der Merwe growth and (d) is simultaneous multilayer growth.

To investigate which growth mechanism is controlling the deposition of Li on Ni(100), SEM images of the surface were obtained immediately following the deposition. Figure 6.12 shows a micrograph of a relatively thick film of ~15 ML, this clearly shows that the film growth

Figure 6.12: SEM micrograph of a Li film deposited on Ni(100) showing island growth.
is not in uniform layers and therefore cannot be FM growth. It is also unlikely to be SM growth as that would exhibit more uniform growth than is visible within the micrograph, the HAS data also showed a non uniform surface through attenuation of the specular reflection. This leaves the two island based growth mechanisms, VW and SK.

AES can be used to obtain the composition from both the surface and the spots of the micrograph in Figure 6.12. A film thickness can also be obtained from the attenuation of the Ni $L_3M_{4.5}M_{4.5}$ peak using the equation given in equation (6.1), where $d_f$ is the film thickness, $\lambda_e$ is the IMFP of the film material, $\theta_t$ is the take off angle, $I$ is the peak intensity and $I_\infty$ is the peak intensity of a clean substrate (Watts and Wolstenholme, 2003). The spectra obtained from the surface and the spots are shown in Figure 6.13, as well as the spectrum acquired from the clean Ni(100) surface. This shows that the black spots visible on the surface of the SEM micrograph are thicker as the Ni $L_3M_{4.5}M_{4.5}$ is more strongly attenuated. The peak intensities for clean Ni, the surface of the Li film and the black spots are 0.594, 0.457 and 0.254 respectively, using a $(I_p - I_b)/I_b$ background correction to account for changes in the incident electron flux. These values equate to thickness of 0.858 nm for the Li surface and 2.774 nm for the spots. In terms of atomic layers, the interlayer spacing in Li(110) (which maximises packing density) is 0.247 nm, and therefore the surface is an average of 3.48 ML thick and the spots are an average of 11.25 ML thick. This demonstrates that the growth mode for the Li films on Ni(100) is SK as there are islands with a few layers of Li in clean films, so, the thickness of the films have been kept below 3.48 ML. Indeed LEED patterns also indicate SK as they show an ordered first layer before forming disordered of three dimensional structures.

$$d_f = \lambda_e \cos(\theta_t) \ln \left( \frac{I}{I_\infty} \right) \quad (6.1)$$

![Figure 6.13: AES spectrum of a Li film on Ni(100) exhibiting island growth. The black line is from the surface of the film, the red line is from the islands and the blue line is a spectrum of the clean Ni crystal for comparison.](image)
6.3 Lithium Hydride

6.3.1 Hydriding of Li Films

Five methods have been attempted for LiH film generation on Ni(100). The first of these was the method used by Engbæk et al. (2006), in which the Ni substrate is exposed to H\(_2\) at reduced temperatures of \(\sim 250 \text{ K}\) causing absorption of H\(_2\) into the bulk of Ni. A Li film is then deposited and annealed to 375 K to diffuse H\(_2\) from the Ni into the Li. The second method was the same as the first, however with an extra H\(_2\) exposure between Li deposition and annealing to provide additional H\(_2\) to the top surface of the Li film. The third method was to only use the second H\(_2\) exposure, so the Li is deposited on clean Ni and then hydrided. The fourth method attempted for generating LiH film was to deposit Li within a H\(_2\) atmosphere. The final method was a modification of the third method; for this method the H\(_2\) pressure was of the order of 1 mbar, whereas the other methods used pressures of the order of \(10^{-6} \text{ mbar}\). Where the pressure of H\(_2\) used was \(10^{-6} \text{ mbar}\) the total exposure was 100 L, for the final method where the exposure was 1 mbar the total exposure was \(9 \times 10^7 \text{ L}\). These films have then been analysed using both AES and TPD to determine the film composition.

6.3.2 Method 1

Initially the Ni crystal was cooled to 250 K, this was then hydrided in a H\(_2\) partial pressure of \(10^{-6} \text{ mbar}\) to form NiH. A Li film was then deposited over this and heated to 375 K to cause the H\(_2\) to diffuse from the Ni into the Li and form LiH.

AES was performed to determine the form of Li present within the film; the Li KLL peak has been shown to shift from 51 eV to 40 eV when hydrided (Powell et al., 1974). It also allows for the presence of oxygen or carbon to be determined, thereby showing whether the film is Li\(_2\)O, LiOH or Li\(_2\)CO\(_3\) rather than LiH. The AES spectrum from a film generated using this method is shown in Figure 6.14. The Li KLL peak within this spectrum is at 54 eV, indicating that the Li is in metallic form. While this spectrum does show that both carbon and oxygen are present, there is not enough for this to be a stoichiometric Li compound film containing these elements; it is likely to be a small amount of contamination leading to some oxygen containing Li compounds being present within the film.

Engbæk et al. (2006) showed that a LiH film decomposes at 610 K with both Li and H\(_2\) being detected. The work presented in § 5.4 showed that on bulk samples, the Li in LiH starts to outgas at \(\sim 750 \text{ K}\); this implies a chemical difference between bulk LiH and the thin film LiH used by Engbæk et al. (2006). Figure 6.15 shows the TPD trace obtained for the film produced using method 1. There are three peaks associated with H\(_2\) desorption and two with Li desorption. The Li peaks are at 560 K and 615 K, implying that both metallic Li and LiH are present; however there is minimal intensity associated with the LiH decomposition. The H\(_2\) peaks are at 565 K, 590 K and 615 K; the peak at 615 K matches well with the Li peak giving further evidence that LiH is present. The peaks at 565 K and 590 K however are unexpected; these could be due to the higher resolution provided by lower ramp rates. It could also be H\(_2\) being outgassed from the Mo sample holder, but this is unlikely as Mo is inert to H\(_2\) (Mueller et al., 1968). The most likely explanation is outgassing of H\(_2\) from the stainless steel cover over the QMS which is undergoing radiative heating.
Figure 6.14: AES spectrum of a LiH film on Ni(100) generated by adsorbing H\textsubscript{2} onto the Ni prior to Li deposition at 250 K.

Figure 6.15: TPD trace of H\textsubscript{2} and Li for a LiH film on Ni(100) generated by adsorbing H\textsubscript{2} onto the Ni prior to Li deposition at 250 K. Ramp rate was 0.5 K s\textsuperscript{-1}.
TPD was also used to confirm that H\textsubscript{2} is sticking to the Ni at the higher temperature of 250 K in comparison to the 100 K used by Engbæk et al. (2006). The TPD trace acquired for this is shown in black in Figure 6.16; this shows no H\textsubscript{2} being outgassed from the Ni when it is exposed at 250 K. The red line shows the trace when the H\textsubscript{2} exposure occurs at the lower temperature of 190 K, here there is a clear H\textsubscript{2} outgassing peak at 300 K. This shows that a temperature of 250 K is too high for this method of forming a LiH film.

![Figure 6.16: TPD trace of H\textsubscript{2} adsorbed on Ni at 250 K (black) and 190 K (red). Ramp rate was 0.5 K s\textsuperscript{-1}.

With the further knowledge that the Ni substrate must be further cooled to \(\sim\)190 K in order for the H\textsubscript{2} to stick, the method for generating LiH films was reattempted. The AES spectrum is shown in Figure 6.17. The Li \textit{KLL} is now split with peaks at 38 eV and 44 eV indicating that the Li is in an oxide or hydride form. Again carbon and oxygen are both present in relatively small amounts.

![Figure 6.17: AES spectrum of a LiH film on Ni(100) generated by adsorbing H\textsubscript{2} onto the Ni prior to Li deposition at 190 K.}
The TPD trace from the sample prepared at 190 K is shown in Figure 6.18. This shows a Li peak at 825 K, which is close to that obtained on bulk LiH, rather than the previous attempt at a thin film. There is also H₂ at 425 K and 830 K; the peak at 830 K corresponds well with the Li peak. The peak at 425 K could correspond with the reaction between LiH and LiOH, indicating the presence of LiOH contamination in the film; however this level of contamination would be minimal as there is no evidence of the decomposition of LiOH and subsequent hydrolysis of LiH at 600 K. This implies that the LiOH is fully consumed by the reaction with LiH.

![Figure 6.18: TPD trace of H₂ and Li for a LiH film on Ni(100) generated by adsorbing H₂ onto the Ni prior to Li deposition at 190 K. The ramp rate was 0.5 K s⁻¹.](image)

### 6.3.3 Method 2

The second method was to repeat the first method, with further H₂ exposure following the deposition; this should provide H₂ from both directions, however may give more opportunity for contamination from any H₂O in the H₂ gas line. The AES shown in Figure 6.19 is very similar to the spectrum obtained in method 1 at 250 K (Figure 6.14); the main difference being that the Li film used for this method appears to be thicker, with a more intense Li KLL peak and the Ni MVV being fully attenuated. There appears to be similar oxygen and carbon content in comparison to the previous film generation method, however the Li KLL peak is again at 53 eV indicating metallic Li rather than LiH.

The TPD acquired using this thin film is shown in Figure 6.20. This method exhibits some bulk like LiH with a Li peak at 825 K and a rising level of H₂ with a potential peak at 875 K. There are also peaks in both the H₂ and Li traces at ~550 K and 610 K; from Engbæk et al. (2006) these would be expected to be Li and LiH, however the 550 K peak appears to correspond with a H₂ desorption.
Figure 6.19: AES spectrum of a LiH film on Ni(100) generated by adsorbing H\textsubscript{2} onto the Ni prior to Li deposition at 250 K, followed by further H\textsubscript{2} exposure.

Figure 6.20: TPD trace of H\textsubscript{2} and Li for a LiH film on Ni(100) generated by adsorbing H\textsubscript{2} onto the Ni prior to Li deposition at 250 K, followed by further H\textsubscript{2} exposure. The ramp rate was 0.5 K s\textsuperscript{-1}.
6.3.4 Method 3

The third method was to only carry out H\textsubscript{2} exposure after deposition of the Li film. The AES from this film is shown in Figure 6.21 and is again very similar to the other methods, with a variation in the thickness of the film shown by changes in the attenuation of the Ni signals and the Li K\textit{LL} is located at 53 eV showing a mainly metallic Li film, this spectrum also contains a shoulder at 43 eV which shows that there is some LiH, LiOH or Li\textsubscript{2}O present.

![AES spectrum of a LiH film on Ni(100) generated by H\textsubscript{2} exposure to a Li film at 300 K.](image)

Figure 6.21: AES spectrum of a LiH film on Ni(100) generated by H\textsubscript{2} exposure to a Li film at 300 K.

The TPD obtained from the film generated using this method (Figure 6.22) is again very similar to the previous method with two changes. The first of these changes is the appearance of a H\textsubscript{2} peak at 510 K, potentially caused by trapped H\textsubscript{2} able to diffuse to the surface. The second is a shift in the temperature at which the bulk like LiH is decomposing from 825 K to 800 K, this is likely to be from small changes in the morphology of the film caused by experimental variability.

6.3.5 Method 4

This method involved depositing the Li within a H\textsubscript{2} atmosphere of 1 × 10\textsuperscript{-6} mbar, the H\textsubscript{2} atmosphere was left for 5 min following the end of deposition to assist with the completion of hydriding. The AES spectrum is shown in Figure 6.23 and again shows the presence of oxygen, carbon and metallic Li.

The TPD trace is shown in Figure 6.24. This is very similar to Figure 6.22 at temperatures less than 700 K, however the bulk like LiH peak is not visible in either the Li or the H\textsubscript{2} traces. This implies that simultaneous deposition and H\textsubscript{2} exposure will not generate a LiH film, in agreement with previous work (Engbæk \textit{et al.}, 2006).
Figure 6.22: TPD trace of H$_2$ and Li for a LiH film on Ni(100) generated by H$_2$ exposure to a Li film at 300 K. The ramp rate was 0.5 K s$^{-1}$.

Figure 6.23: AES spectrum of a LiH film on Ni(100) generated by simultaneous H$_2$ exposure and Li deposition at 300 K.
CHAPTER 6. FORMATION OF LITHIUM BASED THIN FILMS

6.3.6 Method 5

All the above methods used a low pressure of H\(_2\) of the order of 10\(^{-6}\) mbar, the fifth method however uses a higher pressure (1 mbar) to attempt to ensure that the Li film has fully reacted with the H\(_2\) to form a film that does not contain any metallic Li. The AES in Figure 6.25 again shows some carbon and oxygen contamination at similar levels to the other methods. However the main Li KLL peak is now at the 44.8 eV of LiH rather than the 53 eV of Li.

Figure 6.24: TPD trace of H\(_2\) and Li for a LiH film on Ni(100) generated by simultaneous H\(_2\) exposure and Li deposition at 300 K. The ramp rate was 0.5 K s\(^{-1}\).

Figure 6.25: AES spectrum of a LiH film on Ni(100) generated by exposure of high pressure H\(_2\) (1 mbar) to a Li film.

The TPD trace has three peaks between 500 K and 650 K, as well as a peak at high temperatures indicating bulk like LiH and a peak at 400 K attributed to LiOH contamination.
CHAPTER 6. FORMATION OF LITHIUM BASED THIN FILMS

Figure 6.26: TPD trace of H$_2$ and Li for a LiH film on Ni(100) generated by exposure of high pressure H$_2$ (1 mbar) to a Li film. The ramp rate was 0.5 K s$^{-1}$.

6.3.7 Comparison

A comparison of the H$_2$ peaks within the TPDs for the different methods is given in Table 6.1 and Table 6.2 for the Li peaks. The 425 K peak is comparable to that of the solid state reaction between LiH and LiOH, therefore the methods showing this peak may have more H$_2$O contamination than is present within the other methods. Engbæk et al. (2006) attributed the peak at 610 K in the Li and H$_2$ as LiH and the peak in Li at 560 K as metallic Li; LiH decomposition should be at 825 K within the Li trace and starting at around 700 K if bulk-like. All peaks mentioned by Engbæk et al. (2006) are visible within the majority of the methods used for the production of films, however the metallic Li also seems to be matched with a further H$_2$ peak, potentially indicating that this is not Li metal but rather a sub-stoichiometric form of LiH. All of the methods were also attempted with atomic H from the gas cracker, however, this did not result in any changes to the results.

Table 6.1: Overview of H$_2$ TPD peaks

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<th>Method</th>
<th>425 K</th>
<th>510 K</th>
<th>565 K</th>
<th>610 K</th>
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<td></td>
<td>✓</td>
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<td>✓</td>
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<tr>
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</table>

Table 6.2: Overview of Li TPD peaks

<table>
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<th>610 K</th>
<th>825 K</th>
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</tr>
<tr>
<td>Method 5</td>
<td></td>
<td></td>
<td>✓</td>
</tr>
</tbody>
</table>
The AES from 30 eV to 70 eV of all of the above methods are shown in Figure 6.27. Method 2 shows no LiH content at 44.8 eV, this is unexpected as it should be a combination of methods 1 and 3, both of which have a peak at 44.8 eV; it is however worth noting that method 2 was carried out at 250 K whereas for method 1 to work, a temperature of 190 K was required. Methods 3 and 4 both show a peak at 53 eV indicating metallic Li and therefore that the Li film has not fully reacted with the H$_2$. Methods 1 and 5 appear to have fully reacted to form LiH without metallic Li, however method 5 is significantly quicker as it does not require any cooling while method 1 requires a temperature of 190 K, which requires $\sim$1 h of cooling to achieve. The spectrum obtained from method 1 also has a very high background at low KE; this potentially indicates that the quality of the film is low. The AES and TPD have shown that method 5 produces a LiH film which does not contain any metallic Li and while there is some LiOH contamination, this is minimal and therefore this method has been chosen for the production of LiH films. There was a change in the intensities of the Li $KLL$ peak which can be attributed to variations in both the film thickness and the analysis angle. No useful LEED data could be acquired after the Li film had been hydrided; the resulting patterns were diffuse and no discernible structure could be determined.

![AES spectrum](image)

Figure 6.27: AES between 30 eV and 70 eV of the 5 methods used for generation of LiH films.

## 6.4 Lithium Oxide

### 6.4.1 Formation

The starting point for the formation of Li$_2$O films was the reaction shown in equation (6.2). Through which a Li film exposed to O$_2$ reacts to form a Li$_2$O film. In this work, the film was heated whilst in an O$_2$ atmosphere of $1 \times 10^{-3}$ mbar.
6.4.2 XPS Analysis

The Li₂O film formed from heating Li in an O₂ atmosphere has been analysed using XPS. The survey spectrum is shown in Figure 6.28 and is comparable to that of the Li film in Figure 6.8, with the exception that the O 1s and O KLL have both increased substantially.

\[
4\text{Li} + O_2 \rightarrow 2\text{Li}_2O \quad (6.2)
\]

Figure 6.28: XPS survey spectrum of a Li₂O film on Ni(100) formed through the exposure of a Li film to O₂ at 440 K.

The O 1s region between 526 eV and 536 eV is shown in Figure 6.29. This figure shows two components of the O 1s peak, which can be attributed to Li₂O and LiOH. Assuming that a majority Li₂O film has been generated, the larger peak at 530.7 eV is assigned as Li₂O and the smaller peak at 533.2 eV is LiOH. Quantitative analysis of these gives the content of the film as 92 at% Li₂O and 8 at% LiOH (or a ratio of 23 : 2); this purity of Li₂O is sufficient for this work. This peak assignment also agrees with previous work by Haertling et al. (2007); the binding energies here are slightly different however this can be explained by a reduction in charging effects through the use of a thin film on a conducting substrate instead of a bulk insulator. The Li 1s was not visible as a Kα₃ satellite of the Ni 3p is present at the same energy (∼55 eV).

6.4.3 AES Analysis

The survey AES spectrum acquired for this film (Figure 6.30) shows a large increase in the O KLL in comparison to the Li and LiH films (Figures 6.9, 6.17, 6.19, 6.21, 6.23 and 6.25); indicating that the film has been oxidised. The Ni LMM peaks also appear to be more attenuated, this would be expected for an oxidised Li film as the electron IMFP is lower in Li₂O than Li.
Figure 6.29: O 1s XPS spectrum of a Li$_2$O film on Ni(100) formed through the exposure of a Li film to O$_2$ at 440 K.

Figure 6.30: AES survey spectrum of a Li$_2$O film on Ni(100).
The Li $KLL$ region of the AES spectrum is shown in Figure 6.31. This spectrum shows that the Ni $M_{2,3}VV$ has been fully attenuated by the addition of O$_2$ to the film. The Li $KLL$ peak has also shifted from 53 eV to two peaks at 42.2 eV and 36 eV, this is in agreement with previous work on Li$_2$O (Mallinson et al., 2013; Clausing et al., 1973).

![Figure 6.31: AES spectrum between 30 eV and 70 eV of a Li$_2$O film on Ni(100).](image)

The O $KLL$ region is shown in Figure 6.32. This shows one main O $KLL$ peak at 511.5 eV and three loss features, this structure is consistent with the AES of Li$_2$O by Mallinson et al. (2013). The O $KLL$ peak for Li$_2$O has been previously reported as 510 eV (Mallinson et al., 2013; Clausing et al., 1973) whereas for this film it is at 511.5 eV. This could be caused by the bulk samples used in literature having a LiOH surface due to atmospheric exposure, giving a chemical difference between the purer Li$_2$O films.

![Figure 6.32: AES spectrum between 470 eV and 530 eV of a Li$_2$O film on Ni(100).](image)
6.5 Lithium Hydroxide

6.5.1 XPS Analysis

The method first attempted for the generation of LiOH films was to expose a Li metal film to H$_2$O at $1 \times 10^{-5}$ mbar for an exposure of 450 L. This should form LiOH through equation (6.3).

$$2 \text{Li} + 2 \text{H}_2\text{O} \rightarrow 2 \text{LiOH} + \text{H}_2 \quad (6.3)$$

The film generated from this method has been analysed using XPS, the survey from which is shown in Figure 6.33. The spectrum looks similar to that of Li$_2$O shown in Figure 6.28, this is to be expected as the only difference between Li$_2$O and LiOH is the presence of hydrogen which is undetectible to XPS. The only visible change is the intensities of the O$_2$ and Ni peaks; this is likely to be due to slight differences in the thickness of the initial Li film.

![Figure 6.33: XPS survey spectrum of a LiOH film generated by exposing Li to H$_2$O.](image)

The O 1s region of the spectrum (Figure 6.34) shows that the LiOH related peak has increased from that of a Li$_2$O, however it is still significantly smaller than the Li$_2$O peak. This is likely to be caused by a multi-step reaction occurring within equation (6.3) (Zhuang et al., 1998; Wulfsberg et al., 2016). The multi-step reaction is shown in equation (6.4); here the Li reacts with the H$_2$O to form Li$_2$O and H$_2$. The Li$_2$O then reacts with further H$_2$O and the H$_2$ reacts with Li still within the film to form LiOH and LiH respectively. These two constituents of the film then react to form Li$_2$O and H$_2$.

$$2 \text{Li} + \text{H}_2\text{O} \rightarrow \text{Li}_2\text{O} + \text{H}_2 \quad (6.4a)$$
$$2 \text{Li} + \text{H}_2 \rightarrow 2 \text{LiH} \quad (6.4b)$$
$$\text{Li}_2\text{O} + \text{H}_2\text{O} \rightarrow 2 \text{LiOH} \quad (6.4c)$$
$$\text{LiH} + \text{LiOH} \rightarrow \text{Li}_2\text{O} + \text{H}_2 \quad (6.4d)$$
A method to refine this to form a purer LiOH film was attempted; this method is to react the Li film with O$_2$ first to form Li$_2$O, this should then react with H$_2$O to form LiOH directly with minimal LiH and Li$_2$O contamination. The XPS survey spectrum is shown in Figure 6.35, again it is similar to both Figures 6.28 and 6.33. The only difference between them should be the concentration of Li$_2$O and LiOH which should not be easily visible within a survey spectrum.

Looking at the O 1s region in Figure 6.36, the LiOH peak is now significantly more intense than that of the LiOH with a ratio of 11 : 2. This shows that a reasonably pure LiOH film can be created by reacting Li$_2$O with H$_2$O.
CHAPTER 6. FORMATION OF LITHIUM BASED THIN FILMS

Figure 6.36: XPS spectrum of the O 1s region of a LiOH film generated by exposing Li\(_2\)O to H\(_2\)O.

### 6.5.2 AES Analysis

Whilst the reaction of Li with H\(_2\)O did not produce a pure LiOH film as desired, it was still further characterised using both AES and TPD to provide reference data for a LiH/Li\(_2\)O/LiOH tri-layer system. The survey spectrum for the AES from this film is shown in Figure 6.37. This spectrum shows Li, Ni and oxygen as expected, the only difference between this and the Li\(_2\)O film shown in Figure 6.30 appears to be the intensity of Li and Ni. The Li signal decreasing indicates a reduction in the thickness of the film, this is further confirmed by the increase in Ni signal which shows less attenuation. This is unlikely to be an effect of the reaction with H\(_2\)O, rather a variation during the deposition process.

Figure 6.37: AES survey spectrum of a LiOH film generated by exposing Li to H\(_2\)O.

The Li \textit{KLL} region of this tri-layer film presented in Figure 6.38 shows that the Li \textit{KLL} peak has shifted from the 42.2 eV of Li\(_2\)O to 43 eV. This peak cannot be considered to be
LiOH as the XPS (Figure 6.36) showed that the Li$_2$O concentration was higher than that of LiOH. Therefore this peak is likely to be composed of two peaks with a shift that is too small to be able to differentiate within this spectrum.

![Figure 6.38: AES spectrum of the Li KLL region of a LiOH film generated by exposing Li to H$_2$O.](image)

The survey from the LiOH film generated using Li$_2$O and H$_2$O is shown in Figure 6.39. Similar to both the Li$_2$O and tri-layer films, only Li, Ni and oxygen are visible.

![Figure 6.39: AES survey spectrum of a LiOH film generated by exposing Li$_2$O to H$_2$O.](image)

The Li KLL region for this film is shown in Figure 6.40. This shows that the Li KLL peak is now at 44.2 eV, this peak can be identified as LiOH with the XPS providing further evidence of this.
Figure 6.40: AES spectrum of the Li $KLL$ region of a LiOH film generated by exposing Li$_2$O to H$_2$O.

### 6.5.3 TPD Analysis

TPD was carried out on a tri-layer film formed through exposure of Li with H$_2$O at 0.5 Ks$^{-1}$. The mass spectrometer output from this TPD is shown in Figure 6.41. This figure exhibits three clear peaks within the H$_2$ trace at 440 K, 610 K and 860 K, and no clear peaks in either the H$_2$O or the Li. The features within the H$_2$ trace are similar to the features from the TPD of bulk LiH presented in § 5.4; however they are in different concentrations. This can be explained as the reaction between LiH and LiOH will consume the materials until either the thickness of the interstitial Li$_2$O is too thick for the reaction to continue, or one of the compounds has been fully reacted. In the case of bulk material, the Li$_2$O will reach the thickness at which diffusion is limited; however with a thin film, the reduction in thickness is likely to result in the full consumption of either LiOH or LiH before this can happen. A further effect of using a thin film is a reduction in the capability of LiH to react with H$_2$O at $\sim$600 K as the H$_2$O is formed from the decomposition of LiOH. It is therefore likely that the content of LiOH or LiH within the film will be minimal. The change in the shape of the LiH decomposition is also due to a reduction in the amount of material present.

The TPD output for the LiOH film is shown in Figure 6.42. Here the reaction between LiH and LiOH has been reduced, indicating a reduction in the amount of LiH available for reaction. The H$_2$O peak at 440 K is potentially LiOH · H$_2$O, however as no H$_2$O was visible within the XPS spectra it is more likely to be sub-stoichiometric LiOH which decomposes at a lower temperature. The decomposition of LiOH at 540 K appears to be in the same location as was seen with the bulk material.
Figure 6.41: TPD from 375 K to 1000 K at a ramp rate of 0.5 K s\(^{-1}\) of a LiOH film generated by exposing Li to H\(_2\)O.

Figure 6.42: TPD from 350 K to 650 K at a ramp rate of 0.5 K s\(^{-1}\) of a LiOH film generated by exposing Li\(_2\)O to H\(_2\)O.
6.6 Conclusions

This chapter has covered the in-situ growth of films of Li, LiH, Li$_2$O and LiOH. Li films were grown on a Ni(100) substrate and thickness calibrated using known LEED patterns for submonolayer coverages, giving a calibration of 39.2 nA s ML$^{-1}$. A thickness calibration was also carried out using TPD which exhibits two peaks, one for Li to Li bonding (multilayer) and one for Li to Ni bonding (monolayer), this gave a reduced calibration of 25.1 nA s ML$^{-1}$. This reduction was believed to be caused by Li on the Mo sample holder contributing to the multilayer peak, giving an increased peak area and therefore a different calibration. XPS and AES exhibited minimal contamination from oxygen and carbon, implying that the film is clean. The growth mode of the film was investigated using SEM, this showed black spots on the surface. AES showed that Li was present both on and off the spots, indicating that the film was growing under the SK mode.

Multiple techniques for the formation of LiH using H$_2$ were attempted, with varying temperatures, timing of gas dose and H$_2$ pressures used. The most effective at forming LiH was to use 1 mbar of H$_2$ after the Li had been deposited. This method gave an AES spectrum indicative of LiH with minimal contamination, and a TPD showing only two major features, the decomposition of LiH and some H$_2$ outgassing associated with the decomposition of adventitious LiOH.

Li$_2$O was formed by reacting a Li film with $1 \times 10^{-3}$ mbar of O$_2$. XPS showed a large increase in the O$_2$ content and two features within the O 1s peak, assigned as Li$_2$O and LiOH with a ratio of 23 : 2. AES shows a shift in the Li $KLL$ peak from that of Li or LiH, the O $KLL$ is in rough agreement with literature, the small apparent difference able to be explained by having a purer Li$_2$O film.

LiOH synthesis was first attempted by reacting Li with H$_2$O, however this was shown by XPS to have a higher concentration of Li$_2$O than LiOH. This was due to the formation of a trilayer LiH/Li$_2$O/LiOH through multiple reactions rather than the formation of LiOH directly. An alternative method was conducted, using Li$_2$O as the substrate for reaction with H$_2$O, rather than Li. XPS showed that this technique gave a Li$_3$O to LiOH ratio of 2 : 11, much improved over the first attempt. The AES spectrum shows that the Li $KLL$ peak has again shifted, now back to the position of LiH.
Chapter 7

Ageing of LiH Thin Films

7.1 Introduction

This chapter investigates the thermal ageing of LiH using the thin films described in the previous chapter. Firstly, the adventitious contamination of LiH films was investigated. Followed by an analysis of the effects of differing exposures of H₂O on LiH films, to provide further understanding of the hydrolysis (or wet-ageing) process of LiH (equation (5.3)). The exposures used were 45 L and 450 L with a pressure of 1 × 10⁻⁶ mbar.

7.2 Incidental Corrosion of LiH

The fabricated LiH always contained low level (<0.25 ML) corrosion product contamination. Rather than being detrimental to this investigation, it provided further insight into the initial states of LiH hydrolysis. Figure 7.1 shows the O 1s spectra of LiH before (Figure 7.1a) and after (Figure 7.1b) heating to 675 K. Prior to heating, the O 1s spectrum shows two peaks assigned to Li₂O (529.4 eV) and LiOH (532.1 eV). After heating, the LiOH peak has diminished in intensity and the Li₂O peak has shifted by 0.7 eV and broadened by 0.3 eV. The LiOH has decomposed, explaining the decreased peak intensity, while the Li₂O is reasoned to have an increased defect density and reduction in crystallinity due to the relief of interfacial strain incurred during heating. The origin of the interfacial strain is the fact that there is a large lattice mismatch between LiH and Li₂O. For comparison, the intensity of these peaks is more than an order of magnitude less than the film exposed to 45 L of H₂O (§ 7.4).
Figure 7.1: (a) XPS of the O 1s region of an as deposited LiH film. (b) XPS of the O 1s region of a LiH film after heating to 675 K.
7.3 Lithium Hydride Films Exposed to 450 Langmuir of Water

7.3.1 Spectroscopic Analysis

The O 1s XPS spectrum of a LiH film exposed to 450 L of H\textsubscript{2}O is shown in Figure 7.2. This reveals a feature at 535.7 eV; this has not previously been seen on Li films. This feature is believed to be associated with oxygen in the form of H\textsubscript{2}O, this is likely to be due to the presence of either LiOH·H\textsubscript{2}O or adsorbed H\textsubscript{2}O on the surface. Also visible is a peak at 532.4 eV associated with LiOH. Whilst there is no clear peak associated with Li\textsubscript{2}O, it is possible that it is hidden under the H\textsubscript{2}O and LiOH layers and therefore highly attenuated.

![Figure 7.2: XPS spectrum of the O 1s region of a LiH film exposed to 450 L of H\textsubscript{2}O.](image)

7.3.2 Temperature Programmed Desorption

A TPD with a heating rate of 0.5 Ks\textsuperscript{-1} was carried out on the film exposed to 450 L of H\textsubscript{2}O is shown in Figure 7.3. This TPD shows the expected reactions (as shown through bulk desorption in § 5.4) of the decomposition of LiOH, the solid state reaction between LiH and LiOH, the hydrolysis reaction of LiH and the decomposition of LiH; however there is a new feature at 440 K which has been assigned as the desorption of H\textsubscript{2}O. It would be expected for the desorption of H\textsubscript{2}O to appear at a lower temperature than that of LiOH decomposition due to the weaker bonding present, thereby requiring less energy to drive the desorption reaction.
Chapter 7. Aging of LiH Thin Films

7.4 Lithium Hydride Films Exposed to 45 Langmuir of Water

7.4.1 Spectroscopic Analysis

The composition of the film following 45 L H$_2$O exposure has been investigated with XPS of the O 1s region. The spectrum shown in Figure 7.4 contains two peaks at 530 eV and 532.6 eV, these can be attributed to the LiOH and Li$_2$O features found during the analysis of the respective films. The ratio between the LiOH and Li$_2$O is 13 : 7, in comparison with 11 : 2 for a LiOH film and 2 : 23 for a Li$_2$O film. The peak at ~536 eV is no longer present, indicating that 45 L is not in excess of the saturation exposure. This suggests that 45 L of H$_2$O is a reasonable model of a bulk LiH sample which has been exposed to atmosphere (Haertling et al., 2007).

7.4.2 Temperature Programmed Desorption

A TPD was carried out on this film at 1 K s$^{-1}$ which shows that the H$_2$O peak at 440 K is no longer present. This confirms that this peak has been assigned correctly as it is the only peak to have been removed from the TPD output and is also no longer present within the XPS spectrum. Apart from this, the only observable change in the TPD outputs is that the amount of reactant available for each reaction appears to have changed, with much more LiH present for decomposition and a substantially reduced solid state reaction peak. The small increases in temperature can be explained by the increase in the heating rate used.
Figure 7.4: XPS spectrum of the O 1s region of a LiH film exposed to 45 L of H₂O.

Figure 7.5: TPD from 310 K to 1000 K at a ramp rate of 1 K s⁻¹ of a LiH film exposed to 45 L of H₂O.
7.5 Activation Energies

7.5.1 Kissinger Analysis

An effective measure for how comparable these data are with the bulk samples is to examine the values of activation energies. This has first been calculated using Kissinger analysis (§ 3.8.2) using ramp rates of 0.2 K s$^{-1}$, 0.5 K s$^{-1}$, 1 K s$^{-1}$ and 2 K s$^{-1}$ on LiH films with a H$_2$O exposure of 450 L. The H$_2$ and H$_2$O outputs are shown for all of these ramps rates in Figures 7.6 and 7.7, respectively. The exact quantity of H$_2$O adsorbed onto the surface of the film varied with each film due to difficulty in controlling exposure precisely. This is likely to be partly due to the lack of fine control available for gas dosing, and it is also likely that there is H$_2$O contamination within the H$_2$ line. This is not an issue for the determination of the $E_a$ using Kissinger analysis or for full modelling because the experiments have been repeated to ensure that the peak is present in the same location multiple times.

![Figure 7.6: TPD output for H$_2$ at ramp rates of 0.2 K s$^{-1}$, 0.5 K s$^{-1}$, 1 K s$^{-1}$ and 2 K s$^{-1}$. Two peaks are visible, the peak at lower temperature has been assigned as the solid state reaction between LiH and LiOH and the peak at higher temperature has been assigned as the hydrolysis of LiH.](image)

Kissinger analysis requires the temperature at which the peak is a maximum across a variety of ramp rates. These $T_{max}$ values are shown for the four reactions in Table 7.1. Using an Arrhenius plot as described in § 3.8.2, the gradient is equal to $\frac{E_a}{R}$; therefore multiplying the gradient by $R$ gives $E_a$. The Arrhenius plot for the solid state reaction, displaying the linear fit used, is shown in Figure 7.8. This reaction was not possible to analyse with this method with bulk samples as the signal merged with that of LiH hydrolysis. This effect is removed through the use of thin films due to the reduced amount of material, which in turn causes the reactions to complete in less time and therefore improves the resolution of these peaks.
Figure 7.7: TPD output for $\text{H}_2\text{O}$ at ramp rates of 0.2 K s$^{-1}$, 0.5 K s$^{-1}$, 1 K s$^{-1}$ and 2 K s$^{-1}$. Two peaks are visible, the peak at lower temperature has been assigned as the desorption of $\text{H}_2\text{O}$ and the peak at higher temperature has been assigned as the decomposition of LiOH.
This analysis provides the following values for $E_a$: $30 \pm 4 \text{kJ mol}^{-1}$ for the decomposition of LiOH; $82 \pm 8 \text{kJ mol}^{-1}$ for the solid state reaction between LiH and LiOH; $30 \pm 4 \text{kJ mol}^{-1}$ for the hydrolysis of LiH; and $101 \pm 33 \text{kJ mol}^{-1}$ for the desorption of H$_2$O. The value for the solid state reaction is in reasonable agreement with previous values, however both the decomposition of LiOH and LiH hydrolysis are much lower than expected. This is most likely due to the rate-limiting reaction mechanism not being compatible with the mathematical form required for Kissinger analysis. Both of these reactions gave reasonable approximations with bulk samples; this indicates that the reactions are undergoing different mechanisms when in thin films. It would also be expected for the $E_a$ for the desorption of H$_2$O to be the lowest value with the lowest desorption temperature, however this analysis has found it to have the highest $E_a$.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$T_{max}$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.2 K s$^{-1}$</td>
</tr>
<tr>
<td>Decomposition of LiOH</td>
<td>467</td>
</tr>
<tr>
<td>Solid state reaction</td>
<td>425</td>
</tr>
<tr>
<td>Hydrolysis of LiH</td>
<td>475</td>
</tr>
<tr>
<td>Desorption of H$_2$O</td>
<td>445</td>
</tr>
</tbody>
</table>

Figure 7.8: Arrhenius plot of $\ln\left(\frac{T_{max}}{\beta}\right)$ against $\frac{1}{T_{max}}$ for Kissinger analysis of the solid state reaction between LiH and LiOH.

### 7.5.2 Modelling

Explicit modelling using the mechanistic equations presented in Appendix A has been used to improve the $E_a$ values found and to determine the rate limiting mechanisms. The H$_2$ output consists of two peaks, the solid state reaction and the hydrolysis of LiH. Bulk samples showed the solid state reaction to be a $D3$ mechanism and the hydrolysis reaction to be a $F1$ mechanism. This was attempted with a 0.2 K s$^{-1}$ TPD (shown in Figure 7.9);
the fit parameters are $E_a = 80 \pm 3 \text{kJ mol}^{-1}$ and $\nu = 7.31 \pm 5.89 \times 10^6 \text{s}^{-1}$ for the solid state $D3$ reaction and $E_a = 97 \pm 4 \text{kJ mol}^{-1}$ and $\nu = 4.15 \pm 4.47 \times 10^8 \text{s}^{-1}$ for the $F1$ hydrolysis reaction. While the $E_a$ value is similar to that found with bulk samples ($90.5 \pm 0.3 \text{kJ mol}^{-1}$), the fit is clearly not appropriate from Figure 7.9, where the $F1$ related peak does not match the shape of the hydrolysis peak. The shape of the $D3$ peak matches the solid state reaction peak, however the $E_a$ is significantly different from the $63.9 \pm 0.2 \text{kJ mol}^{-1}$ found from bulk samples. This change in $E_a$ is probably due to a reduction in the defect density and the number of grain boundaries present within the Li$_2$O layer, and thus provides an inhibiting effect on diffusion. As the $D3$ is a good fit it is likely that diffusion is still the rate limiting mechanism with thin films; the $F1$ mechanism is almost certainly not correct for hydrolysis, in agreement with the change in the effectiveness of Kissinger analysis.

By keeping the $D3$ but trying different mechanisms for the hydrolysis reaction, it is found that the best mathematical fit is using an $A3$ reaction mechanism. This fit is shown in Figure 7.10. An $A3$ mechanism is three dimensional Avrami-Erofeev nuclei growth; this mechanism assumes that reactions initiate at random nucleation points and then propagate three dimensionally through the material, in which the rate-limiting step is the rate of propagation. This is also consistent with Kissinger analysis not producing physically sensible results, as the requirement for this is for the equation that models the rate limiting step to be of the form $(1 - \alpha)^n$; while $F1$ is of this form, $A3$ is not. The parameters for this fit are $E_a = 80 \pm 3 \text{kJ mol}^{-1}$ and $\nu = 5.38 \pm 4.35 \times 10^6 \text{s}^{-1}$ for the solid state reaction and $E_a = 93 \pm 1 \text{kJ mol}^{-1}$ and $\nu = 1.43 \pm 0.13 \times 10^8 \text{s}^{-1}$ for the hydrolysis reaction. However, as with the bulk samples, this $E_a$ for the hydrolysis value is not a true $E_a$, the rate limiting factor is the availability of H$_2$O; this is formed from the decomposition of LiOH. Therefore the mechanism would be expected to be the same, with a slightly higher $E_a$ for the hydrolysis to account for a time lag caused by the time taken for H$_2$O to diffuse through the Li$_2$O interlayer. The proposed model does not fit the the leading edge or trailing edges particularly well, this is potentially caused by changes in the time lag. The time lag is linked to the thickness of the Li$_2$O layer between the LiOH and LiH which will increase with the reaction takes place. As
this thickness increases it is possible that this causes a distortion in the peak shape, where the reaction occurs quicker than average early on and takes longer as the reaction continues.

![Figure 7.10: TPD output for H$_2$ with a ramp rate of 0.2 K s$^{-1}$. Data is fitted with the sum of a D3 mechanism and an A3 mechanism.](image)

The best fit for both the desorption of H$_2$O and for the decomposition of LiOH are an A3 mechanism. The fit is shown in Figure 7.11, the parameters for this fit are $E_a = 72 \pm 1$ kJ mol$^{-1}$ and $\nu = 2.26 \pm 0.11$ s$^{-1}$ for the H$_2$O desorption and an $E_a = 86 \pm 1$ kJ mol$^{-1}$ and $\nu = 4.53 \pm 0.21 \times 10^{-7}$ s$^{-1}$ for the LiOH decomposition. This is reasonable for the decomposition of LiOH; as mentioned previously this should be the same as for the hydrolysis reaction with a slightly reduced $E_a$, this is the case here.
Figure 7.11: TPD output for H$_2$O with a ramp rate of 0.2 K s$^{-1}$. Data is fitted with the sum of two $A\beta$ mechanisms.

### 7.6 Summary of Thermal Ageing

The $E_a$ values found through modelling are shown in Table 7.2, along with the values found for bulk samples. This shows that the values obtained using thin films are similar in the majority of cases to those obtained using bulk material, with the exception of the solid state reaction. The thin film results should be more accurate as a result of the reduction in bulk contributions and any issues in thermal transport through the material.

Table 7.2: Comparison of $E_a$ values determined with bulk LiH samples and with LiH thin films. Desorption of H$_2$O was not observed in the bulk material.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Activation Energy (kJ mol$^{-1}$)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Bulk</td>
</tr>
<tr>
<td>Decomposition of LiOH</td>
<td>96 ± 4</td>
</tr>
<tr>
<td>Solid state reaction</td>
<td>63.9 ± 0.2</td>
</tr>
<tr>
<td>Hydrolysis of LiH</td>
<td>90.5 ± 0.3</td>
</tr>
<tr>
<td>Desorption of H$_2$O</td>
<td>—</td>
</tr>
</tbody>
</table>

### 7.7 Conclusions

This chapter has presented work on the ageing of LiH thin films which were deposited on a Ni(100) crystal as described in § 6.3. This film was exposed to 450 L and 45 L of H$_2$O and analysed using XPS and TPD.

XPS analysis of the 450 L revealed an extra O 1s peak present at 535.7 eV, this was attributed to H$_2$O adsorbed onto the surface. An additional peak also appeared within the TPD,
attributable to the same species. Both of these features are removed when the H$_2$O exposure of the LiH film is reduced to 45 L, confirming adsorbed H$_2$O as the cause.

The $E_a$ of the reactions were initially determined using Kissinger analysis. The value obtained from this for the reaction between LiH and LiOH is in reasonable agreement with the value obtained from the TPD of bulk LiH. However, the values obtained for LiOH decomposition and LiH hydrolysis are clearly different from bulk, this would imply that the rate limiting mechanism is different than in bulk as the validity of the Kissinger analysis depends on the reaction mechanisms.

Peak modelling was also undertaken, this provided further evidence that the limiting mechanism is different for thin films of LiH. The $F1$ mechanism, evident in bulk samples, no longer fits to the TPD peak and now fits to an $A3$ mechanism. This mechanism fitted all of the reactions with the exception of the solid state reaction which remained as a $D3$ limited reaction.
Chapter 8

Uranium

8.1 Introduction

This chapter describes the work carried out into the effect of various gases on U and UO$_2$. Initially the sample preparation is detailed, followed by the adsorption and reaction of H$_2$, H$_2$O and O$_2$ with U using XPS and TPD. The sample was then oxidised to UO$_2$ so that the interactions of UO$_2$ with H$_2$ and H$_2$O could be investigated using molecular beam techniques and TPD.

8.2 Sample Preparation

8.2.1 Sputtering

The U sample used for this work was cleaned using SiC paper within an Ar glove box prior to supply, this removed the gross oxide. The sample was then transferred to the UHV system in air so contained a thin (~10 nm (Harker, 2006)) oxide layer. XPS analysis was carried out to check the surface composition, this confirmed that the surface was heavily oxidised and that further in-situ cleaning would be required. The U 4f region of the XPS spectrum of the as-received surface is shown in Figure 8.1. This figure has been peak fitted and reveals two main component pairs, one at 380.3 eV and 391.2 eV and one at 387.2 eV and 398.2 eV; both of these pairs are consistent with UO$_2$ and its shake-up satellite. The shake-up satellite is the excitation of an electron from the U 6d–O 2p band to the localised U 5f state (Allen et al., 1982). The other peaks are created by the Al K$_{\alpha3,4}$ X-ray lines as the source is not monochromated.
Figure 8.1: Fitted XPS spectrum of the U 4f region of an as received uranium sample.

Cleaning was performed using Ar\(^+\) ion sputtering, the sample was analysed using XPS, AES and UPS after each sputter cycle. The drain current during sputtering was monitored, allowing for the total sputter flux to be calculated for each cycle; these fluxes were 0 mA s, 1.5 mA s, 9.3 mA s, 21 mA s and 32.7 mA s. XPS spectra of the U 4f, O 1s and the C 1s regions are shown in Figures 8.2 to 8.4, respectively. The U 4f shows that as the amount of sputtering increases, the UO\(_2\) peaks decrease and peaks appear at 387.7 eV and 377 eV; these energies are consistent with metallic U (Ilton and Bagus, 2011). After 32.7 mA s, the UO\(_2\) related peaks have been removed from the spectrum, indicating that the U sample has been cleaned sufficiently. The O 1s region reveals similar information, where with sputtering the intensity of the peak is reduced; with only negligible amounts of oxygen present after 32.7 mA s of sputtering. The C 1s region initially shows a large peak related to a layer of adventitious carbon on the surface, after 9.3 mA s this has been removed and a peak appears at 281.6 eV, this peak is likely to be linked to a small concentration of U carbide or oxycarbide.
Figure 8.2: XPS spectra of the U 4f region of a uranium sample after varying amounts of Ar\(^+\) ion sputtering.

Figure 8.3: XPS spectra of the O 1s region of a uranium sample after varying amounts of Ar\(^+\) ion sputtering.
Figure 8.4: XPS spectra of the C 1s region of a uranium sample after varying amounts of Ar\(^+\) ion sputtering.

The UPS spectra acquired for the different sputter fluxes are shown in Figure 8.5. This shows that prior to any sputtering the spectrum is dominated by C 2p. After the first sputter cycle this C 2p has been removed and the UPS shows a spectrum in agreement with that published for a UO\(_2\) surface (Gouder et al., 1989). This consists of both the U 6d - O 2p bonding orbital (5.2 eV) and the U 5f\(^2\) (2.5 eV) peaks and no Fermi edge. As the sputter cleaning continues, the oxygen content does not appear to decrease; however the Fermi edge becomes visible and increases in intensity with increased sputter flux. The change in the Fermi edge is expected as UO\(_2\) is a semiconductor whereas U metal conducts (Idriss, 2010). This is contrary to the U 4f peaks which show a clean surface devoid of any UO\(_2\). This apparent contradiction can be reconciled by appreciating that XPS and UPS have different information depths. The IMFP of electrons in UPS is material dependent (Woodruff and Delchar, 1994) and so may be longer than for U 4f XPS and therefore UPS spectra contain information from deeper within the sample, indicating that the sample contains sub-surface oxide.

AES taken with sputter fluxes of 0 mA s, 1.5 mA s and 9.3 mA s is shown in Figure 8.6. The region of 50 eV to 120 eV is considered to be U and comprises of a mix of U OPP, U OVV, U OOV, U OPV and U OOP peaks (Allen and Wild, 1974). As the sample is sputtered, the C KLL and O KLL peaks are reduced, in agreement with the previous XPS and UPS. There is also further structure appearing within the U region; this occurs as the U metal is less attenuated and able to be better resolved with the loss of the carbon surface layer.
Figure 8.5: UPS spectra of a uranium sample after varying amounts of Ar\(^+\) ion sputtering.

Figure 8.6: AES spectra between 0 eV to 650 eV of a uranium sample after varying amounts of Ar\(^+\) ion sputtering. See text for uranium peak assignments.
8.2.2 Annealing

After the sputtering had been completed and confirmed to give a clean U metal surface, annealing was carried out to aid with restructuring of the sputtered surface. The annealing was performed isothermally for an hour, before allowing to cool and performing XPS to determine any effect on the surface composition. The temperatures used for the annealing process were 475 K, 575 K, 675 K and 775 K, with 300 K used to indicate room temperature for an unannealed sample. The anneal to 475 K also includes the sample being subsequently left under UHV conditions for 20 h to determine if the residual gas within the chamber had any effect on the composition.

The U 4f, O 1s and C 1s regions of the XPS are shown in Figures 8.7 to 8.9 respectively. The U 4f region shows that annealing at 475 K had minimal effect upon the U structure, the figure exhibits a change in peak intensity however this is likely to be from the sample being in a slightly different position relative to the source and detector. At 575 K the oxygen within the bulk of the U has redistributed throughout the sample, forming UO$_{2-x}$ at the surface. When annealed to at least 675 K, a new feature appears at 378.0 eV which is attributed to a carbide or oxycarbide species. This is in agreement with C 1s and O 1s which show an increase in the surface carbon and oxygen content. At higher temperatures the amount of UO$_2$ relative to the combination of U and UO$_x$C$_y$ does not change, indicating equilibrium between the bulk and surface concentrations of carbon and oxygen, further confirmed by consistency in the O 1s peak at anneal temperatures of 575 K, 675 K and 775 K. A sample was left under UHV conditions for 20 h to confirm if oxygen and carbon were being picked up from the vacuum, however this showed no change and therefore this increase in oxygen and carbon are unlikely to be from background gases.

The thermally induced diffusion of oxygen and carbon to the surface has been observed elsewhere. Orlov et al. (2003) mixed $^{14}$C into bulk U, which was shown to segregate to the surface with temperatures of above 875 K. While this temperature is significantly higher than observed here, this can be explained by the differing information depths and sensitivities of the two probes. The detection of β emission from $^{14}$C is less sensitive to the small changes that occur at lower temperatures in comparison XPS.

The U 4f region has also been fitted after annealing to 775 K, shown in Figure 8.10. The fit reveals that the annealed film comprises U metal (28 at%), UO$_{2-x}$ (51 at%) and UO$_x$C$_y$ (21 at%). Elemental quantifications give 51 at% uranium, 33 at% oxygen and 16 at% carbon. Atomic quantification was calculated using an arbitrary cut off at 390 eV for the metal because the Doniach-Sunjic peak shape is ill-defined in terms of area. The fit also includes shake-up satellites from the UO$_{2-x}$ and UO$_x$C$_y$ lines, both of which are separated by 6.9 eV from their respective parent peak. However, for UO$_x$C$_y$ the satellite peak is broader and more intense than for UO$_{2-x}$, which implies a modification to the electronic states involved in the shake-up process (i.e. a change to either U 6d – O 2p or U 5f). Previous work on thin films has shown that the valence band structure has significant differences between UO$_x$C$_y$ and UO$_2$, for example, the contribution of the C 2p state to the valence band. Furthermore, the de-localised nature of the U 5f in UO$_x$C$_y$ has been demonstrated which is fundamentally different to UO$_2$ and therefore it is reasonable that the shake-up lines would also exhibit differences (Eckle and Gouder, 2004).
Figure 8.7: XPS spectra of the U 4f region of a uranium sample after annealing at different temperatures.

Figure 8.8: XPS spectra of the O 1s region of a uranium sample after annealing at different temperatures.
Figure 8.9: XPS spectra of the C 1s region of a uranium sample after annealing at different temperatures.

Figure 8.10: Fitted XPS spectrum of the U 4f region of a uranium sample after annealing to 775 K.
The data presented above shows that sputtering can be used to provide a clean surface, however the use of annealing to reform the surface results in the reformation of UO$_2$ when temperatures of 575 K and above are used. Due to this, the temperature of sample annealing must be kept below 475 K and be followed by a light sputter to remove the small amounts of surface UO$_2$ formed whilst also minimising the impact on the surface structure. An overview of the energies for the XPS and AES peaks are presented in Table 8.1.

Table 8.1: Overview of XPS and AES peaks.

<table>
<thead>
<tr>
<th>Peak</th>
<th>Compound</th>
<th>Binding Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>U 4f$_{5/2}$</td>
<td>U</td>
<td>387.7</td>
</tr>
<tr>
<td>U 4f$_{5/2}$</td>
<td>UO$_2$</td>
<td>391.2</td>
</tr>
<tr>
<td>U 4f$_{5/2}$</td>
<td>UO$_x$C$_y$</td>
<td>388.9</td>
</tr>
<tr>
<td>U 4f$_{7/2}$</td>
<td>U</td>
<td>377.0</td>
</tr>
<tr>
<td>U 4f$_{7/2}$</td>
<td>UO$_2$</td>
<td>380.3</td>
</tr>
<tr>
<td>U 4f$_{7/2}$</td>
<td>UO$_x$C$_y$</td>
<td>378.1</td>
</tr>
<tr>
<td>O 1s</td>
<td>UO$_2$</td>
<td>530.6</td>
</tr>
<tr>
<td>C 1s</td>
<td>UO$_x$C$_y$</td>
<td>281.6</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Peak</th>
<th>Kinetic Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>U</td>
<td>50-120</td>
</tr>
<tr>
<td>C KLL</td>
<td>266.3</td>
</tr>
<tr>
<td>O KLL</td>
<td>512.7</td>
</tr>
</tbody>
</table>

8.3 Gas Phase Reactions on Uranium Metal

8.3.1 Hydrogen

H$_2$ was dosed onto a clean sputtered U surface at 200 K at exposures of 1 L, 5 L, 9 L, 20 L and 30 L. TPD was subsequently performed, shown in Figure 8.11 for a sample exposed to 9 L. This TPD is in general agreement with previous work (Bazley et al., 2008). The main feature of this profile is a peak centred at 450 K which is the recombinational desorption of H$_2$ from both U and traces of UO$_2$, and a small shoulder at 550 K. This shoulder is the desorption of H$_2$ from step edges or other defects in the UO$_2$.

The exposure of 9 L provided a saturated surface. Previous saturation coverages have been given between 0.15 ML and 0.22 ML (Balooch and Hamza, 1996; Bazley et al., 2008). As the data here is comparable to previous data it is reasonable to assume that the saturation coverage would be similar and therefore in the range of 0.15 ML to 0.22 ML.

XPS was performed on samples of U metal exposed to H$_2$, however this did not show any significant change from that of a clean surface and is not displayed here. This indicates that there is no formation of UH$_3$ occurring, as this would be the only reaction that would cause changes to the XPS spectrum. It was not expected that UH$_3$ would be formed, as this has been shown to require exposures of $10^{10}$ L with sample temperatures of 475 K (Allen and Stevens, 1988).
8.3.2 Water

Clean U samples have also been exposed to up to 100 L of H$_2$O at a temperature of 200 K. The XPS from a sample exposed to 100 L is shown in Figure 8.12. The U 4f (Figure 8.12a) shows four main peaks, consisting of the U 4f$_{5/2}$ and U 4f$_{7/2}$ for two oxidation states of U; metallic U$^0$ and U$^{4+}$. There is also a shake up satellite separated from the main peak by 6.5 eV. The U 4f$_{7/2}$ oxide peak is at 380.3 eV, this is 0.3 eV higher than would be expected for stoichiometric UO$_2$, indicating a sub-stoichiometric UO$_{2-x}$ film. This would be consistent with partial oxidation of the surface. The O 1s region (Figure 8.12b) can be fitted with two peaks. The main component is a peak at 530.9 eV which is consistent with a UO$_{2-x}$ species. The second component is at 533.0 eV, this indicates a -OH group, likely to be surface hydroxyl terminations.

TPD of a sample exposed to 15 L of H$_2$O is shown in Figure 8.13. H$_2$ (m/z = 2), H$_2$O (m/z = 18) and O$_2$ (m/z = 32) were followed with the QMS, however the O$_2$ trace was featureless and therefore is not shown. The TPD shows five features; four H$_2$ peaks and a H$_2$O peak, this is consistent with dissociative adsorption which is typical of the reaction between H$_2$O and a clean U surface (Manner et al., 1999; Henderson, 2002; Shamir et al., 2006). Dissociative adsorption is when the incoming molecule splits into its respective atoms on the surface (equation (8.1) in this case). This is also supported by the appearance of UO$_{2-x}$ within the XPS as incorporation of oxygen into the U surface would require the H$_2$O to dissociate.
Figure 8.12: Fitted XPS spectra of U exposed to 100 L of H$_2$O showing (a) the U 4f region, (b) the O 1s region.
CHAPTER 8. URANIUM

The first H\(_2\) peak (300 K) is accompanied by a H\(_2\)O peak, these are assigned to the decomposition of a weakly bound hydroxyl species. The fact that H\(_2\) and H\(_2\)O are both evolved from this surface indicates that there are two decomposition pathways. H\(_2\)O is produced from the recombination of 2 OH groups, leaving an oxygen atom that presumably further oxidises the surface. It is not attributable to multilayers of H\(_2\)O physisorbed onto the surface, as the sample temperature used in this work is greater than the 150 K required for this (Manner et al., 1999). H\(_2\) is likely formed from the cleavage of the O−H bond and then the recombination of 2 H. The assignment of the -OH group is further supported by the O 1s XPS (Figure 8.12b). The second H\(_2\) peak (400 K) is assigned as desorption of H\(_2\) from U oxide in the proximity of metal (e.g. step edges). The third H\(_2\) peak (500 K) is hypothesised as the desorption of H\(_2\) from a defective U oxide surface. The final H\(_2\) peak (>800 K) is reasoned to be the desorption of H\(_2\) from a more strongly bound species on the U oxide surface.

\[
\text{H}_2\text{O} \rightarrow \text{H} + 2\text{O} \quad (8.1)
\]

Figure 8.13: TPD of a U sample exposed to 15 L of H\(_2\)O with a heating rate of 1 K s\(^{-1}\) showing H\(_2\) and H\(_2\)O traces.

### 8.3.3 Oxygen

The reaction between U and O\(_2\) has been investigated using a molecular beam to acquire a SP against surface coverage, shown in Figure 8.14. Kisliuk analysis (§ 3.9.2) was carried out on this data, giving a \(K\) value of 2.5. This implies that intrinsic adsorption is more favourable than extrinsic adsorption, in other words O\(_2\) molecules that adsorb onto adatoms rather than the U surface are more likely to desorb than to chemisorb. As \(K\) is essentially the ratio between intrinsic and extrinsic adsorption, a value of 2.5 implies that there will still be some extrinsic adsorption. For example, on average for every 5 molecules adsorbed intrinsically, there will be 2 adsorbed extrinsically.
Figure 8.14: Sticking probability of O$_2$ on U. Fitted with Kisliuk model with $K = 2.5$.

XPS was used to determine the amount of oxidation that had occurred during the beam exposure, the U 4f region is shown in Figure 8.15. It is evident that there is only limited oxidation as the metallic U 4f peaks dominate, with only a shoulder of UO$_{2-x}$ visible, which is in agreement with the low exposure calculated from the seeding % and total beam flux (1L to 5L).

Figure 8.15: XPS spectrum of U 4f region of a U sample exposed to a H$_2$O molecular beam.
8.4 Gas Phase Reactions on Uranium Dioxide

8.4.1 Formation of a Uranium Dioxide Layer

The next stage of the investigation required a UO\(_2\) surface, this was formed by heating a clean metallic U surface in an O\(_2\) atmosphere. The conditions used for this were a temperature of 800 K in an O\(_2\) pressure of 10\(^{-6}\) mbar, these were based upon previous studies by Allen and Wild (1974); Ellis (1976); Winer \textit{et al.} (1986, 1987). The sample surface was assessed using XPS after exposures of 135 L, 1125 L and 2700 L (equivalent to times of 3 min, 25 min and 60 min). The 135 L and 1125 L exposures were cooled under UHV conditions whilst the 2700 L was cooled in an O\(_2\) atmosphere. Following the 2700 L exposure, the sample had visibly changed appearance; the surface appeared to be slightly darkened and had lost its metallic appearance. The XPS for each exposure, along with that of the clean metallic surface, is shown in Figure 8.16 for the U 4f and O 1s regions. Both of these regions show partial oxidation (UO\(_{2-x}\)) for exposures of 135 L and 1125 L, and oxidation (UO\(_2\)) for the 2700 L sample. The C 1s region was also recorded, however only showed trace amounts and so is not displayed here.

The U 4f spectrum for the sample exposed to 2700 L was fitted and is shown in Figure 8.17. This was fitted with U metal, U\(^{4+}\), U\(^{5+}\) and U\(^{6+}\) species and respective satellites, which confirmed that the only species present was U\(^{4+}\) (UO\(_2\)). The partially oxidised surfaces show a small shift of 0.2 eV in the peak energy of the U\(^{4+}\) species, consistent with a sub-stoichiometric form. The O 1s spectra (Figure 8.16b) show a shift in binding energy in agreement with that of the U 4f, in that there is UO\(_{2-x}\) with the lower exposures and after a 2700 L exposure UO\(_2\) is the sole constituent. There is no evidence of UO\(_{2+x}\), in agreement with previous studies where this has been found to require pressures of the order of 10\(^{-3}\) mbar and exposure times of over 100 h (Allen \textit{et al.}, 1982). The composition of the sample after each exposure is shown in Table 8.2.

<table>
<thead>
<tr>
<th>Exposure (L)</th>
<th>U (at%)</th>
<th>O (at%)</th>
<th>C (at%)</th>
<th>O:U Ratio</th>
<th>Surface Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>94</td>
<td>3</td>
<td>3</td>
<td>0.03</td>
<td>U</td>
</tr>
<tr>
<td>135</td>
<td>49</td>
<td>50</td>
<td>1</td>
<td>1.02</td>
<td>U, UO(_{2-x})</td>
</tr>
<tr>
<td>1125</td>
<td>47</td>
<td>52</td>
<td>1</td>
<td>1.11</td>
<td>U, UO(_{2-x})</td>
</tr>
<tr>
<td>2700</td>
<td>33</td>
<td>66</td>
<td>1</td>
<td>2</td>
<td>UO(_2)</td>
</tr>
</tbody>
</table>
Figure 8.16: XPS spectra of U exposed to 0 L, 135 L, 1125 L and 2700 L of O$_2$ at 800 K showing (a) the U 4f region, (b) the O 1s region.
8.4.2 Deuterium

As a result of the background level of H$_2$ within the chamber, it was not possible to obtain molecular beam results using H$_2$. Instead it was attempted using D$_2$ as this is chemically similar, however as the mass is different it allows for it to be differentiated from the background H$_2$ signal by the mass spectrometer. This was unsuccessful as the sticking probability was still too low to detected, so isothermal desorption was attempted. Here a D$_2$ beam is impinged on the surface until the surface is in equilibrium (observed SP = 0 as the amount desorbing is equal to the amount adsorbing), the beam is then turned off which causes a change in the equilibrium state and therefore desorption occurs. However this was also unsuccessful as the desorption was too rapid to observe, meaning that no useful information could be extracted from this experiment.

Inelastic scattering measurements were also made on this surface using a D$_2$ beam to gain information on the nature of the interaction. This technique requires knowledge of the quantum mechanics of scattering. Therefore knowledge of the rotational constant, $B$, is required for the molecule of interest. For D$_2$ this is 30.44 cm$^{-1}$ or 3.74 meV (Haynes, 2012). In addition, as D$_2$ is a homonuclear diatomic molecule (nuclear spin of 1), it exists in two forms, ortho-D$_2$ and para-D$_2$. For rotational motion, ortho-D$_2$ can only have an even J value, whereas para-D$_2$ can only have an odd J value, where J is the rotational quantum number. Conversion between ortho and para states is strongly forbidden, and therefore $\Delta J = \pm 2$ (Mattera, 1992). Scattering was carried out with the QMS normal to the sample, and the sample at 48° to the beam direction.

Figure 8.18 shows the ToF spectra obtained for both the direct (Figure 8.18a) and the scattered (Figure 8.18b) beams for the same distance with both the nozzle and sample at 300 K. The average velocities for these beams are 2076 m s$^{-1}$ and 2032 m s$^{-1}$ for the direct scattered beams respectively. The actual velocity after scattering from the sample can be calculated using the distances and times related to before and after the scattering event. This gives an actual scattered velocity of 1481 m s$^{-1}$. Converting the velocities to kinetic energy ($E = \frac{1}{2}mv^2$) gives an energy drop of 46 ± 2 meV, corresponding to approximately 12B or a transition of $J = 0 \rightarrow 3$. However, this transition is not possible as $\Delta J = 3$, implying
a change in nuclear spin which is forbidden. An alternative to the transfer of translational kinetic energy to rotational energy is that the molecule is temporarily sticking to the surface and then desorbing at thermal energies equivalent to that of the sample surface, also known as trap-desorption. In this case with both the sample and nozzle at 300 K this would require a residence time (τ) of 7.9 μs.

![Graph](image_url)

**Figure 8.18:** ToF spectra of a D₂ molecular beam (a) direct to QMS over a known distance, (b) scattered from a UO₂ sample with the same total distance,

This was repeated with a variety of surface and nozzle temperatures, which are summarised in Table 8.3, where $E_i$ is the average energy of a molecule in the incident beam, $E_s$ is the average energy of a molecule in the scattered beam and $\Delta E$ is the change in energy. The table shows that $E_s$ does not appear to change with $T_N$, in that the energies for all experiments when the sample is at 300 K all appear to be the same after scattering, even though $T_N$ varies between 300 K and 700 K. This correlation implies that there is some extent of thermal equilibration occurring, in other words a form of trapped desorption. Another
point of interest is that all values of $\tau$ are similar (i.e. around $10 \pm 5 \mu s$) even with thermal energies above 800 K. This may be an effect of the large mass difference between $\text{D}_2$ (4 amu) and U (238 amu). $\text{H}_2$ has been shown to adsorb onto the surface of oxidised U by Balooch and Hamza (1996). TPD shows that this desorbs between 350 K and 650 K and therefore there may be different scattering mechanisms with changing sample temperature; where at lower temperatures the $\text{D}_2$ is scattering off D already adsorbed onto the surface whereas at higher temperatures there is only the UO$_2$ surface.

Table 8.3: Table showing the parameters for inelastic scattering and trap-desorption for D$_2$ on UO$_2$.

<table>
<thead>
<tr>
<th>$T_N$ (K)</th>
<th>$T_S$ (K)</th>
<th>$E_i$ (meV)</th>
<th>$E_s$ (meV)</th>
<th>$-\Delta E$ (meV)</th>
<th>$-\Delta E/B$</th>
<th>$\tau$ (µs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>300</td>
<td>91</td>
<td>46</td>
<td>45</td>
<td>12.15</td>
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<td>72</td>
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<td>-7.05</td>
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<td>300</td>
<td>169</td>
<td>52</td>
<td>117</td>
<td>31.16</td>
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<tr>
<td>700</td>
<td>300</td>
<td>215</td>
<td>42</td>
<td>173</td>
<td>46.38</td>
<td>14.1</td>
</tr>
</tbody>
</table>

### 8.4.3 Water

Similarly to $\text{H}_2$ there was a low signal compared to the background noise for the $\text{H}_2\text{O}$ data, therefore $\text{D}_2\text{O}$ was used. A UO$_2$ sample was exposed to 40 L of $\text{D}_2\text{O}$ at 190 K, and then investigated using TPD at $1 \text{ K s}^{-1}$, shown in Figure 8.19. One feature is present within the $\text{D}_2\text{O}$ trace at 240 K, this is similar to the feature observed on clean U metal at 270 K (Figure 8.13). No features are present in the $\text{D}_2$ trace, implying that $\text{D}_2\text{O}$ does not dissociate on the UO$_2$ surface, unlike on metallic U; this lack of dissociation is typical for a well ordered metal oxide surface (Henderson, 2002). The intensity of the feature within the TPD is an order of magnitude lower than that of the clean metal, implying that the adsorption of $\text{H}_2\text{O}$ is inhibited by the oxide. This is consistent with the model proposed by Winer et al. (1987).

In this model the only reactions that can occur is between $\text{H}_2\text{O}$ (or $\text{D}_2\text{O}$) and either lattice or interstitial O$^{2-}$, shown in equation (8.2) for $\text{D}_2\text{O}$. The reverse of this reaction is likely to be the source of the $\text{D}_2\text{O}$ in Figure 8.19.

$$\text{D}_2\text{O} + \text{O}^{2-} \rightarrow 2 \text{OD}^-$$  \hspace{1cm} (8.2)

The SP of $\text{D}_2\text{O}$ on UO$_2$ was observable using the modified King-Wells method as described in § 3.9.2. Figure 8.20 shows the sticking probability against time. The initial sticking probability of 0.9 is surprisingly high in comparison with previous work by Balooch and Hamza (1996), where it was found to be 0.001 at room temperature. It is likely that this discrepancy is due to the differences in surface temperature; this work has used a temperature of 190 K which is very close to the temperature required to form permanent ice multilayers (Winer et al., 1987). In other words, the high sticking probability is related to the formation of transient multilayers. Ideally the $\text{D}_2\text{O}$ mass spectrometry signal would have been calibrated to pressure, however there was insufficient time for this process; which also means that it was not possible to carry out Kisliuk analysis or measure the sample dose.
Figure 8.19: TPD output of a UO$_2$ sample exposed to 40 L of D$_2$O with a heating rate of 1 K s$^{-1}$.

Figure 8.20: Sticking probability of D$_2$O on UO$_2$, with a sample temperature of 190 K.
Isothermal desorption has also been carried out; the D$_2$O signal decay against time from this is shown in Figure 8.21a for a sample temperature of 220 K, where \( t=0 \) s is the time at which the beam was removed from the sample surface. The D$_2$O trace has been fitted with an exponential decay, modelling a first order process for desorption, with a rate constant of 0.21 s$^{-1}$. A rate constant of 0.07 s$^{-1}$ has also been obtained with the sample at 190 K, the trace and exponential decay fit for which are shown in Figure 8.21b. Although the dose could not be measured, the sample was exposed multiple times with similar results, implying that the system was indeed in equilibrium.

Figure 8.21: Isothermal desorption of D$_2$O from UO$_2$ with a sample temperature of (a) 220 K, (b) 190 K.
8.5 Conclusions

This chapter has described the preparation of clean U and UO$_2$ surfaces. It has been shown that annealing U causes surface segregation of oxygen and carbon to form a mixed metal/oxide/oxycarbide surface at lower temperatures than previously observed. A layer of UO$_2$ was formed on U by exposure to O$_2$ at an elevated temperature.

The interaction of H$_2$, H$_2$O and O$_2$ with U and UO$_2$ were studied. Due to background gases and low signal intensity, the hydrogen was substituted with deuterium for the oxide surface. H$_2$ and H$_2$O on U both show dissociative adsorption modes, in agreement with previous studies. The adsorption and reaction of O$_2$ with U was modelled using Kisliuk kinetics. The data indicated that intrinsic adsorption was favoured over extrinsic adsorption with the ratio being about 2.5.

On UO$_2$, the interaction with D$_2$ was studied inelastically. The data was consistent with two models, the conversion of incident kinetic energy to rotational energy or the trap-desorption of D$_2$ on the surface. The more likely scenario was reasoned to be trap-desorption due to the invariance of the scattered kinetic energy with nozzle temperature. D$_2$O showed a high initial sticking probability which was attributed to multilayer formation. However, both isothermal desorption and TPD indicated that this was a short lived state at the temperatures explored here (190 K to 220 K).
Chapter 9

Conclusions

The objectives of the work presented within this thesis were to:

1. Install and commission a surface science instrument, known colloquially as the inorganic surface science capability.

2. Investigate the early stages of LiH ageing.

3. Further the understanding of the adsorption and reaction of H$_2$ on U and UO$_2$.

4. Further the understanding of the adsorption and reaction of H$_2$O on U and UO$_2$.

5. Further the understanding of the adsorption and reaction of O$_2$ on U.

The commissioning work on the ISSC was presented in Chapter 4. This chapter showed the FAT and SAT that was carried out on analytical equipment as part of the commissioning, it also discussed the required calibration work which gives additional meaning to data acquired using the system. The system passed the majority of tests to specification and those that were not passed were deemed to be satisfactory for use. The molecular beam was also characterised, for example, the drift velocity (1758 m s$^{-1}$), Mach number (19) and angular divergence (0.5° for the 1 mm collimator) were determined for a He beam. The data obtained indicated that the performance of the molecular beam system was comparable with similar systems reported in the literature. This chapter also described software developed to increase system automation and therefore the usability of the system. For example, stage control allowed for reproducible sample positioning, which is central for all experimental work performed using the instrument.

This system has had both positives and negatives relating to its use within this work. The molecular beam generation system has performed well throughout. Another advantage is the range of techniques available within a single system, however one issue with this is that the techniques cannot be fully optimised due to geometric constraints from other techniques. The transfer system to move samples between chambers has regularly broken, such that the locking mechanism no longer engages with the sample holder. There are a few ways through which this could be improved; the first would be to use an automated central distribution chamber, or to use multiple smaller instruments with a vacuum suitcase to transfer between systems without atmospheric exposure. Both of these would also allow work to be carried out on multiple samples in parallel, whereas the current design does not allow for this due
CHAPTER 9. CONCLUSIONS

to its linear transfer. The film deposition could be improved through the use of a quartz crystal microbalance to measure the amount of material deposited without relying on flux measurements. Another major improvement which could be made to the system would be to fit a monochromated X-ray source to remove addition X-ray lines. This would allow for the Li 1s to be visible against Ni without competing with a Kα3 satellite.

The early stages of LiH ageing was investigated using both bulk and thin film samples of LiH in Chapters 5 to 7. Four reactions were identified within the thermal ageing of bulk LiH:

- \( \text{LiOH} + \text{LiH} \rightarrow \text{Li}_2\text{O} + \text{H}_2 \) (solid state reaction)
- \( \text{LiOH} \rightarrow \text{Li}_2\text{O} + \text{H}_2\text{O} \) (LiOH decomposition)
- \( 2\text{LiH} + \text{H}_2\text{O} \rightarrow \text{Li}_2\text{O} + 2\text{H}_2 \) (LiH hydrolysis)
- \( 2\text{LiH} \rightarrow 2\text{Li} + \text{H}_2 \) (LiH sublimation)

The activation energies have been determined as 63.9 kJ mol\(^{-1}\), 96.4 kJ mol\(^{-1}\) and 90.5 kJ mol\(^{-1}\) respectively for the reactions above with the exception of the sublimation; these are in agreement with previous studies. Fitting of the TPD peaks to known rate-limiting mechanisms has provided the most likely mechanisms as \( F1 \) (nucleation limited) for LiOH decomposition and \( D3 \) (3D diffusion limited) for the solid state reaction. Heating has been shown to cause blisters to form on the surface of the LiH sample, believed to be formed either through the relief of sub-surface pressure build-up or from the spallation of LiOH due to differences in density and lattice parameter with Li\(_2\)O.

Li films were grown \textit{in-situ} through deposition onto a Ni(100) substrate. Deposition flux was calibrated to overlayer thickness using LEED. These films were then converted to various Li compounds. LiH was formed by exposure of the Li film to 1 mbar of H\(_2\). Li\(_2\)O was generated using a pressure of 1 \( \times 10^{-3} \) mbar of O\(_2\). Exposing the Li film to H\(_2\)O was attempted for the formation of LiOH, however this formed a LiH/Li\(_2\)O/LiOH trilayer system. A LiOH film was formed by converting to Li\(_2\)O before exposing to H\(_2\)O. These compounds were necessary precursors for the study of the hydrolysis of LiH thin films.

LiH films exposed to an excess of H\(_2\)O exhibited additional features in XPS and TPD which have been attributed to H\(_2\)O adsorbed on the surface. Kissinger analysis did not provide meaningful values of \( E_a \) for films, implying that different mechanisms are likely to be rate-limiting, compared to those for bulk. This was confirmed by modelling, which showed that the \( A3 \) (3D nuclei growth limited) mechanism applied for LiOH decomposition and LiH hydrolysis, where it was \( F1 \) within bulk material. The combination of TPD of bulk samples and XPS of thin films have shown that the Li\(_2\)O overlayer is fundamentally different from native Li\(_2\)O. It is likely that the Li\(_2\)O is of variable crystallinity due to the large lattice mismatch with LiH; this changes its reactivity towards further hydrolysis.

This work on LiH did not include any molecular beam experiments and therefore this is a potential area for future work. For example, the sticking probability and inelastic scattering parameters could be obtained for H\(_2\)O on LiH. Reactive scattering could also be performed on this system, for example, the dynamics of H\(_2\) evolution during hydrolysis could be probed. As outlined in this thesis, the comparison between bulk and thin film LiH allows for greater insight into corrosion phenomena, thus this comparison could be extended to molecular beam experiments in future work.
The reactions between U and UO$_2$ with various gases (O$_2$, H$_2$ and H$_2$O) were investigated in Chapter 8. Annealing a clean U surface to a temperature of 575 K was shown to cause surface segregation of both sub-stoichiometric UO$_{2-x}$ and UO$_x$C$_y$. A similar effect has been observed on UO$_2$ surfaces. Dissociative adsorption was observed for H$_2$ and H$_2$O on U, indicating that U behaves in a similar fashion to transition metals. The adsorption of O$_2$ onto U caused irreversible surface oxidation and was modelled with Kisliuk kinetics which showed that intrinsic adsorption is 2.5 times more likely than extrinsic adsorption. For the temperatures explored (190 K to 220 K), D$_2$O exhibited a high initial sticking probability on UO$_2$, attributed to the formation of short lived (of the order of seconds) ice multilayers. This could not be analysed using Kisliuk analysis as the system was not fully calibrated, ideally this would be calibrated in the future to enable such measurements.

D$_2$ appeared to exhibit trap-desorption, with a residence time of under 10 µs, however further investigation would be required to confirm that this is the case, rather than the conversion of kinetic energy to rotational energy. The most straightforward method to distinguish between trap-desorption and inelastic scattering is to obtain the angular distribution of the scattered molecules. A trap-desorption process should give a cosine angular distribution (cos$^n$θ), whereas for inelastic scattering it would be lobular in the specular direction. However, rotational state distributions are known to broaden angular distributions which may make determination of the interaction mode unclear. Therefore state-resolved measurements (e.g. laser-induced fluorescence and IR excitation) would be required for an unambiguous determination of the interaction dynamics.

The work on U described here could be expanded to include explicit studies of UC inclusions on U or UO$_2$ surfaces. It has recently been shown that UC inclusions form preferential hydriding sites (Harker et al., 2013). It was argued that the inclusions disrupt the passivating oxide layer, thereby allowing easier passage of hydrogen into the bulk metal. Surface science is well suited to provide further information to support or rebut this hypothesis. For example, TPD and XPS measurements would provide a wealth of information regarding the interaction of H$_2$ with these surfaces. Another extension of the hydride work could be to determine the behaviour of H$_2$ on different oxide stoichiometries.

Thin films of U compounds could be used in similar experiments; these specimens would be of high purity and also allow for control of surface stoichiometry. Previous work on thin films has focussed solely on characterisation, leaving gas reactions a relatively unstudied topic. As shown in this thesis, thin films of LiH has revealed much about the hydrolysis reaction and therefore the same techniques can be directly applied to study gas reactions on U thin films.

A further area in which both the LiH and U work could be expanded is through the use of single crystal samples. These would enable structural experiments involving LEED and HAS that would expand upon compositional measurements and reaction kinetics determined here. Furthermore, angular distributions of reaction products can be obtained with a higher degree of fidelity than on polycrystalline crystalline. The lack of grain boundaries in single crystal specimens would permit the unambiguous determination of their role in the diffusion of H$_2$ and H$_2$O in LiH hydrolysis and dry ageing.
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REFERENCES


REFERENCES


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Appendix A

Reaction Mechanism Models

Equations for $f(\alpha)$ and $g(\alpha)$ for a variety of reaction mechanisms. Equations taken from Dinh et al. (2001).

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Mechanism</th>
<th>$f(\alpha)$</th>
<th>$g(\alpha)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>F1</td>
<td>Mampel unimolecular law</td>
<td>$1 - \alpha$</td>
<td>$- \ln(1 - \alpha)$</td>
</tr>
<tr>
<td>A1</td>
<td>Prout-Tompkins branching nuclei</td>
<td>$\alpha(1 - \alpha)$</td>
<td>$\ln \left( \frac{\alpha}{1 - \alpha} \right)$</td>
</tr>
<tr>
<td>A2</td>
<td>2D Avrami-Erofeev nuclei growth</td>
<td>$2(1 - \alpha)[- \ln(1 - \alpha)]^{\frac{3}{2}}$</td>
<td>$[-\ln(1 - \alpha)]^{\frac{3}{2}}$</td>
</tr>
<tr>
<td>A3</td>
<td>3D Avrami-Erofeev nuclei growth</td>
<td>$3(1 - \alpha)[- \ln(1 - \alpha)]^{\frac{3}{2}}$</td>
<td>$[-\ln(1 - \alpha)]^{\frac{3}{2}}$</td>
</tr>
<tr>
<td>D1</td>
<td>Parabolic law</td>
<td>$\alpha^{-1}$</td>
<td></td>
</tr>
<tr>
<td>D2</td>
<td>2D diffusion</td>
<td>$[- \ln(1 - \alpha)]^{-1}$</td>
<td>$(1 - \alpha) \ln(1 - \alpha) + \alpha$</td>
</tr>
<tr>
<td>D3</td>
<td>3D spherical diffusion (Jander)</td>
<td>$(1 - \alpha)^{\frac{2}{3}}[(1 - \alpha)^{\frac{2}{3}} - 1]^{-1}$</td>
<td>$\frac{3}{2}[1 - (1 - \alpha)^{\frac{2}{3}}]^2$</td>
</tr>
<tr>
<td>D4</td>
<td>3D diffusion (Brounshtein-Ginstling)</td>
<td>$[(1 - \alpha)^{\frac{2}{3}} - 1]^{-1}$</td>
<td>$\frac{3}{2} \left[ 1 - \frac{2\alpha}{3} - (1 - \alpha)^{\frac{2}{3}} \right]$</td>
</tr>
<tr>
<td>R1</td>
<td>1D phase boundary movement</td>
<td>Constant</td>
<td>$\alpha$</td>
</tr>
<tr>
<td>R2</td>
<td>2D phase boundary movement</td>
<td>$\alpha^{\frac{2}{3}}$</td>
<td>$2[1 - (1 - \alpha)^{\frac{2}{3}}]$</td>
</tr>
<tr>
<td>R3</td>
<td>3D phase boundary movement</td>
<td>$\alpha^{\frac{2}{3}}$</td>
<td>$3[1 - (1 - \alpha)^{\frac{2}{3}}]$</td>
</tr>
</tbody>
</table>

Power law

$(1 - \alpha)^n$
Appendix B

Vacuum Schematic of ISSC

Image is ©VACGEN Ltd. Reproduced with permission.
Appendix C

Time of Flight Fitting Script

```
%% TOF FITTING
% Determines beam parameters for ToF spectra using peak fitting.
% Can be used for single or multi peak spectra, and for pure
% or mixed beams.

clear all
close all
clc % clear saved variables, figures and workspace
addpath('C:\xxxx') % Path of data

%% Variables
a = 1; % Normalisation Constant
t = 1E-7:1E-7:1E-3; % time range (s) for TOF equation
R = 8.315; % Gas Constant (JK^(-1)mol^(-1))
beam_width = 1E-3; % width of beam (estimate)
slit_radius = 0.03925; % slit radius from centre of chopper
slit_width = 1E-3; % slit opening width
l = 0.325; % distance from chopper to 0 degree
distance = (2*sqrt(152.7^2+181.9^2))/1000; % distance
between 0 and 180 degree peaks
MHe = 0.004; % mass of He (kg/mol)
gammaHe = 5/3; % gamma of He

%% Load Data for 0 degrees
[filename,pathname] = uigetfile('*.txt','Choose 0 degree file')
; % Choose the 0 degree data
cd(pathname); % Change to correct directory
formatspec = '%6f%f[^\n\r]'; % Format of ToF Data
filenamefull = [pathname,filename]; % Generates filename with path
fileID = fopen(filenamefull,'r'); % Opens file
dataArray = textscan(fileID,formatspec,'Delimiter',',','WhiteSpace',',','EmptyValue',NaN,'ReturnOnError',false);
% Reads in data from file
```
fclose (fileID); % Closes file
Data_Time0 = dataArray{1}; % Reads time data from file
Data_Intensity0 = dataArray{2}; % Reads intensity data from file

for i = length(filename):-1:length(filename)-3 % Loop removes extension from filename for saving
    filename(i)=
end

filename0 = [pathname, filename,' fitted.xls']; % Generates name and location for saved data
clearvars filename pathname formatspec fileID dataArray ans filenamefull; % Clears variables no longer needed

%% Select Baseline and find peaks for 0 degrees
Data_Time0 = Data_Time0*1E-3; % Convert time to seconds from ms
iterations = 1000; % Number of iterations to carry out smoothing for
uiwait(msgbox('Define the baseline of the spectrum'));
figure(1)
plot(Data_Time0, Data_Intensity0) % Plots data
[~, baseline0] = ginput(1); % Click on baseline
close(1) % Closes figure

Data_Intensity0 = Data_Intensity0 - baseline0; % Remove baseline
Data_Intensity0 = smooth2(Data_Intensity0, iterations, Data_Time0); % Smooth data

plot(Data_Time0, Data_Intensity0) % Plots smoothed data
peaks0 = peaksnum(); % GUI to request number of peaks in spectrum.

x0 = Data_Time0;
y0 = zeros(length(Data_Time0),1);
rough_max = max(Data_Intensity0); % Maximum intensity, used for normalisation.
Data_Intensity0 = Data_Intensity0/rough_max; % Normalisation to max = 1
peak_x_coordinate0 = zeros(peaks0,1);
ii = 1;

for i = 1:peaks0 % Loop searches for peaks
    while Data_Intensity0(ii) < 0.9
APPENDIX C. TIME OF FLIGHT FITTING SCRIPT

```
ii = ii + 1; % Ignores values until intensity is greater than 0.9

while Data_Intensity0(ii) < Data_Intensity0(ii+1)
    ii = ii + 1; % Checks if peak is still increasing
end

peak_x_coordinate0(i) = ii; % Saves time value at which peak occurs
y0(ii) = 1; % Sets y at peak to 1 to give an impulse function

while Data_Intensity0(ii) > 0.1
    ii = ii + 1; % Ignores values until intensity is less than 0.1
end

Data_Intensity0 = Data_Intensity0 / max(Data_Intensity0(peak_x_coordinate0)); % Renormalise to the value at peak.

figure(1)
plot(y0) % Plot impulse function of found peaks and smoothed data together
hold on
plot(Data_Intensity0)
hold off

%% Load Data for 180 degrees - This is a repeat of 0 degree

[filename,pathname] = uigetfile('*.txt','Choose 180 degree file ');
formatspec = '%6f%f%[\n\r];
filenamefull = [pathname,filename];
fileID = fopen(filenamefull,'r');
dataArray = textscan(fileID, formatspec, 'Delimiter', '', ', ', 'WhiteSpace', '', ', 'EmptyValue', NaN, 'ReturnOnError', false);
close(fileID);
Data_Time180 = dataArray{1};
Data_Intensity180 = dataArray{2};
for i = length(filename):-1:length(filename)-3
```
filename(i)=[];
end

filename180 = [pathname,filename,' fitted.xls'];
clearvars filename pathname formatspec fileID dataArray ans filenamefull;

%% Select Baseline and Peaks for 180 degrees
Data_Time180 = Data_Time180*1E-3; %convert to seconds
uiwait(msgbox('Define the baseline of the spectrum'));
figure(2)
plot(Data_Time180,Data_Intensity180)
[~,baseline180] = ginput(1);
Data_Intensity180 = Data_Intensity180 - baseline180;
Data_Intensity180 = smooth2(Data_Intensity180,iterations, Data_Time180);
plot(Data_Time180,Data_Intensity180)
peaks180 = peaksnum();

x180 = Data_Time180;
y180 = zeros(length(Data_Time180),1);
rough_max180 = max(Data_Intensity180); % rough max to allow routine to find peak between 0 and 1
Data_Intensity180 = Data_Intensity180/rough_max180;
peak_x_coordinate180 = zeros(peaks180,1);
ii = 1;

for i = 1:peaks180
    while Data_Intensity180(ii) < 0.9 %this values is dataset defined from noise level. This value has to be outside the noise
        ii = ii + 1;
    end
    while Data_Intensity180(ii) < Data_Intensity180(ii+1)
        ii = ii + 1;
    end
peak_x_coordinate180(i) = ii;
y180(ii) = 1;

while Data_Intensity180(ii) > 0.1
    ii = ii + 1;
end

Data_Intensity180 = Data_Intensity180 / max(Data_Intensity180(peak_x_coordinate180));
figure(2)
plot(y180)
hold on
plot(Data_Intensity180)
hold off

%% Beam Parameters

if peaks0 > 1 % Parameters can only be calculated if there is more than one peak.

    period = (x0(peak_x_coordinate0(peaks0))-x0(peak_x_coordinate0(1)))/(peaks0-1); % Calculate period of chopper as average over spectrum.
    frequency = 1/period; % Convert period to frequency
    disp(['Chopper Frequency = ',num2str(frequency),' Hz']);
end

else % If only one peak then frequency must be defined by user

    frequency = input('What is the frequency of the chopper [Hz ]?');

end

Pure = PureBeam; % GUI to ask if beam is pure He

if Pure == 1 % If beam is pure He then mass and gamma are taken as He.

    M = MHe;
    gamma = gammaHe;
else

end
APPENDIX C. TIME OF FLIGHT FITTING SCRIPT

[MS, gammaS, conc] = SeededBeam; % GUI to determine concentration of beam if not pure He
conc = conc/100; % Convert to decimal from percentage
M = conc*MS + (1-conc)*MHe; % Calculate weighted average of mass
gamma = conc*gammaS + (1-conc)*gammaHe; % Calculate weighted average of gamma

end

%% Gate Function and TOF distribution
T_start = 1;

vd = distance/(Data_Time180(peak_x_coordinate180(1)) - Data_Time0(peak_x_coordinate0(1))); % Calculate drift velocity using d/t

disp(['Drift velocity = ', num2str(vd), ' m/s']) % Display drift velocity to user

T_nozzle = (vd^2*M*(gamma-1)) / (2*R*gamma); % Calculate nozzle temperature from drift velocity

disp(['Nozzle Temperature = ', num2str(T_nozzle), ' K']) % Display nozzle temperature to user

[gate] = Gating_Function_circular_trapazodial(x0, frequency, beam_width, slit_radius, slit_width); % Function to calculate gate function for beam parameters

yconv0 = conv(y0, gate); % Convolution of delta functions with gate for 0 degrees

yconv0 = yconv0/max(yconv0); % Normalise to 1

yconv180 = conv(y180, gate); % Convolution of delta functions with gate for 180 degrees

yconv180 = yconv180/max(yconv180); % Normalise to 1

 [~,j] = max(gate);

for i = 1:length(yconv0) % Loop corrects times within the matrix
    if i + j <= length(yconv0) % Ensures requested index is within the array
        yconv0(i) = yconv0(j+i);
    else
        yconv0(i) = 0;
    end

yconv0 = yconv0(1:length(y0)); % Ensures length of matrix is correct

end

figure(1)
plot(x0,yconv0) % Plot convolution and data together
hold on
plot(Data_Time0,Data_Intensity0,'-r')
hold off

for i = 1:length(yconv180) % Loop corrects times within the matrix
  if i + j <= length(yconv180) % Ensures requested index is within the array
    yconv180(i) = yconv180(j+i);
  else
    yconv180(i) = 0;
  end
end
yconv180 = yconv180(1:length(y180)); % Ensures length of matrix is correct

figure(2)
plot(x180,yconv180) % Plot convolution and data together
hold on
plot(Data_Time180,Data_Intensity180,'-r')
hold off

%% Convolution of Delta + Gate + TOF for 0 degrees
iterations = 250;
Chi_matrix = zeros(2,iterations); % Setting up matrix for chi values
T = linspace(1,50,iterations); % Creates a vector of beam temperatures between 1 and 50 K
x_fit_index0 = zeros(2,peaks0);

ii=1;
for i = 1:peaks0 % Determines data to be used for fitting if noise allows from 0.2 on raising edge to 0.7 on trailing edge. Does not fit well to noise or pump tails.
while Data_Intensity0(ii) < 0.2  % This values is defined from noise level.
    ii = ii + 1;
end

x_fit_index0(1,i) = ii;
while Data_Intensity0(ii) < Data_Intensity0(ii+1)
    ii = ii + 1;
end

while Data_Intensity0(ii) > 0.7
    ii = ii + 1;
end

x_fit_index0(2,i) = ii;
while Data_Intensity0(ii) > 0.1;
    ii = ii + 1;
end
end

for i = 1:iterations
    [y2conv0] = Gate_Convolution2(yconv0,x0,M,1,T(i),R,vd,y0);
        % Generates a convolution of Gata and ToF fit for a set beam temperature
    [Chi] = Chi_squared(y2conv0,Data_Intensity0,x_fit_index0);
        % Determines the chi value for set beam temperature
    Chi_matrix(1,i) = Chi;  % Saves chi values for later comparison
end

 [~,index] = min(Chi_matrix(1,:));    % Determines lowest chi value
T_best0 = T(index);  % Beam temperature which matches lowest chi value
disp(['Beam Temperature (0 degrees) = ',num2str(T_best0),' K'])
    % Displays beam temperature of best fit to user
[y2conv0] = Gate_Convolution2(yconv0,x0,M,l,T_best0,R,vd,y0);

% Regenerates fit for determined beam temperature

figure(1)
plot(Data_Time0,Data_Intensity0,:k') % Plots data and fit together
hold on
plot(x0,y2conv0,'-g')
hold off

y2conv0 = y2conv0.'; % Transposes the fit data, required for saving

%% Convolution of Delta + Gate + TOF for 180 degrees - This is a repeat of 0 degree

x_fit_index180 = zeros(2,peaks180);

ii=1;
for i = 1:peaks180
    while Data_Intensity180(ii) < 0.2
        ii = ii + 1;
    end
    x_fit_index180(1,i) = ii;
    while Data_Intensity180(ii) < Data_Intensity180(ii+1)
        ii = ii + 1;
    end
    while Data_Intensity180(ii) > 0.7
        ii = ii + 1;
    end
    x_fit_index180(2,i) = ii;
    while Data_Intensity180(ii) > 0.1;
        ii = ii + 1;
    end
end
for i = 1:iterations
    [y2conv180] = Gate_Convolution2(yconv180,x180,M,1+distance,
        T(i),R,vd,y180);
    [Chi] = Chi_squared(y2conv180,Data_Intensity180,
        x_fit_index180);
    Chi_matrix(2,i) = Chi;
end
 [~,index] = min(Chi_matrix(2,:));
 T_best180 = T(index);
 disp(['Beam Temperature (180 degrees) = ',num2str(T_best180),' K'])
 [y2conv180] = Gate_Convolution2(yconv180,x180,M,1+distance,
    T_best180,R,vd,y180);
 figure(2)
 plot(Data_Time180,Data_Intensity180,':k')
 hold on
 plot(x180,y2conv180,'-g')
 hold off
 y2conv180=y2conv180.';

 % Export data to .xls file
 Exporttitles = {'0 degree','0 degree','0 degree','180 degree','180 degree','180 degree';'Time (s)','Data','Fit','Time (s)','Data','Fit'};
 ExportData = [x0,Data_Intensity0,y2conv0,x180,Data_Intensity180,
    y2conv180];
 disp('Writing Data File')
 xlswrite(filename0,Exporttitles);
 xlswrite(filename0,ExportData,'Sheet1','A3');
 xlswrite(filename0,{'Drift Velocity','Nozzle Temperature','Beam Temp (0 deg)','Beam Temp (180 deg);vd,T_nozzle,T_best0,
    T_best180','Sheet1','H1'});
 disp('Completed')

 function [Intensity] = smooth2(Intensity,iterations,Time)
 for iter = 1:iterations
     for i = 1:length(Intensity)
         if i == 1
APPENDIX C. TIME OF FLIGHT FITTING SCRIPT

Intensity(i) = Intensity(i);
elseif i == length(Intensity);
Intensity(i) = Intensity(i);
elseif i == 2 || i == length(Intensity)-1;
Intensity(i) = (Intensity(i-1) + 3*Intensity(i) +
Intensity (i+1))/5;
else
Intensity(i) = (Intensity(i-2) + 3*Intensity(i-1) +
5*Intensity(i) + 3*Intensity (i+1) + Intensity(i+2))/13;
end
end

%%
%%
function [gate] = Gating_Function_circular_trapazodial(t,
frequency,beam_width,slit_radius,slit_width)

% Variables
beam_radius = beam_width/2; % radius of beam (estimate)
slit_length = 7.5E-3; % slit height
offset = 0;

% Calculated Variables
period = 1/frequency; % period of gate, also used as maximum
time value
velocity = 2*pi*slit_radius/period; % linear velocity of
slit

% Find projected areas
r1 = zeros(1,length(t));
r2 = zeros(1,length(t));
A1 = zeros(1,length(t));
A2 = zeros(1,length(t));

for i = 1:length(t)
    r = offset-(beam_radius-(t(i)*velocity)); % finds the
distance slit has travelled into the beam
    if r < 0
        r1(i) = -r; % replaces negative values
    else
        r1(i) = r;
    end
    if r1(i) > beam_radius % provides a limit of movement
        on end of beam
r1(i) = beam_radius;
end

theta = 2 * acos(r1(i)/beam_radius); % finds angle of segment caused by slit crossing beam
A1(i) = (beam_radius^2)/2 * (theta - sin(theta)); % finds area of circle segment from leading edge
if r1(i) > beam_radius
    A1(i) = 0; % provides minimum value of 0 on data
end
r2(i) = r-slit_width; % finds position of trailing edge
if r2(i) < 0
    r2(i) = -r2(i); % replaces negative values
end
theta = 2 * acos(r2(i)/beam_radius); % finds angle of segment caused by slit crossing beam
A2(i) = (beam_radius^2)/2 * (theta - sin(theta)); % finds area of circle segment from trailing edge
if r2(i) > beam_radius
    A2(i) = 0; % provides minimum value of 0 on data
end
clear R;

% Gate Function
gate = zeros(1,length(t));
[~,maxA1] = max(A1); % Finds peak positions
[~,maxA2] = max(A2);

for i = 1:length(t)
    if i <= maxA1 % up to leading edge reaching beam centre
        gate(i) = A1(i) - A2(i); % gate given by leading edge area minus trailing edge area
    elseif i<= maxA2 % up to trailing edge reaching beam centre
        gate(i) = pi * beam_radius^2 - A1(i) - A2(i); % gate given by full beam minus leading edge and trailing edge areas
    else % for rest of gate
        gate(i) = A2(i) - A1(i); % gate given by trailing edge area minus leading edge area
    end
end
gate

%%
function [y2conv] = Gate_Convolution2(yconv,x,M,l,T,R,vd,y)

f = TOF_equation(x,M,l,T,R,vd); % Function to calculate Boltzmann distribution.

f(1) = 0; % Replace infinity at t=0 with 0.
f = f'; % Transpose data
y2conv = conv(f,yconv); % Convolute ToF with gate
y2conv = y2conv/max(y2conv); % Normalise to 1
[~,j] = max(f);

for i = 1:length(y2conv) % Loop corrects times within the matrix
    if i + j <= length(y2conv) % Ensures requested index is within the array
        y2conv(i) = y2conv(j+i);
    else
        y2conv(i) = 0;
    end
end
y2conv = y2conv(1:length(y)); % Ensures length of matrix is correct

end
end
end

function [f] = TOF_equation(t,M,l,T,R,vd)

f1 = t.^( -4);
f2 = exp(-1*M*0.5*T^( -1)*R^( -1)*((l./t)-vd).^2);
f = f1.*f2; % Performs multiplication between elements of matrix rather than a matrix multiplication.
f = f/max(f); % Normalise peak to 1

end
end
end

function [Chi] = Chi_squared(fit_y,data_y,fit_idx)

fit_y = fit_y';
Total_Chis = abs(fit_y-data_y);
Chi = zeros(length(fit_idx)/2,1);

if length(fit_idx) == 1
    Chi = sum(Total_Chi(fit_idx(1):fit_idx(2)));
else
    for i = 1:2:length(fit_idx)
        Chi(i) = sum(Total_Chi(fit_idx(i):fit_idx(i+1)));  
        Find chi for each peak
    end
end

Chi = sum(Chi);

end
Appendix D

Publications

Published articles that have resulted from this work are referenced below and are reproduced with permission following this page.


Note: A versatile mass spectrometer chamber for molecular beam and temperature programmed desorption experiments

James P. Tonks,1,2,a) Ewan C. Galloway,2,b) Martin O. King,2 Gwilherm Kerherve,3,c) and John F. Watts1

1Department of Mechanical Engineering Sciences, University of Surrey, Guildford, Surrey GU2 7XH, United Kingdom
2AWE Plc, Aldermaston, Reading, Berkshire RG7 4PR, United Kingdom
3VACGEN Ltd, St. Leonards-On-Sea, East Sussex TN38 9NN, United Kingdom

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A dual purpose mass spectrometer chamber capable of performing molecular beam scattering (MBS) and temperature programmed desorption (TPD) is detailed. Two simple features of this design allow it to perform these techniques. First, the diameter of entrance aperture to the mass spectrometer can be varied to maximize signal for TPD or to maximize angular resolution for MBS. Second, the mass spectrometer chamber can be radially translated so that it can be positioned close to the sample to maximize signal or far from the sample to maximize angular resolution. The performance of this system is described and compares well with systems designed for only one of these techniques. [http://dx.doi.org/10.1063/1.4960083]

Molecular beam scattering (MBS) and temperature programmed desorption (TPD) are complementary techniques that have been widely applied to study interactions at the solid-gas interface. Both techniques have played a leading role in determining adsorption dynamics,1–11 surface structure and physics,4,4 and reaction kinetics.1,5–9 However, the experimental geometry demanded by MBS and TPD are entirely different. To provide increased time and angular resolution, MBS experiments are performed with the mass spectrometer positioned typically 10s of cm from the sample, with a narrow entrance aperture.10–12 Conversely, TPD requires the signal to be maximized; therefore, a short sample detector distance, typically 1 mm, with a large entrance aperture is required.13 Although TPD and MBS have been previously reported with the same detector, it has been at the expense of resolution.14,15 This has led to systems being designed either for MBS or TPD or having separate chambers for TPD and MBS. This note describes an instrument that allows TPD and high resolution MBS to be performed with the same mass spectrometer, in which the spectrometer can be moved along both the polar and radial axes and the width of the entrance aperture varied.

The system comprises five separate ultra high vacuum (UHV) chambers. There is a sample preparation chamber with standard cleaning facilities (Ar+ sputtering, annealing), gas dosing, and metal deposition. An analytical chamber is also present, which has the capability for x-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), Auger electron spectroscopy (AES), and scanning electron microscopy (SEM). The scattering, mass spectrometer, and molecular beam forming chambers are described below.

The molecular beam is generated through free-jet expansion of a high pressure gas through a converging nozzle into a low pressure background. The system described here uses a Gottingen type design, which utilizes a relatively low pressure within the nozzle with a faster pumping speed to provide the pressure difference. This type of source has been comprehensively described by many different authors.11,12,16–19 The molecular beam used here features a 50 µm quartz nozzle pressurized between 4 and 5 bars (typically 4.5 bar), with expansion and modulation stages pumped by 4600 and 3600 l s−1 baffled oil diffusion pumps, respectively. The base pressure of these chambers is 10−8 mbar. The beam is extracted by a 500 µm skimmer, situated between the expansion and modulation chambers. Separation between the nozzle and skimmer was adjusted to optimise beam intensity. During use, the pressure in the expansion chamber increases from 10−8 to 10−4 mbar at He flows of typically 2.5–3.3 mbar 1 s−1. The beam is mechanically chopped by a rotating disk to provide a pulsed beam of frequency up to 1000 Hz. The chopper has two different sized slits allowing for the beam to be chopped into ~1.5% or 50% pulses. The time of flight (ToF) of the beam is measured by a LED and a photodiode system, whereby a timing signal is sent to the mass spectrometer to begin detection. A time channel width of 0.1 µs was used. There is also a pneumatically driven shutter that allows the beam to be turned on or off in under 100 µs. A variety of collimating apertures are installed (4, 2, 1.5, 1, 0.5, and 0.2 mm), allowing for the size of the beam to be changed. The nozzle can be heated up to 1000 K, via resistive heating.

The 635 mm diameter scattering chamber achieves a base pressure of 2 × 10−10 mbar through a combination of a 1100 1 s−1 turbomolecular pump and a titanium sublimation pump. The sample manipulator in this chamber has 6 degrees of freedom (x, y, z, and rotations in polar and 2 azimuthal directions) and a temperature range of 180–1000 K. The quadrupole mass spectrometer (HIDEN...
HAL 7, 0–200 amu range) is housed in a separate, differentially pumped, chamber. Figure 1 shows a photograph of the mass spectrometer chamber, housed within the larger scattering chamber. The mass spectrometer chamber is mounted on a goniometer which is sealed from the scattering chamber with a PTFE ring. The rotational range of the mass spectrometer is ∼200°, driven by an externally mounted stepper motor with a step resolution of 0.01°. Radial motion of the chamber is enabled by a linear drive and bellows, providing about 240 mm of travel. The linear drive is operated by a stepper motor driven screwdriver with a step increment of 1 µm. The mass spectrometer housing contains different sized apertures (5, 3, 2, and 1 mm diameter) selectable by rotating the housing using a screwdriver mounted to a feedthrough, thereby allowing the aperture size to be selected for the experiment. To reduce the background signal in the mass spectrometer chamber, an additional 1300 l s⁻¹ magnetically levitated turbomolecular pump backed by a 70 l s⁻¹ turbomolecular pump and a titanium sublimation pump are fitted. The maximum and minimum distances between sample and mass spectrometer are 237 and 1 mm, respectively. Using a 237 mm sample-detector distance and a 1 mm entrance aperture, the angle subtended from the sample to detector is ∼0.24°. The selectable aperture diameter and linear motion are the two key design features allowing this mass spectrometer to perform TPD, He atom scattering (HAS), and MBS experiments.

The drift velocity (v_d) of the He beam was measured by noting the arrival time with the mass spectrometer positioned at 0° and 180° in the scattering chamber. For a nozzle temperature of 298 K (E = 64 meV), v_d is calculated as 1758 m s⁻¹, in agreement with theory. The monochromaticity of the beam was determined from the width of the He pulse. The obtained ToF signal was fitted to the convolution of mathematical description of the gate function and the velocity distribution through least squares fitting. The fit gives a velocity spread (∆v/v) of 8.4% ± 0.6%, corresponding to a beam temperature (T_B) of 2.8 ± 0.1 K and a Mach number of 19 ± 1, similar to other sources of this type.\(^{11,12,16–19}\) The beam number density was measured by calibrating the response of the mass spectrometer to a spinning rotor gauge. A high molecular beam flux is desirable as scattered molecular beams are typically of the order of a few percent of the incident beam flux. The intensity of a beam can be defined as the number density, the number of atoms per unit volume, N_0. Using a collimating aperture of 1 mm diameter and a He beam stagnation pressure of 4.5 bar, a pressure of 8.4 × 10⁻³ mbar was measured on the calibrated mass spectrometer, which gives N_0 = 2.04 × 10¹⁵ cm⁻³. The He atom flux, N_f, is the number of atoms impinging on a unit area per unit time, which was calculated using v_d to be 3.59 × 10²⁸ cm⁻² s⁻¹. Such a flux is of the order of 10 monolayer s⁻¹, which is appropriate for reactive scattering studies; however, it is at the upper end of the desired range and can be reduced through the use of a smaller collimating aperture or the 1.5% or 50% duty cycles on the chopper. The beam divergence was measured by rotating the mass spectrometer so that it crossed the beam. The divergence places a limit on the angular resolution achievable in an experiment. It was found that a 1 mm collimating aperture provided the best compromise between intensity and resolution. The angular resolution of the beam in this configuration is 1.44°.

A series of experiments were conducted to determine the experimental performance of this system. HAS was performed on an atomically clean Ni(100) surface at 295 K and is shown in Figure 2(a). The detector was placed at 237 mm from the sample with a 1 mm diameter entrance aperture. As Ni is a free electron metal, only the specular reflection was visible. The full width half maximum of the specular reflection of the He beam from Ni(100) surface was measured to be 1.91°. The

FIG. 1. Labelled photograph of the mass spectrometer chamber. Arrows show the axes of motion; (1) rotatable mass spectrometer housing; (2) linear drive; (3) linear drive socket; (4) linear drive screwdriver; (5) bellows; (6) goniometer.

FIG. 2. (a) Specular reflection of a He beam from a Ni(100) surface using an incidence angle of 47°. The black dots show the data and the red line shows the fitted Lorentz distribution. (b) TPD trace of m/z = 2 from H₂ adsorbed on Ni(100) at 200 K using a ramp rate of 0.5 K s⁻¹.
increase in the beam width with respect to the intrinsic width is probably due to the Debye-Waller effect.\textsuperscript{21}

A TPD profile was obtained for H\textsubscript{2} adsorbed on Ni(100) with a detector sample distance of 1 mm and an entrance aperture diameter of 5 mm. The sample was prepared by exposing Ni(100), cooled to 200 K, to 10 L (1 L = 10\textsuperscript{-6} Torr s) of H\textsubscript{2}. A TPD was then performed from 250 – 450 K at a ramp rate of 0.5 K s\textsuperscript{-1}. The result of this experiment is shown in Figure 2(b), a clear H\textsubscript{2} peak is evident at 300 K.\textsuperscript{22}

In addition, reactive scattering was performed by exposing the Ni(100) surface at 295 K to a He beam containing 1\% O\textsubscript{2}. The detector was placed normal to the sample surface at a distance of 35 mm, with an entrance aperture of 5 mm. An initial sticking probability of 0.58 was measured in this arrangement, comparable to literature.\textsuperscript{23}

The performance of a multi purpose mass spectrometer chamber has been described. A series of experiments verified the effective operation of the mass spectrometer. A sharp Ni(100) specular reflection was obtained for HAS; for TPD, H\textsubscript{2} desorption was characterised; and for reactive scattering, the sticking probability of O\textsubscript{2} was obtained. All experiments compare well with literature.

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Corrosion studies of LiH thin films
J.P. Tonks a, b, M.O. King b, *, E.C. Galloway b, J.F. Watts a

a Department of Mechanical Engineering Sciences, University of Surrey, Guildford, Surrey, GU2 7XH, UK
b AWE plc, Aldermaston, Reading, RG7 4PR, UK

HIGHLIGHTS

• Thin films of high purity LiH, LiOH and Li2O have been produced.
• O1s XPS shows separate peaks for LiOH and Li2O.
• LiH exposed to low H2O doses shows the presence of both LiOH and Li2O.
• With higher doses, chemisorbed H2O is observed.
• Decomposition kinetics of thin films are similar to previous bulk studies.

ABSTRACT

Thin films of LiH and its corrosion products were studied using temperature programmed decomposition (TPD), x-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES). Thin films were grown on Ni(100) in an ultra high vacuum system using an electron beam evaporator. Characteristic Li KLL AES peaks were identified for Li, LiH, Li2O and LiOH which facilitated identification of thin film composition. XPS of the O 1s region revealed three distinct chemical shifts which were attributed to Li2O, LiOH and chemisorbed H2O. We show that exposing LiH to very low H2O partial pressures results in formation of LiOH/Li2O domains on LiH. We also show that these XPS peaks can be linked to reaction mechanisms in the TPD profiles. TPD traces have been explicitly modelled to determine the activation energies of the reactions and compare favourably with previous measurements on bulk LiH samples.

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1. Introduction

Lithium hydride (LiH) has several attractive properties that have sustained interest in the material for well over a century. From a theoretical point of view, LiH is the lightest molecular solid and its simple electronic structure means that the material offers an excellent test of first principle calculations [1–6]. From a practical point of view, LiH finds application as a hydrogen storage material [7], a strong reducing agent [8] and in the nuclear industry as an efficient neutron moderator [9–11].

The labile reaction between LiH and H2O (equation (1a)) is of interest in the aforementioned practical applications due to its deleterious effects on the hydrogen density, increased oxygen content, and an increase in the presence of H2 gas when in a hermetic environment. Consequently, LiH hydrolysis has produced a wealth of literature which will now be summarised. The current understanding of LiH hydrolysis involves the formation of a trilayer system of LiOH/Li2O/LiH (bulk), which is formed by the reactions shown in equation (1) [8,12–16].

\[ 2\text{LiH} + \text{H}_2\text{O} \rightarrow \text{Li}_2\text{O} + 2\text{H}_2 \] (1a)

\[ \text{LiH} + \text{H}_2\text{O} \rightarrow \text{LiOH} + \text{H}_2 \] (1b)

\[ \text{Li}_2\text{O} + \text{H}_2\text{O} \rightarrow 2\text{LiOH} \] (1c)

Experimental evidence tends to favour the formation of a Li2O layer on LiH for low H2O exposures (up to 1 ML (monolayer)) [12,15,17]. Theory also points toward equation (1a) as the enthalpy of formation of this process is more favourable compared to equation (1b) [8,15]. The subsequent thermal decomposition of the trilayer LiOH/Li2O/LiH (bulk) system causes the release of H2O and H2. There are two proposed decomposition routes leading to the formation of a surface layer of Li2O only. These processes are given

* Corresponding author.
E-mail address: Martin.King@awe.co.uk (M.O. King).

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in equation (2) \[8,14,18,19\].

\[
\begin{align}
2\text{LiOH} & \rightarrow \text{Li}_2\text{O} + \text{H}_2\text{O} \\
\text{LiH} + \text{LiOH}/\text{Li}_2\text{O} & \rightarrow \text{Li}_2\text{O} + \text{H}_2 
\end{align}
\] (2a)

\[ (2b) \]

The key aspect of the current investigation with respect to previous work is that LiH specimens here are fabricated in a clean environment, within an ultra high vacuum (UHV) chamber. To the authors knowledge, all previous hydrolysis studies have involved powder or bulk specimens \[14,16,18–23\], the latter being produced from powder compaction. Given the high reactivity of LiH to moisture, it is inevitable that impurities will be incorporated within the bulk material (for LiH this is primarily O), even in dry Ar glovebox conditions \[24\]. The work presented here therefore has the advantage of sample purity and associated identification of chemical species over previous studies.

In order to investigate the fundamental chemistry of LiH hydrolysis we have produced pure LiH films and exposed them to known quantities of moisture. The use of thin films and model systems has been very successful in developing a mechanistic description of many surface processes, for example: heterogeneous catalysis \[25–29\], thin film photovoltaics \[30\] and in the growth of thin film semiconductors \[31\]. The work described here is a study of the fundamental interactions of H2O with pure LiH thin films and the nature of the solid state corrosion processes. This has been achieved with several surface sensitive probes (x-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES) and temperature programmed decomposition (TPD)) and provides interesting new insight into the hydrolysis phenomena.

2. Experimental

This work was carried out using an UHV system with a base pressure of 10−10 Pa which has been described in more detail elsewhere \[32\]. The system is equipped with XPS and AES for spectroscopic analysis, low energy electron diffraction (LEED) for surface crystallography and TPD for thermal analysis. Also present is an electron beam deposition source for metallic thin films and the analysis of the Ni Auger attenuation, the thickness of LiH films. In their recent paper, Guichard et al. \[17\] examined the fundamental interactions of H2O with pure LiH thin films. However a survey spectrum revealed that the C and O contamination was minimal at ~3 at%, whilst the adventitious O contamination was negligible. From the two point LEED calibration of the evaporation source and the analysis of the Ni Auger attenuation, the thickness of LiH films examined here were estimated to be 10–12 ML. XPS was unable to resolve the Li 1s emission due to its relatively low photoionisation cross-section, and close proximity to the Ni 3p emission. However a survey spectrum revealed that the C and O contamination was minimal at ~3 at%, whilst the adventitious O contamination could be resolved into LiO and Li2O components at a ratio of approximately 1:1 \[Fig. 2a\], with a Guassian/Lorentzian product peak shape (30% Guassian) and full width half maximum (FWHM) values of 2.18 and 1.43 eV, respectively. O contamination is likely to be from residual H2O in the H2 supply as the pressure during Li deposition was less than 2 × 10−7 Pa. The observation of co-existing Li2O and LiOH indicates that even at very low H2O exposures, the LiOH/Li2O/LiH trilayer corrosion model remains valid. The high reactivity of H2O with Li2O would suggest that H2O mobility on a Li2O surface is low, effectively promoting the formation of LiOH islands. In their recent paper, Guichard et al. \[17\] examined the hydrolysis of bulk LiH under low humidity. The authors concluded that no LiOH could be observed below a pressure of 1.3 Pa, which is produced from the electrolysis of demineralised H2O. Hydrolysis studies were performed by allowing H2O vapour through a leak valve, which in turn originated from a heated flask of freeze-pump-thawed demineralised H2O.

XPS and AES have been carried out on all of these thin film compounds in order to determine the surface composition. XPS was performed using an Al Kα (hv = 1486.7 eV) source and a concentric hemispherical analyser (CHA) to determine the kinetic energy of the emitted electron. A 2 point calibration of the XPS energy scale was done with the Ni 2p1/2 and the C 1s lines at 852.6 and 285.0 eV, respectively. AES used a 12 kV electron source operating with a sample current of approximately 10 nA and the same CHA as used for XPS. This surface chemical analysis was followed by TPD from ambient to 1000 K at a variety of heating rates to investigate the mechanisms and kinetic parameters of LiH hydrolysis and subsequent thermal decomposition. The heating rates used for TPD were 0.2, 0.5, 1 and 2 K s−1.

3. LiH thin films

After synthesis, the Li thin film was immediately characterised with AES and XPS. Previous work shows that the AES spectrum of Li exhibits a single transition, the Li KLL line at 53 eV which is shifted to between 38 and 41 eV for oxides \[20,38–42\]. This is sufficiently separated from the Ni MNN transition at 60 eV to allow it to be clearly observed. The black line in \[Fig. 1\] shows the Li KLL AES spectrum of a typical Li film; which shows a large Li signal at 53 eV in comparison to the attenuated Ni MNN signal at 60 eV \[33,38\]. For LEED patterns of Li greater than 0.55 ML, a gradual attenuation of the 5 × 5 pattern was observed, indicating three dimensional growth above this coverage.

Upon exposure of the Li film to 200 Pa H2, a shift in the KLL line from 53 eV to 44.8 eV (the red line in \[Fig. 1\]) is observed with minimal contamination of the sample by O and C. In order to obtain AES spectra for LiO, a Li film was exposed to 10−4 Pa O2 for 120 s. For LiOH, this LiO film was exposed to 10−4 Pa H2O for 360 s. The AES spectra for LiO and LiOH are shown in \[Fig. 1\]. The AES spectrum for Li2O shows a single transition at 42 eV close to what has been previously reported. To the authors knowledge no high resolution Li KLL data for LiOH has been reported. AES spectra for LiH, Li2O and LiOH were used throughout this study to corroborate XPS and TPD experiments. No structural information could be obtained from LEED patterns of Li films. This indicates that the films generated were either amorphous, three dimensional or a combination of both.

From the two point LEED calibration of the evaporation source and the analysis of the Ni Auger attenuation, the thickness of Li films examined here were estimated to be 10–12 ML. XPS was unable to resolve the Li 1s emission due to its relatively low photoionisation cross-section, and close proximity to the Ni 3p emission. However a survey spectrum revealed that the C and O contamination was minimal at ~3 at%, whilst the adventitious O contamination could be resolved into LiO and Li2O components at a ratio of approximately 1:1 \[Fig. 2a\], with a Guassian/Lorentzian product peak shape (30% Guassian) and full width half maximum (FWHM) values of 2.18 and 1.43 eV, respectively. O contamination is likely to be from residual H2O in the H2 supply as the pressure during Li deposition was less than 2 × 10−7 Pa. The observation of co-existing Li2O and LiOH indicates that even at very low H2O exposures, the LiOH/Li2O/LiH trilayer corrosion model remains valid. The high reactivity of H2O with Li2O would suggest that H2O mobility on a Li2O surface is low, effectively promoting the formation of LiOH islands. In their recent paper, Guichard et al. \[17\] examined the hydrolysis of bulk LiH under low humidity. The authors concluded that no LiOH could be observed below a pressure of 1.3 Pa, which is...
several orders of magnitude higher than the H2O pressure during experiments here, approximately 10^{-6} \text{ Pa}. This apparent contradiction can be explained by recognising that Guichard et al. used probes (x-ray diffraction and infra-red spectroscopy) which are not surface sensitive and therefore would not be able to resolve any trace hydroxide species. Indeed, the authors point out that the formation of LiOH is possible if its concentration were less than the detection limit of the techniques used.

Prior to LiH thin film experiments, two control experiments were performed, with the results displayed in the m/z = 7 trace of Fig. 3. In the first of which, Li metal was deposited onto the Ni(100) substrate and a TPD performed (magenta dashed line in Fig. 3). This resulted in a peak at 640 K, similar to that obtained by Engbæk [33]. The second control experiment involved performing a TPD on a crystalline bulk LiH specimen, formed through the compaction of powders in a die press. This TPD (dotted green line in Fig. 3) produced a single exponential feature beginning around 775 K which was ascribed to LiH sublimation and is close to the melting point of bulk LiH [43]. Sublimation was not monitored to completion due to the concern that excess Li may damage the mass spectrometer. TPD was then performed on the LiH thin film, the result of which is displayed in Fig. 3. Two peaks are evident from the TPD profile of H2. One of which is associated with a Li desorption peak at 825 K, which is close to the sublimation temperature of bulk LiH indicating a high degree of crystallinity. The lack of any features at 640 K in the LiH TPD indicates that there is no free Li metal and that the film has fully hydried. As a result of these observations we conclude that we have successfully synthesised a thin film of high purity LiH, in agreement with the assertion that the single Li KLL emission at 44.8 eV originates from LiH. The other H2 peak is a broad feature centred at 425 K which is not associated with water desorption, as evidenced by the lack of any peaks in the TPD trace of H2O. This result, combined with the O 1s XPS, indicates that very thin overlayers (less than 0.2 ML) of LiOH on LiH decompose to Li2O to produce H2 without H2O. There are two possible models that explain the lack of any evolved H2O. Firstly, the decomposition may be entirely through the solid state reaction, equation (2b). This assertion fits well with the fact that equation (2b) has been proposed to be mechanistically a solid state reaction, in which species must diffuse to the reaction interface [19,23]. An extremely thin layer will drastically reduce the distance over which chemically active species must travel before reacting and therefore would be favoured in thin layers. Also the temperature of the LiOH conversion to Li2O is in agreement with other studies on bulk LiH compacts, indicating similar decomposition kinetics [19]. Alternatively, there may be some H2O evolved from LiOH, and as the Li2O layer is extremely thin, the H2O will be entirely consumed by the LiH layer. Thermodynamically, the solid state reaction (equation (2b)) is more favourable than the thermal decomposition of LiOH to Li2O and H2O (equation (2a)). The heat of reaction of equation (2b) is \(-22.9\) \text{ kJ mol}^{-1} compared to \(-124\) \text{ kJ mol}^{-1} for equation (2a) at 298 K [8]. Given the more favourable thermodynamics, it is reasoned that the solid state reaction is the more probable reason for the lack of evolved H2O.

Additional characterisation of the decomposition process was provided in the O 1s XPS spectrum obtained after heating the film to 675 K, shown in Fig. 2b. In comparison to the XPS spectrum prior to heating (Fig. 2a), the XPS spectrum collected after heating to 675 K reveals that partial conversion of LiOH to Li2O has occurred, as the ratio is now approximately 1:4 where it was 1:1 previously. The residual LiOH component may be a result of incomplete conversion of LiOH to Li2O. However, as samples were allowed to cool after TPD for about an hour, it is not possible to discount that the small LiOH component is a result of H2O adsorption from the background gases in the chamber. The O 1s spectrum obtained after TPD is very similar to what has been observed for a Li2O pellet exposed to 0.8 L of H2O [44]. At this thickness of LiOH, it is probably better described as a \(-OH\) terminated Li2O surface. This is an apparent contradiction to previous studies that report heating to modest temperatures (for example 473 K [21] and 550 K [14]) resulted in the full conversion of LiOH to Li2O. Again, the techniques used in these studies lacked surface sensitivity and therefore it is likely that small amounts of LiOH were still present on the surface after heating but were not able to be observed.

The peak shape used for fitting was the same as prior to heating and the FWHM values here are 2.45 and 1.75 eV, respectively. This represents an increase of 0.28 \pm 0.01 eV in the FWHM upon heating. There is also an increase in binding energy of 0.7 eV in the Li2O component of the O 1s spectrum upon heating. A similar effect has been recently observed using Raman spectroscopy, in which extra features associated with the Li2O vibration emerged after heating [45]. In this paper, the authors argued that the appearance of multiple Li2O vibrations arise because there is a large lattice mismatch between LiH and Li2O. As the Li2O layer grows with heating, it is likely that to relieve the increasing interfacial strain, multiple domains of Li2O of varying crystallinity are required. Indeed cracking and blistering has been previously observed upon heating, attributed to stress relieving mechanisms [19]. Although these studies used bulk specimens, an increase in interfacial stress and a subsequent decrease in Li2O crystallinity is consistent with...
the O 1s spectra reported here. The O 1s peak associated with Li2O shifts to higher binding energy, indicating that there is less oxide-like character to the Li2O layer, in other words there are fewer O ions with a formal O2-/C0 charge, which is consistent with a decrease in crystallinity. In addition, an increase in the FWHM of the Li2O component upon heating is consistent with a decrease in the structural order of this layer. Deliberately exposing a LiH film to H2O produces a Li2O layer (Fig. 4b) that has an O 1s binding energy very close to that of the adventitious Li2O at room temperature, suggesting that the ambient temperature Li2O structure is independent of H2O dose, within the limits investigated in this work (0–450 L at a H2O partial pressure of 10⁻⁴ Pa).

4. LiH films exposed to H2O

In order to investigate the hydrolysis reaction further, LiH samples were then intentionally exposed to increased pressures of H2O to generate LiOH according to equation (1). LiH films were exposed to 450 and 45 L of H2O at a pressure of 10⁻⁴ Pa. O 1s XPS spectra of the 450 and 45 L films are presented in Fig. 4. Fig. 4 in comparison to Fig. 2a shows that the LiOH quantity has increased as expected with exposure to moisture. In comparison with the non H2O exposed LiH, the O 1s emission is approximately 10 times more intense in both spectra. An additional emission is observed at 535 eV in the film exposed to 450 L which is a binding energy typical for adsorbed H2O [46,47]. No Li2O is observed in this film which was presumed to be a result of attenuation by the H2O(ad) and LiOH layers, consistent with the proposed trilayer corrosion model, in which LiOH and adsorbed H2O form the outermost layers. With high H2O exposures, there is evidence of some charging related binding energy shifts in the O 1s features [48]. It is not possible to categorically determine if the H2O exists on the surface as a simple chemisorbed species or as LiOH·H2O, a compound known to exist for high partial pressures of H2O, 520 Pa [23]. However, as the sample was dosed at 10⁻⁴ Pa, it appears unlikely that there would be sufficient pressure to generate the formal LiOH·H2O compound and therefore suggests that the chemisorbed species is more likely. Indeed, a recent report has shown that exposure of a Li film at 100 K to 15 L of H2O results in the physisorption of H2O [49]. It is therefore plausible that LiOH could chemisorb H2O at higher temperatures.

The 450 and 45 L films were then studied using TPD (Figs. 5 and 6 respectively) and reveal H2O desorption features associated with the H2O(ad) and LiOH O 1s peaks. All TPDs performed left a residual Li2O layer (with a trace amount of LiOH) on the Ni substrate, as a result, the peak at 520 K was attributed to the decomposition of LiOH (equation (2a)) and desorption of H2O at 425 K. Although XPS has been used to characterise LiOH and Li2O corrosion layers in bulk LiH samples, to our knowledge, this is the first time that XPS has been used to study these decomposition/desorption reactions. O 1s binding energy assignments of corrosion and decomposition products are summarised in Table 1 and are similar to findings in

![Figure 2](https://example.com/fig2.png)

**Figure 2.** XPS spectra of the O 1s region of a LiH film on Ni(100). Two peaks are present, assigned as LiOH (red) and Li2O (green). (a) is from a LiH film as fabricated at ambient temperature and (b) is a LiH film after heating to 675 K. LiOH (red) has reduced and Li2O (green) has increased in comparison to the film as deposited. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
Previous studies \cite{23, 44, 48, 50}. Also presented within this table are the fitting parameters for the peaks.

In both 45 L and 450 L exposures, LiOH decomposition at 520 K is followed by an associated evolution of H$_2$ from the sample at 535 K. We attribute this to be the result of reaction according to Fig. 3.

**Fig. 3.** TPD traces for the decomposition of thin film LiH, with thin film Li and bulk LiH decomposition given for reference. TPD traces for thin film LiH are given as solid lines (black – H$_2$, blue – H$_2$O and red – Li), a TPD trace for thin film Li is given as a dashed line (magenta – Li), and a TPD trace for bulk LiH is given as a dotted line (green – Li). A ramp rate of 0.5 K s$^{-1}$ was used. Peaks are labelled with assigned reactions. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

**Fig. 4.** XPS spectra of the O 1s region of a LiH film on Ni(100) exposed to (a) 450 L of H$_2$O and (b) 45 L of H$_2$O. Three peaks are present, assigned as adsorbed H$_2$O (cyan), LiOH (red) and Li$_2$O (green). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

**Fig. 5.** TPD traces for m/z of 2 (H$_2$) in black and 18 (H$_2$O) in blue for a LiH film on Ni(100) exposed to 450 L of H$_2$O at a ramp rate of 1 K s$^{-1}$. Peaks are labelled with assigned reactions. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

LiH + LiOH → Li$_2$O + H$_2$

2LiH → 2Li$_{\text{(g)}}$ + H$_2$

Li → Li$_{\text{(g)}}$

$\text{m}/\text{z} = 2$

m/z = 7 (LiH Film)

m/z = 7 (Li)

m/z = 7 (LiH Bulk)

m/z = 18

previous studies \cite{23, 44, 48, 50}. Also presented within this table are the fitting parameters for the peaks.

In both 45 L and 450 L exposures, LiOH decomposition at 520 K is followed by an associated evolution of H$_2$ from the sample at 535 K. We attribute this to be the result of reaction according to
equation (1a), whereby the liberated H2O from LiOH decomposition can react with the LiH substrate to form Li2O and a new H2 peak, in addition to the one produced by equation (2b). The effect of adsorbed on the H2 evolution at 425 K is not as clearly defined as that of LiOH decomposition, as the solid state reaction between LiH and LiOH (equation (2b)) proceeds concurrently. In order to resolve these features and to elucidate kinetics, TPDs were performed at a variety of ramp rates. This causes the temperature at which reactions occur to shift as a function of the mechanism and thermodynamics of the reaction. The H2 and H2O traces are shown in Fig. 7 for ramp rates of 2, 1, 0.5, and 0.2 K s⁻¹. The peaks are labelled as:

a. LiH + LiOH → Li2O + H2

b. 2LiH + H2O → Li2O + 2H2

c. H2O(ad) → H2O(g)

d. LiOH → Li2O + H2O

Fig. 7 shows that as the decomposition of LiOH (reaction d) varies with heating rate, the hydrolysis of LiH (reaction b) also shifts temperature to be slightly higher than that of the decomposition. This provides further evidence to show that reactions d and b are linked with some of the H2O evolved diffusing through the Li2O layer to the LiH to cause further reaction. Another reason for varying the heating rate was to determine if peak a, which is quite broad, comprised of two components (solid state reaction and hydrolysis from the H2O(ad)). However, as both reactions shift with ramp rate by similar amounts, it was not possible to provide clarification on this. Indeed peaks c and d are sharp and therefore it is reasonable to expect a feature similar in shape to b to be present within the H2 profile. This is evidently not the case and therefore it is unlikely that the H2O(ad) interacts with the LiH. In summary, the LiOH layer (which is still present when the H2O desorbs) must therefore provide a physical barrier to H2O propagation toward the LiH, causing the H2O to desorb rather than react.

Attempts to determine the activation energy (Ea) were performed using Kissinger analysis [51], these proved to be unsuccessful for all reactions. Kissinger analysis assumes that the reaction rate can adopt the form (1 − α)n, where α is the reacted fraction and n is the reaction order. Reactions schemes of this type are not generally valid for solid state reactions [52] and therefore may explain why the Kissinger analysis fails to adequately calculate Ea.

Explicit modelling was performed on both the H2O and the H2 TPD traces. The best mathematical fits were determined to be an A3 (three dimensional Avrami-Erofeev nuclei growth) mechanism for the H2O related reactions and D3 (three dimensional spherical diffusion) for the solid state reaction [18]. D3 has also been previously identified as the best chemical mechanism for the solid state reaction within bulk LiH due to the requirement for diffusion across the Li2O interlayer [19]. Fig. 8 shows the fits for the H2 and H2O traces respectively. The fit parameters are given in Table 2 where r is a pre-exponential factor. The values determined for the Ea of the

![Fig. 6. TPD traces for m/z of 2 (H₂) in black and 18 (H₂O) in blue for a LiH film on Ni(100) exposed to 4.5 L of H₂O at a ramp rate of 1 K s⁻¹. Peaks are labelled with assigned reactions. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)](image1)

![Fig. 7. H₂ and H₂O TPD traces at ramp rates of 2 K s⁻¹ (black), 1 K s⁻¹ (red), 0.5 K s⁻¹ (green) and 0.2 K s⁻¹ (blue). The peaks are labelled as 'a' - the reaction of LiH and LiOH, 'b' - the reaction of LiH and H₂O, 'c' - the desorption of H₂O(ad) and 'd' - the decomposition of LiOH. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).](image2)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Binding Energy (eV)</th>
<th>FWHM (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li₂O</td>
<td>529.4–530.3</td>
<td>1.68 ± 0.05</td>
</tr>
<tr>
<td>LiOH</td>
<td>531.9–532.6</td>
<td>1.79 ± 0.05</td>
</tr>
<tr>
<td>H₂O(ad)</td>
<td>534.6</td>
<td>1.76 ± 0.05</td>
</tr>
</tbody>
</table>
decomposition of LiOH (90 kJ mol\(^{-1}\)) and the solid state reaction between LiH and LiOH (82 kJ mol\(^{-1}\)) are comparable to previous studies of the corrosion layers formed on bulk LiH which were 97 and 70 kJ mol\(^{-1}\), respectively [18,19]. The discrepancy between these values could be a result of different mechanisms being rate limiting in thin films in comparison to the bulk; differences in thermal transport; or the use of a high purity thin film which will result in less interference from mass transport, which may have influenced the results obtained from the bulk sample in comparison to a thin film. In addition, the lack of a LEED pattern could indicate poorly ordered surface which could alter any grain boundary effects within the reaction mechanisms. As a result of the close link between the decomposition of LiOH and the reaction between LiH and H\(_2\)O, the slight increase in \(E_a\) (3.1 kJ mol\(^{-1}\)) shown here is proposed to be a result of a slight time delay in which the H\(_2\)O must diffuse across the Li\(_2\)O layer. An analogous study has been reported which is in agreement with this hypothesis. Using a H\(_2\)O molecular beam, Balooch et al. [22] showed that there is a phase lag (and therefore a time lag) between H\(_2\) production and scattered H\(_2\)O molecules, which increases with increasing H\(_2\)O exposure. A greater phase lag for thicker LiOH and Li\(_2\)O films is consistent with a diffusion process for the transfer of H\(_2\)O to LiH. However, in the case described here, nuclei growth (A3) provided the best fit to this process, indicating that diffusion across the Li\(_2\)O region is not the rate limiting process. Instead the process is governed by the decomposition of the LiOH layer.

The precise nature of the solid state reaction is a subject of debate. For example, Myers [14] and Dinh [19] have proposed mechanisms based primarily upon H\(_2\)O and H\(^+\) transport across the Li\(_2\)O layer, respectively. Here, we reason that an alternative model is consistent for the experimental data obtained. Instead of the transport of a species across the film to react at the LiH surface, the diffusion process is equivalent to Li–O bond rearrangement in the Li\(_2\)O layer and H\(_2\) evolution at the interfaces. Fig. 9 provides a graphical summary of the proposed model for the solid state reaction. At the LiH – Li\(_2\)O interface:

\[
2\text{LiH} + \text{Li}_2\text{O} \rightarrow \text{Li}_2\text{O} + \text{H}_2 + 2\text{Li}
\]  

(3)

In essence, equation (3), describes the splitting of LiH into its constituent elements. The heat of formation of reaction 3 is 774 kJ mol\(^{-1}\) at 298 K. It is likely that this process will be mediated by the fact that the interface layer will be highly defective due to the large lattice mismatch and thus the heat of formation will be significantly lower. In equation (3), the Li atoms are actually switching bonds from H to O at the LiH/Li\(_2\)O interface, causing nearest neighbour shifting of Li–O bonds throughout the Li\(_2\)O layer. This will leave an excess of Li atoms at the Li\(_2\)O/LiOH interface, which converts LiOH to Li\(_2\)O. The process at the Li\(_2\)O/LiOH interface is therefore:

\[
2\text{LiOH} + 2\text{Li} \rightarrow 2\text{Li}_2\text{O} + \text{H}_2
\]  

(4)

This process has a heat of formation of \(-227\) kJ mol\(^{-1}\) at 298 K.

---

**Table 2**

\(E_a\) and \(\varepsilon\) determined for decomposition reactions of LiH. The error is the standard error on the mean from all ramp rates.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>(E_a) (kJ mol(^{-1}))</th>
<th>(\varepsilon) (10(^6) s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{LiOH}_{\text{ad}} \rightarrow \text{LiOH} )</td>
<td>72.7 ± 2.8</td>
<td>2.3 ± 1.8</td>
</tr>
<tr>
<td>(\text{LiOH} \rightarrow \text{Li}_2\text{O} + \text{H}_2)</td>
<td>90.1 ± 3.6</td>
<td>27 ± 2.6</td>
</tr>
<tr>
<td>(\text{LiH} + \text{LiOH} \rightarrow \text{Li}_2\text{O} + \text{H}_2)</td>
<td>81.6 ± 3.8</td>
<td>6.2 ± 2.4</td>
</tr>
<tr>
<td>(2\text{LiH} + \text{H}_2\text{O} \rightarrow \text{Li}_2\text{O} + 2\text{H}_2)</td>
<td>93.2 ± 2.4</td>
<td>52.2 ± 8.8</td>
</tr>
</tbody>
</table>

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Fig. 8. Fitted H\(_2\) and H\(_2\)O TPD traces of a LiH film exposed to H\(_2\)O at 0.2 K s\(^{-1}\). The line in black is the data with a background correction applied and the line in red is the applied fit. The fit consists of a D3 mechanism for the solid state reaction of LiH and LiOH and an A3 mechanism for the reaction of LiH with H\(_2\)O, the decomposition of H\(_2\)O\(_{\text{ad}}\), and the decomposition of LiOH. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 9. Schematic of the proposed Li–O bond shift model for the solid state reaction between LiH and LiOH. The chemical equations indicate the reactions occurring at the interface, which sum to the overall solid state reaction. The only gaseous species realised in this scheme is H\(_2\).
The overall reaction is the same as the observed reaction, \( \text{LiH} + \text{LiOH} \rightarrow \text{Li}_2\text{O} + \text{H}_2\text{O} \), equation (2b). Diffusion, in this model, is in the sense of bond shifting in the \( \text{Li}_2\text{O} \) layer.

5. Conclusions

Thin films of Li, LiH, Li\(_2\)O and LiOH have been synthesised and characterised using AES, XPS and TPD. Characterisation has shown peak shifts in both the Li KLL and the O 1s spectra, allowing for identification of these Li compounds. LiH films were then analysed using TPD and characterised using XPS after heating to 675 K; this showed a H\(_2\) desorption peak at 425 K associated with a solid state reaction between adventitious LiH and LiOH, resulting in the formation of Li\(_2\)O and H\(_2\). The XPS shows a reduction in the LiOH present and an increase in the amount of Li\(_2\)O, providing further evidence of the prevalence of the solid state reaction in very thin corrosion layers. Also present within the TPD are decomposition and sublimation of LiH to Li and H\(_2\) at 825 K.

After exposing LiH films to an excess (450 L) of H\(_2\)O, XPS of the O 1s region indicated the presence of LiOH and adsorbed H\(_2\)O. The TPD of this film contained two peaks within the H\(_2\)O trace, attributed to the desorption of chemisorbed H\(_2\)O at 425 K and the decomposition of LiOH into Li\(_2\)O and H\(_2\)O at 535 K. The former, to our knowledge, is the first observation of desorbing H\(_2\)O ad-layers from the LiOH/LiH surface. A fraction of the H\(_2\)O liberated from LiOH diffuses through the Li\(_2\)O to the LiH surface and reacts with the LiH to form further Li\(_2\)O and H\(_2\). The use of multiple ramp rates caused these peaks to shift and shows that the reaction of LiOH and H\(_2\)O closely follows the decomposition of LiOH at all rates. There was no evidence to suggest that adsorbed H\(_2\)O diffuses through LiOH and Li\(_2\)O to react with LiH. Reducing the H\(_2\)O exposure, such as from the LiOH/LiH surface. A fraction of the H\(_2\)O liberated from LiOH and Li\(_2\)O to react with LiH. Reducing the H\(_2\)O exposure, such that the XPS of the O 1s region shows no adsorbed H\(_2\)O, eliminates the adsorbed H\(_2\)O in the TPD profile.

Kissinger analysis was unsuccessful in determining the \( E_\text{k} \) for the decomposition reactions. The failure was suggested to be a result of the mechanisms involved being of an inappropriate mathematical form. Instead, explicit modelling was carried out to determine \( E_\text{k} \) and \( f \) for each reaction. The values for \( E_\text{k} \) were 72.7 kJ mol\(^{-1}\) for the desorption of H\(_2\)O; 90.1 kJ mol\(^{-1}\) for the decomposition of LiOH both with an A3 mechanism; and 81.6 kJ mol\(^{-1}\) for the solid state reaction with a D3 mechanism, which are in reasonable agreement with the values obtained for bulk specimens. The increase in \( E_\text{k} \) for the reaction of LiOH with H\(_2\)O is reasoned to be an artefact caused by a transport process of H\(_2\)O through the Li\(_2\)O layer. A model for the solid state reaction is proposed based upon Li-O bond shifting.

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