X-RAY PHOTOELECTRON SPECTROSCOPY STUDIES
OF ALUMINIUM OXIDE THIN FILM SYSTEMS

A Dissertation
Presented to the Faculty of the Graduate School
of Cornell University
in Partial Fulfillment of the Requirements for the Degree of
Doctor of Philosophy

by
Ei-leen Tan
May 2005
X-RAY PHOTOELECTRON SPECTROSCOPY STUDIES OF ALUMINIUM OXIDE THIN FILM SYSTEMS

Ei-leen Tan, Ph.D.
Cornell University 2005

This dissertation describes an investigation of the growth and processing of aluminium oxide thin films. These oxide films, used as insulating barriers in magnetic and superconducting tunnel junctions, are typically formed by exposing an aluminium thin film to a controlled dose of pure oxygen at room temperature. The x-ray photoelectron spectroscopy results presented in this dissertation show that aluminium oxide layers grown using this method are oxygen deficient, and that their surfaces are covered with a layer of negatively-charged clusters of oxygen molecules weakly bonded to the positively-charged oxygen vacancies in the oxide.

The deposition of a metallic overlayer drives the chemisorbed oxygen into these oxide vacancies, provided that the work function of the overlayer metal is high enough to produce an electrochemical potential difference across the oxide. A low energy electron bombardment, in the range of 10–20 eV, can also be used to produce such a potential difference. The enhanced potential difference results in an increase in the oxide thickness as well as its oxygen content, pushing its stoichiometry closer to an ideal value of 1.5 (i.e., Al$_2$O$_3$).

Micron-sized aluminium oxide-based tunnel junctions which incorporate electron bombarded oxide layers show a significantly lower resistance noise figure at 4.2 K compared to tunnel junctions whose oxide layers were not electron bombarded.
The decrease in the noise level is attributed to the filling of the oxygen vacancy sites in the oxide as a result of the electron bombardment, as the charge trapping behaviour of these vacancy sites is a major source of noise in tunnel junctions.
BIOGRAPHICAL SKETCH

Ei-leen Tan was born in 1975 in Malaysia. After going through the traditional education system in Singapore, she was accepted into Imperial College, UK, where she read Physics and graduated in 1997 with first class honours. She entered Cornell University that same year, receiving both an M.S. (2001) and a Ph.D. (2005) in Physics. In 2005 she will return to Singapore to continue her scientific career.
To Mom and Dad
ACKNOWLEDGEMENTS

Gone are the days of one master, one apprentice. And a good thing too, for I would never have become what I am today without the invaluable help and guidance from the folks I have met on this one journey.

At the top of my acknowledgements list is of course my advisor, Bob Buhrman. Like a good fraction of graduate students, I had joined Bob’s research group without really knowing what I was getting into. Looking back, this turned out to be one of the better decisions, perhaps even the best, that I had made throughout my entire graduate school career. The scientific discussions we’ve had over the years have been thoroughly enjoyable and stimulating. I am extremely grateful for the guidance Bob has provided, and I’ve learnt a lot while trying to collect data to meet the high standards that he sets. I would also like to thank Professors Piet Brouwer and Rob Thorne for serving on my committee.

My fellow compatriots in the Buhrman group come next on the list — in particular the BEEM team (Andrew, Phil and John), without whom much of the data shown in this thesis would not have been possible; and the nanofabrication experts whose advice have saved me countless hours of frustration at CNF. Then there’s all the postdocs, undergrads and alumni, many of whom I know only from the tomes of knowledge scattered all over the lab. A big thank you, and here’s wishing all of you the best in your future endeavours.

Experiments these days inevitably requires more resources than a single research group can ever have. I would like to acknowledge the assistance of the staff at the various facilities I’ve used one time or the other — the Cornell Center for Materials Research, the Cornell Nanofabrication Facility and the Center for Nanoscale Systems.
On the social side of things, the members of the Buhrman group again play a dominant role, both in and out of the lab. The fellow grad students with whom I started this journey at the end of the last century; it’s been a real privilege to know you all. Keep in touch, guys.

I would like to thank my family for their encouragement and support, past, present and future; and especially for giving me the freedom to pursue my dreams. And finally, a big Danke! to Wulf for being there whenever I needed him, and for putting up with all my idiosyncrasies over the past few years.
# TABLE OF CONTENTS

1 Introduction ................................. 1
1.1 Aluminium oxide — a historical perspective .... 1
1.1.1 XPS studies of aluminium oxide ............ 3
1.1.2 STM/BEEM studies .......................... 4
1.2 Overview .................................. 5
References for Chapter 1 ......................... 7

2 X-Ray Photoelectron Spectroscopy — Principles and Practice 8
2.1 Introduction ................................ 8
2.2 The photoemission process ......................... 8
2.3 The spectroscope ................................ 13
2.3.1 X-ray source ............................... 15
2.3.2 Sample mounting ............................. 16
2.3.3 Analyser and detector ....................... 16
2.4 Experimental procedures ......................... 19
2.4.1 Sample handling ............................ 19
2.4.2 XPS energy calibration ....................... 20
2.4.3 Charging effects ............................. 22
2.4.4 Scan parameters ............................. 23
2.4.5 Angle resolved scans ....................... 23
2.5 XPS data analysis ............................. 24
2.5.1 Spectra fitting ............................. 24
2.5.2 Binding energies and shifts ................... 24
2.5.3 Calculating chemical concentrations .......... 25
2.5.4 Thin films and multilayer films ............... 28
References for Chapter 2 ......................... 34

3 Aluminium Oxide Thin Film Growth .............. 35
3.1 Introduction ................................ 35
3.2 Aluminium film growth .......................... 35
3.3 XPS spectra analysis ........................... 36
3.4 Single layer aluminium films ..................... 43
3.4.1 Sample preparation and oxidation ............... 43
3.4.2 Oxide thickness and stoichiometry ............. 49
3.4.3 Chemisorbed oxygen and the Al/AlO₅ system ...... 53
3.4.4 Oxygen 1s peak intensities .................... 53
3.4.5 Binding energy ............................. 56
3.4.6 Air oxidation ............................... 63
3.5 Multilayer films ............................... 67
3.5.1 Experimental details and XPS analysis .......... 69
3.5.2 Metal XPS scans ............................. 70
6.4 Tunnel Junctions with AlO$_x$ barrier ................. 165
References for Chapter 6 ........................................... 166
LIST OF FIGURES

2.1 Photoemission and measurement process energy levels ............ 10
2.2 The photoemission and Auger processes .......................... 12
2.3 An XPS survey scan ........................................ 13
2.4 Schematic of an x-ray photoelectron spectroscopy .................. 14
2.5 X-ray source block diagram ..................................... 15
2.6 Sample positioning .............................................. 17
2.7 Analyser block diagram .......................................... 18
2.8 Gold 4f XPS spectrum ........................................... 21
2.9 Schematic of the photoemission process ............................ 27
2.10 Analysis for a an aluminium/aluminium oxide film stack .......... 30
2.11 Aluminium 2p XPS spectrum .................................... 31

3.1 XPS survey scan, unoxidised aluminium film ....................... 38
3.2 Aluminium 2p spectrum, unoxidised aluminium film ............... 39
3.3 Oxygen 1s spectrum, unoxidised aluminium film ................... 42
3.4 Aluminium 2p spectra, aluminium film, various oxygen doses . 44
3.5 Absolute intensities of Al 2p metal and oxide peaks as a function of oxygen dose ........................................ 45
3.6 Measured and expected change in Al 2p oxide peak intensity ... 47
3.7 Measured and expected change in Al 2p metal peak intensity ... 48
3.8 Thickness vs. oxygen exposure ................................... 49
3.9 Calculated variation of oxide aluminium atomic concentration as a function of stoichiometry ............................... 50
3.10 Variation of calculated thickness with aluminium atomic concentra- tion ......................................................... 51
3.11 Oxide stoichiometry vs. oxygen exposure .......................... 52
3.12 Measured and expected change in O 1s peak intensity .......... 54
3.13 Absolute intensities of O 1s peak vs. oxygen dose ............... 55
3.14 Normalised absolute intensities of O 1s peaks vs. oxygen dose .. 57
3.15 Normalised absolute intensities of Al 2p peaks vs. oxygen dose ... 58
3.16 Binding energy difference between Al 2p peaks vs. oxygen dose, large dose steps .................................. 59
3.17 Binding energy difference between Al 2p peaks vs. oxygen dose, small dose steps .................................. 60
3.18 Schematic of the Al/AlO_x bilayer ................................ 62
3.19 Oxygen 1s spectra of air-transferred and vacuum-transferred aluminium films ........................................ 64
3.20 Oxygen 1s spectra of an air-transferred aluminium film, 6 days in vacuum ...................................................... 65
3.21 Oxygen 1s chemisorbed and oxide peak intensities for an air-transferred sample as a function of time in UHV ................................. 66
3.22 Oxygen 1s relative peak intensities for samples grown at different times of the year ............................................. 68
3.23 Schematic of the photoelectron process for multilayer samples ................................................................. 71
3.24 Cobalt 2p spectra, oxidised and unoxidised cobalt film ...................................................................................... 72
3.25 Oxygen 1s spectra, cobalt film, before and after annealing .............................................................................. 73
3.26 Niobium 3d spectrum, 300 Å niobium sample, air transferred ................................................................. 75
3.27 Oxygen 1s spectrum of a 300 Å niobium sample, air transferred .............................................................. 76
3.28 Yttrium 3d spectrum of a 300 Å yttrium sample, vacuum transferred .......................................................... 77
3.29 Oxygen 1s spectrum of a 300 Å yttrium sample, vacuum transferred .......................................................... 78
3.30 Aluminium 2p binding energy shift in a gold/aluminium bilayer film ......................................................... 80
3.31 Oxygen 1s binding energy shift in a gold/aluminium bilayer film .............................................................. 81
3.32 Aluminium 2p spectra, tantalum/aluminium films for different starting thicknesses of aluminium ....................... 83
3.33 Oxygen 1s spectra, tantalum/aluminium films for different starting thicknesses of aluminium ...................... 84
3.34 Aluminium 2p spectra, oxidised aluminium film with and without a cobalt overlayer ................................ 86
3.35 Oxygen 1s spectra, oxidised aluminium film with a cobalt overlayer ........................................................ 87
3.36 Aluminium 2p spectra, oxidised aluminium film with a niobium overlayer ................................................... 89
3.37 Oxygen 1s spectra, oxidised aluminium film with a niobium overlayer ........................................................ 90
3.38 Niobium 3d spectra, oxidised aluminium film with a niobium overlayer ...................................................... 92
3.39 Aluminium 2p spectra, oxidised aluminium film with an yttrium overlayer .................................................. 93
3.40 Oxygen 1s spectra, oxidised aluminium film with an yttrium overlayer ........................................................ 94
3.41 Thicknesses of the buried aluminium oxide layers for three different overlayer metals .................................. 97

4.1 Survey scans of an aluminium film, before and after annealing ................................................................. 103
4.2 Survey scans of Au/Cu/Co/Al multilayer film, before and after annealing ..................................................... 104
4.3 Aluminium 2p spectra of Au/Cu/Co/Al multilayer film, before and after annealing ........................................... 105
4.4 Aluminium 2p spectra of unannealed and 500°C annealed aluminium films ...................................................... 107
4.5 Oxygen 1s spectra of unannealed and 500°C annealed aluminium films ........................................................... 108
4.6 Oxygen 1s spectra of Co/Al films annealed at 300°C and 500°C ............................................................. 109
4.7 Aluminium 2p spectra of an air-transferred aluminium film after 10 eV floodgun exposure, 15 hours .................. 112
4.8 Oxygen 1s spectra of an air-transferred aluminium film after 10 eV floodgun exposure, 15 hours ...................... 113
4.9 Aluminium 2p spectra of an air-transferred aluminium film after 10 eV floodgun exposure, 85 min ...................... 115
4.10 Oxygen 1s spectra of an air-transferred aluminium film after 10 eV floodgun exposure, 85 min .................................................. 116
4.11 Oxygen 1s spectra after 10 eV floodgun exposure followed by re-
oxidation .......................................................................... 118
4.12 Oxygen 1s spectra after re-oxidation followed by a 10 eV floodgun
exposure .............................................................................. 119
4.13 Oxide O/Al ratio of an air-oxidised aluminium film after a series of
floodgun exposures and re-oxidation steps ....................... 120
4.14 Chemisorbed oxygen peak intensity of an air-oxidised aluminium
film after a series of floodgun exposures and re-oxidation steps . 121
4.15 Oxide thickness of an air-oxidised aluminium film after a series of
floodgun exposures and re-oxidation steps ...................... 122
4.16 Oxide O/Al ratio of a vacuum-transferred aluminium film after a
series of 10 eV floodgun exposures and re-oxidation steps ..... 123
4.17 Oxide thickness of a vacuum-transferred aluminium film after a
series of 10 eV floodgun exposures and re-oxidation steps ..... 124
4.18 Normalised chemisorbed oxygen intensity of a vacuum-transferred
aluminium film after a series of 10 eV floodgun exposures and re-
oxidation steps ................................................................. 125
4.19 Aluminium 2p spectra of a vacuum-transferred aluminium film ex-
posed to a 20 eV floodgun for 1 hour ................................. 127
4.20 Oxygen 1s spectra of a vacuum-transferred aluminium film exposed
to a 20 eV floodgun for 1 hour ........................................ 128
4.21 Normalised chemisorbed oxygen intensity of a vacuum-transferred
aluminium film after a series of 20 eV floodgun exposures and re-
oxidation steps ............................................................. 129
4.22 Oxide thickness of a vacuum-transferred aluminium film after a
series of 20 eV floodgun exposures and re-oxidation steps ..... 130
4.23 Oxide O/Al ratio of a vacuum-transferred aluminium film after a
series of 20 eV floodgun exposures and re-oxidation steps ...... 131
4.24 Chemisorbed oxygen peak intensity vs. oxide stoichiometry for
floodgun-exposed aluminium samples ............................... 133
4.25 Oxygen 1s spectra of an air-transferred cobalt film after a 20 eV
floodgun exposure. ........................................................... 135
4.26 Oxygen 1s spectra of an air-transferred cobalt film after re-exposure
to oxygen ....................................................................... 136
4.27 Relative intensities of oxygen 1s peaks for a floodgun exposed cobalt
sample as a function of exposure time .............................. 137

5.1 Sidewall shorting during ion milling ................................. 145
5.2 Junction fabrication, step one ........................................... 148
5.3 Junction fabrication, step two ......................................... 149
5.4 Junction fabrication, step three ........................................ 150
5.5 Junction fabrication, step four .......................................... 151

xii
5.6 Noise measurement setup ........................................ 154
5.7 Room temperature low frequency noise, control junction .......... 156
5.8 Noise figures as a function of temperature ........................... 157
5.9 Spread of noise figures at 4.2 K ..................................... 158
CHAPTER 1

INTRODUCTION

Aluminium oxide (AlO$_x$) is commonly used as an insulating barrier material in magnetic and superconducting tunnel junctions, the basis of many new nanoscale electronic devices. Magnetic tunnel junctions (MTJs) [1] are used in the development of fast, nonvolatile magnetic memory cells which have the potential to significantly increase performance in portable computing products. Superconducting Josephson junctions (JJs) [2] are promising candidates for the construction of quantum bits (qubits), a first step in the realisation of practical quantum computers. More recently, aluminium oxide layers have been used as gate insulators in molecular electronics based transistors [3].

Although much research has been carried out on the oxidation of aluminium in the last few decades, the focus has mostly been on thick aluminium oxide layers for corrosion protection. For device applications, particularly in nanoscale electronics, it is essential that the aluminium oxide barrier be several orders of magnitude thinner. The growth and processing of such ultrathin films present several new challenges which must be met in order for aluminium oxide based technology to be commercially viable.

1.1 Aluminium oxide — a historical perspective

Being the most abundant metal on the planet, aluminium is widely employed in almost all aspects of daily life — automobile construction, the food service industry, in the fine arts scene, to name but a few. What makes aluminium so desirable for such uses (apart from being light and cheap) is the natural tendency for the surface to oxidise and form a protective barrier which prevents further
corrosion of the metal beneath.

Hence, the problem of aluminium oxide growth is not a new one; it has been thoroughly investigated over the last century by research groups interested in its corrosion protection properties. Their main goal, of course, was to obtain oxide barriers that would last under various harsh environmental conditions, such as situations of high mechanical and thermal stress or continuous salt water exposure. These barriers would naturally need to be as thick and continuous as possible, without regard to its electronic properties.

For devices though, a much different and stringent set of requirements must be fulfilled. Once it was demonstrated that aluminium oxide was a suitable material for use in MTJs and JJs, interest in its growth process revived, but now with the aims of producing ultrathin and yet electrically robust barriers. A further issue is reproducibility — for any modern technology to be commercially viable, it must lend itself well to large scale production, where device-to-device variation is kept to an absolute minimum. An even more ambitious goal would be the ability to strictly control the electrical properties of the barrier, enabling the production of devices tailored for one specific need or other.

For aluminium and other metals, the thermal oxidation process can be described by the model proposed by Cabrera and Mott [4]. In this model, the oxidation process is initiated when molecular oxygen lands on a bare aluminium surface. As both oxygen and aluminium are highly reactive species, a monolayer of aluminium oxide quickly forms on the surface. After the formation of this initial oxide layer, further oxygen molecules landing on the surface will dissociate and pick up electrons tunneling from the metal across the oxide, due to a difference in the chemical potentials. The negatively charged oxygen ions (O\(^{-}\)) then set up
a potential across the oxide which draws aluminium cations towards the surface, where they react with the oxygen to form more oxide. As the oxide becomes thicker, the electron tunneling rate and consequently the aluminium diffusion rate both decrease. The oxide growth process is thus self limiting, and stops\(^1\) when the oxide thickness is about 15 Å [5].

### 1.1.1 XPS studies of aluminium oxide

X-ray photoelectron spectroscopy (XPS) is a surface sensitive technique which allows for the chemical analysis of the top 5–10 nm of a sample. This makes the technique ideal for studying changes at sample surfaces, such as oxidation. Earlier XPS studies (before 1995) of aluminium oxide concentrated mainly on bulk aluminium samples and how effective various surface treatments were at producing a passivating oxide layer (see, for example, Reference [6]). Later oxidation studies [7, 8] have examined the initial stages of aluminium oxidation (a process not described by the Mott-Cabrera model). Both these studies involved single crystals of aluminium, and in particular the Al(111) face. The sticking coefficient of oxygen\(^2\) for this face is low, making the oxidation process slow enough to be studied by XPS and other means.

Although XPS investigations of bulk materials and single crystals provide much insight into the oxidation process in the Al/AlO\(_x\) system, they may not be an accurate representation of the Al/AlO\(_x\) layers found in tunnel junctions. The basis of a tunnel junction device is a trilayer stack where the AlO\(_x\) layer is sandwiched between two metal electrode layers. The AlO\(_x\) layer is formed by first depositing

\(^1\)Or at least, slows down considerably.

\(^2\)The sticking coefficient of a gas on a surface is the ratio of the rate of adsorption of the gas to the rate at which the gas strikes the surface.
a thin layer of Al onto the base electrode, and then exposing it to pure oxygen at room temperature, or to an oxygen plasma. A top electrode is then deposited onto
the AlO_x layer, finishing the trilayer stack. Hence, not only do we have to take
into account the smaller vertical size of the Al/AlO_x layer, but also the interactions
between the electrodes and the Al/AlO_x layer. A few groups have recently carried
out XPS studies in this area (e.g. References [9, 10]).

1.1.2 STM/BEEM studies

Among the many surface and thin film characterisation methods used to investigate
the Al/AlO_x system, one other method has been extensively used by the Bulirman
group — ballistic electron emission microscopy (BEEM), an extension of scanning
tunneling microscopy (STM) [11].

In BEEM, ballistic electrons are injected into a sample consisting of a multilayer
film stack, with a Schottky barrier placed at the base of the stack. Depending on
band structure and interfacial scattering, some, all, or none of the injected electrons
will have enough energy to pass over the Schottky barrier and be collected at the
base. By varying the energy at which the electrons are injected, a map of electron
transport through the multilayer stack can be obtained. Holes can similarly be
injected and collected and their transport mapped out.

One important criterion for tunnel junctions is the completeness and uniformity
of the insulating oxide barrier. Shorts across the barrier (known as “pinholes”) can
severely degrade the quality of the tunnel junction. With BEEM, such pinholes
can be readily detected. Hence, it is possible to find out the growth and oxidation
conditions which would produce extremely thin and yet pinhole-free oxide barriers.
This is particularly useful in the fabrication of magnetic tunnel junctions, where
one of the main goals is to have as thin an oxide layer as possible.

One further observation from the BEEM studies is the presence of clusters on the ALO$_x$ surface. These clusters are mobile and can be dragged around the surface with the STM tip, but remain indefinitely on the surface even under ultrahigh vacuum (UHV) conditions. Furthermore, the proportion of the surface covered by these clusters increases as the oxygen exposure increases. It is therefore highly probable that these clusters are oxygen molecules on the surface of the ALO$_x$.

As chemical identification of the clusters cannot be achieved with the BEEM technique, XPS becomes the analytical tool of choice.

1.2 Overview

This thesis is primarily concerned with the following questions: What is the role of these clusters in the aluminium oxidation process, and how do they influence tunnel junction properties?

The next chapter is an overview of the XPS technique. The construction and functioning of the spectroscope is described, as well as the spectral analysis methods used to obtain quantitative information for the samples. Chapter 3 describes the oxidation process of aluminium thin films, as tracked by XPS. Both single layer aluminium films, as well as the multilayer stacks used in tunnel junction fabrication, are investigated. Chapter 4 presents more XPS data showing the chemical changes in the oxide as a result of two oxide modification methods — thermal annealing and low energy electron bombardment. Chapter 5 examines the effectiveness of the electron bombardment method in improving the oxide quality. Micrometer-scale Al/ALO$_x$/Al tunnel junctions incorporating the electron-bombarded oxide layers are fabricated for this purpose. The low frequency junction
resistance noise is then measured and used as a gauge of oxide quality. A summary of the major results is presented in Chapter 6, together with suggestions for future investigations.
References for Chapter 1


CHAPTER 2
X-RAY PHOTOELECTRON SPECTROSCOPY — PRINCIPLES AND PRACTICE

2.1 Introduction

Although the photoelectric effect was first discovered by Heinrich Hertz in 1887, it was not until 1955 that laboratory technology was advanced enough for this process to be utilised as a form of spectroscopy. This new technique was called electron spectroscopy for chemical analysis (ESCA) by its developer, Kai Siegbahn [1]. Today, the term ESCA is used interchangeably with XPS, the latter standing for x-ray photoelectron spectroscopy, a name which reflects the type of photons used in the spectroscopy process. The first part of this chapter describes the theory behind the photoemission process and how it is used in an XPS spectroscope. The second part of the chapter discusses the experimental techniques and data analysis methods.

2.2 The photoemission process

When a photon of sufficient energy $h\nu$ is incident on an atom in a solid, an electron can be ejected from a core level within the atom. As energy is conserved in this process, the kinetic energy of the photoelectron, $E_k$, and the photon energy are related by:

$$h\nu = E_k + E_b + \phi$$  \hspace{1cm} (2.1)

where $\phi$ is the work function of the material, and $E_b$ is the binding energy of the photoelectron (Figure 2.1a).
From this simple equation, it would appear that, if the photon energy and work function of the material were known, it is a straightforward matter to measure the kinetic energy of the photoelectron and calculate its binding energy. However, as the work function often depends on factors such as sample crystallinity, obtaining an accurate value for the work function is not an easy task.

There is a second problem inherent in converting this process into an experimental procedure which can reliably measure electron binding energies. When leaving the sample, the photoelectron must overcome the work function of the material; similarly, when the photoelectron enters the spectrometer (a necessary condition for a measurement), the photoelectron must overcome the work function of the spectrometer. The binding energy obtained using the spectrometer is thus measured relative to the Fermi level of the spectrometer, which in general is not the same as the Fermi level of the sample (see Figure 2.1a). Binding energies measured in this way would be therefore dependent on the spectrometer used, and such a measurement would be of limited usefulness.

Fortunately, in most cases, there is a solution for both problems — just make a good electrical connection between the sample and the spectrometer. Doing so will equalise both Fermi levels, and hence the measured binding energy will be the same as the electron binding energy (Figure 2.1b). We still need to determine the work function of the spectrometer; however this is readily done by measuring a sample with known binding energies. Section 2.4.2 describes the calibration process in more detail.

In the above argument, we have assumed that the sample to be measured is a good conductor, i.e., it has a well defined Fermi level. This is not true for a good insulator, where the Fermi level, and hence the binding energy, is not well
Figure 2.1: Energy level diagrams for the photoemission and measurement process. (a) The Fermi levels of the sample and spectrometer are generally not the same, hence the measured binding energy $E_b'$ is different from the electron binding energy $E_b$. (b) When the sample is in electrical contact with the spectroscope, the Fermi levels of the sample and spectroscope match, and the measured binding energy is equal to the binding energy of the electron. $E_k$ is the kinetic energy of the electron, $E'_k$ is the measured kinetic energy, $\phi$ and $\phi_{sp}$ are the work functions of the sample and spectroscope respectively.
defined. In this case, binding energies are not measured relative to the Fermi level; instead, the binding energies are measured relative to that of a known constituent on the sample whose binding energies are easily identified and reproduced (carbon, for example). A more serious problem with insulating samples is charging; this is discussed in Section 2.4.3.

The vacancy left behind by the ejected photoelectron can be filled either by a radiative process (x-ray emission), or a nonradiative one (Auger process). In the latter case, an electron from a less tightly bound orbital fills the hole, while a second electron is ejected from another orbital. The energy of this ejected electron (the Auger electron) depends on the orbitals involved in the transition process. A doubly charged ion remains after the ejection of the Auger electron; the vacancies in this ion are then filled by x-ray emission or further Auger transitions. Figure 2.2 is a schematic of the photoemission and Auger processes.

Although the high energy x-rays are able to penetrate deep into the sample, the emitted photoelectrons and Auger electrons typically have mean free paths on the order of a few nanometers. Hence, only photoelectrons generated close to the surface of the sample will be able to reach the detector without being scattered. XPS is thus a surface sensitive technique which probes only the top 5–10 nm of the sample.

An XPS spectra typically consists of several narrow photoemission lines as well as a few broader Auger lines (Figure 2.3). Each elemental species has a set of unique binding energies corresponding to different core levels within the atom; the same is true for Auger transitions. By matching the binding energies obtained from an unknown sample with those from known elements, it is possible to identify different chemical species within the unknown sample. More importantly,
Figure 2.2: (a) The photoemission process: An incident x-ray ejects a photoelectron from one of the core levels of an atom. (b) The Auger process: A vacancy in a lower core level can be filled by an electron in a higher level via a nonradiative transition process. An electron (the Auger electron) is ejected from an outer shell of the atom in this process, carrying away the energy released in the transition.
Figure 2.3: An XPS survey scan of an oxidised aluminium thin film, showing oxygen and aluminium peaks. A carbon line is also present (a small amount of contamination is always inevitable).

Deviations in the binding energies from their elemental values provide information about the chemical state of the atoms within the sample. Finally, with careful line intensity measurements, accurate estimates of the chemical composition of the sample can be made.

2.3 The spectroscope

The XPS system used in this work is a Surface Science Laboratories Model SSX-100. A schematic of the spectroscope is shown in Figure 2.4. The spectroscope consists of two main subsystems. The first subsystem, the source volume, contains the x-ray source and the sample, and is where the photoemission process occurs.
Figure 2.4: Schematic of an x-ray photoelectron spectroscope.
The second subsystem of the XPS contains the electron energy analyser and detector. In this subsystem, the photoelectrons pass through a dispersion analyser before being collected at a multichannel plate detector. All the components of the spectroscopic are housed within an ultrahigh vacuum (UHV) chamber. An ion pump maintains the system base pressure in the mid to high $10^{-10}$ torr range. When the spectroscopic is operating, the pressure rises to $1 - 2 \times 10^{-9}$ torr.

### 2.3.1 X-ray source

Figure 2.5 shows the block diagram for the x-ray source. Electrons emitted from the filament of the electron gun are accelerated towards a water cooled aluminium anode. The x-rays generated at the anode consist of the aluminium K lines on top of a background of bremsstrahlung radiation. A quartz monochromator selects only the $K_\alpha$ x-ray line, as well as filtering out the background radiation. The resulting x-ray beam is reduced in intensity, but with a clean, flat background and a narrow linewidth of about $0.2$ eV. The SSX-100 has 4 different beam spot size...
settings: 150, 300, 600 and 800 $\mu$m. All the data shown in this thesis was taken using the 800 $\mu$m spot size setting.

### 2.3.2 Sample mounting

Samples are transferred in and out of the XPS UHV chamber via an attached load lock. Vacuum conditions in the load lock are achieved with a turbomolecular pump, backed by a rotary pump. An isolation gate valve separates the two vacuum systems.

For standard scans, the sample is mounted onto a flat sample holder, with the detector axis at an angle of 55 degrees to the sample surface normal (See Figure 2.6). The sample is clamped down onto the sample holder with a clip, while the sample holder itself sits on a stage which can be moved horizontally and vertically. This movable stage allows the sample to be positioned correctly (with the help of an optical microscope) under the x-ray beam. The final fine focusing is done by moving the stage along the z-axis until a maximum count rate is achieved.

The sample holders and clips are made of aluminium or stainless steel, while the sample stage is made from stainless steel. The sample stage is connected to the ground of the spectrometer. This provides the necessary electrical path between the sample and the spectrometer (See Section 2.2).

### 2.3.3 Analyser and detector

A block diagram of the analyser subsystem is shown in Figure 2.7. Like many other commercial spectrosopes [1], the SSX-100 uses a hemispherical analyser to measure the velocities (and hence kinetic energies) of the photoelectrons. After passing through the analyser, the photoelectrons are collected at a multichannel
Figure 2.6: (a) Schematic of sample stage. The analyser axis is at an angle of 55 degrees to the sample normal, and has a 30 degree field of view. (b) Stage degrees of freedom. (c) The sample should be at the right height to obtain maximum signal intensities.
Figure 2.7: Analyser block diagram.
plate detector. The output of the detector is then preprocessed and relayed via an A/D converter to the controlling computer, which then translates the signals to a human readable form. References [1, 2] contains an in-depth discussion of XPS electron energy analyser design, and in particular, how a good energy resolution and low noise background can be achieved. Details on the SSX-100 detector and signal preprocessing can be found in Reference [3].

The SSX-100 has 4 different resolution settings. The lowest setting has an energy resolution of about 5 eV and is primarily used during quick survey scans of the sample. For analysing individual peak structures, the highest setting is used; this has an energy resolution of about 0.6 eV [3].

### 2.4 Experimental procedures

While it is extremely easy to collect data with the spectroscope, getting useful and reproducible data requires care in preparing the sample, as well as in the setting up and calibration of the spectroscope.

#### 2.4.1 Sample handling

Since XPS is a surface sensitive technique, even small amounts of surface contamination will adversely affect the quality of the data. Samples should therefore be handled under clean conditions at all times; ideally samples should be grown and measured in-situ. This is not always achievable, in which case the sample should be transferred into the XPS vacuum chamber as quickly as possible after being grown.

Even with these precautions, there will still be a tiny amount of carbon contamination on the surface. This contamination is mainly due to the almost negligible
backstreaming of the roughing pump oil, through the turbopump, into the load lock during sample transfers.

Samples should be outgassed thoroughly in the load lock before being transferred into the XPS chamber, so as to preserve clean, UHV conditions in the XPS chamber.

2.4.2 XPS energy calibration

As mentioned in Section 2.2, for reliable binding energy measurements, the work function of the spectrometer must first be determined. This calibration procedure is done by measuring the binding energies of a known sample.

Since chemical changes such as oxidation produce shifts in binding energies, it is necessary to use a pure, inert material for the calibration. Gold, silver and (to a lesser extent) copper are commonly employed for this purpose. These materials do not readily oxidise, and their XPS spectra have strong, sharp peaks. In this work, thermally evaporated gold films are used for calibration; the energy reference scale of the SSX-100 spectrometer is set to give a value of 83.96 eV for the binding energy of the gold 4f$_{7/2}$ peak (Figure 2.8).

One commonly used method of spectroscope calibration involves the use of the 1s peak of carbon. Since carbon is often present as a small contamination layer on the sample, this is a quick and convenient method of calibration. The carbon 1s spectra consists of a few peaks; the largest of which lies at 284.6 eV and arises from C–C bonded carbon atoms. Some XPS studies have used this adventitious carbon as a means of spectroscope calibration (Reference [4], for example). This method can be used reliably in most cases, especially those involving metal samples [5].

However, for samples with surface layers which are semiconducting and insulating,
such as oxidised metal films, this calibration method results in a slightly shifted energy reference scale, when compared to that obtained using a pure gold film. This is most likely due to the carbon contamination layer charging up (see Section 2.4.3) when it sits atop the insulating oxide layer. As a result, the main carbon peak binding energy increases from 284.6 eV to a higher value. An energy reference scale calibrated according this apparent binding energy will therefore produce a systematic error in the measured binding energies of the peaks.

The energy reference scale does not stay constant but drifts slightly as a result of environmental changes within the spectroscope. Gold scans done before and after each data collection run (whose durations are around 6–12 hours) show that there is negligible drift (around 0.05 eV) during a run. Between different data collection runs, the drift is usually also insignificant, although in rare occasions the drift becomes as large as 0.1 eV. In most cases therefore, it is usually enough
to recalibrate the spectrometer once a week. If good accuracy is crucial, calibration is recommended before the actual data collection run.

### 2.4.3 Charging effects

During the photoemission process, electrons are ejected from the sample surface, leaving behind a positively charged surface. If the surface is in good electrical contact with the rest of the spectroscopic, the positive charge will be quickly neutralised by a flow of electrons from the spectroscope to the sample. If there is no good electrical contact, for instance, in the case of insulating samples, the positive charge which quickly builds up makes it harder for subsequent electrons to leave the surface. This produces a positive shift in the measured binding energy, as well as a broadening of the peak. In this case, it is thus necessary to use a charge neutraliser, so as to keep the Fermi surfaces of the sample and spectrometer as close together as possible.

In the SSX-100, an adjustable low energy (between 0 and 20 eV) electron floodgun is used to neutralise charging when scanning insulating samples. The floodgun voltage must be selected so as to produce an electrically neutral surface. If the voltage is set too low, the positive charge on the sample will not be completely neutralised; if the voltage is set too high, it is possible to “overcharge” the sample negatively and produce a binding energy shift in the negative direction. Comparing binding energies with standard values is not really an accurate measure of whether the optimum floodgun voltage is achieved, due to chemical shifts. A better indicator would be the width of the measured peaks; at the optimum voltage, the peak widths will be at their minimum value.

Naturally, applying the floodgun to a metallic sample will have little or no
effect on the binding energies and widths of the measured peaks.

2.4.4 Scan parameters

When doing measurements in which the primary goal is to obtain quantitative information about the chemical composition of a sample, it is essential to carry out the scans of different regions with the same spectroscopy parameters. In particular, scans of different regions should be done under the same resolution, with the same spot size, and within the same data collection run. Also, the x-ray beam can produce localised heating of the sample, so it is important to ensure that there is no or minimal damage to the sample during scans.

2.4.5 Angle resolved scans

By mounting the sample on an angled stage, and rotating that stage about the z-axis, it is possible to observe photoelectron emission at different angles to the sample surface. The mean free path of the photoelectrons in the sample depends on the electron energy and the sample material, but they are typically around 20–30 Å. Therefore, when viewing along a grazing angle to the sample surface, the majority of observed photoelectrons will be those produced close to the sample surface, since the deeper photoelectrons cannot escape through the larger distance needed without undergoing some scattering. Hence, the contribution from the top few monolayers to the total signal intensity is higher than that at larger angles. This allows us to identify which peaks come from the surface, and which from the bulk, giving a rough depth profile of the sample. Such a scan is extremely useful when there is reason to believe that the sample is not homogeneous, but whose composition changes with depth.
2.5 XPS data analysis

2.5.1 Spectra fitting

Most XPS spectra can be fitted with a gaussian line shape, summed with a lorentzian. A gaussian-lorentzian weight factor of 90%:10% is typically used.

For certain metals, a gaussian-lorentzian peak with an additional asymmetric tail is required to fit the peaks arising from the bulk. In these metals, the photoelectron emission process leaves behind a positive potential, off which the ejected photoelectrons can scatter. This results in an asymmetric broadening of the lineshape, with a long tail towards the high binding energy [6, 7].

When peaks in a given spectral region are separated by a few eV, such as the aluminium 2p peaks, it is straightforward to identify the individual peaks belonging to different states of the aluminium atoms. In cases where the peak is broad, it is often possible to find various different combinations of peaks which will provide a good fit for the spectra. Hence, getting the “best fit”, as determined from a least squares analysis, may not in reality be the “correct fit”. A fitting scheme employing consistent constraints in binding energies and peak widths should be used, and any type of fitting scheme used must be justified through experiments and theoretical models.

2.5.2 Binding energies and shifts

The primary use of XPS is to identify unknown chemical species within a sample. A survey scan of a wide energy region (typically between 0 to 1000 eV) is usually first obtained, and the binding energies of the observed peaks can be checked against a database. Most spectroscope manufacturers provide a database of ener-
gies, but more precise values can be found in the XPS database published by the National Institute of Standards and Technology (NIST) [8]. As in most spectroscopic techniques, more than one element can share a given binding energy, so it is important to match not just a single line, but as much of the complete spectrum as possible.

The second piece of information that can be obtained from binding energy positions is the chemical state of the atom, for instance, what the atom is bonded to, as well as its valence state. When an atom is involved in a chemical bond, electrons are either drawn toward or pushed away from its valence shell. A core electron of the atom will then see an altered potential. This is observed as a shift in its binding energy.

Since it is often impractical or impossible to measure binding energies of an element in its pure atomic state, binding energy shifts are usually measured relative to some standard “reference” state of the element. For instance, for a metallic element, the measured binding energies of the pure metal are taken as the reference values, and binding energy shifts are calculated relative to these values.

### 2.5.3 Calculating chemical concentrations

The most powerful feature of XPS lies in its ability to determine the chemical composition of materials with a fair degree of accuracy.

Figure 2.9 shows schematically a flux $F$ of x-rays incident on a uniform, homogeneous, sample. The number of photoelectrons emitted from a given atomic species, per unit volume of the sample, $N_0$ is:

$$N_0 = \sigma CF$$

(2.2)

where $C$ is the concentration (number of atoms per unit volume) of that atomic
species in the sample, and $\sigma$ is the photoelectron ejection cross section for a given orbital of the atom. Before reaching the detector, these emitted photoelectrons will have to pass through the overlying atomic layers. The probability $P$ that a photoelectron at a depth $z$ below the surface makes it to the top of the surface and into the detector is given by:

$$P = e^{-z/\lambda \sin \theta}$$  \hspace{1cm} (2.3)

where $\lambda$ is the mean free path of the photoelectron as it traverses the overlying atomic layers, and $\theta$ is the angle between the sample normal and the detector. The mean free path $\lambda$ is dependent on both the energy of the photoelectron as well as the material it passes through.

When the sample thickness is much greater than the photoelectron mean free path, the total number of emitted photoelectrons (per unit area of surface) can therefore be obtained by integrating the unit volume elements from the surface down to infinity (assuming no attenuation of the x-ray beam as it passes through the sample):

$$N = \int_{-\infty}^{0} N_0 P dz = \lambda N_0 \sin \theta$$  \hspace{1cm} (2.4)

To obtain the actual number of photoelectrons picked up by the detector, a detector constant $K$ must be factored in, thus giving the measured signal intensity $I$:

$$I = K \lambda N_0 \sin \theta = K \lambda \sigma CF \sin \theta$$  \hspace{1cm} (2.5)

This expression therefore provides a relationship between the concentration of a given atomic species in a material and the photoelectron signal intensity. By itself, this equation is not very useful or practical, since it requires knowledge of the detector constant $K$ as well as the x-ray flux $F$, both of which vary between different spectrometers and run conditions.
Figure 2.9: The photoemission process. An x-ray flux $F$ penetrates deep into the sample. At any given depth $z$, photoelectrons are produced.
Useful comparisons of absolute intensities between different samples can still be made, provided that care is taken to ensure that scanning conditions remain as similar as possible for the different samples, and that the samples are prepared and handled under the identical conditions (as far as possible, within the scope of the experiment). For example, doing a quick scan of a calibration sample (such as gold) before each data collection run and comparing peak intensities can give a rough idea of how much the x-ray flux changes between runs.

In most cases however, we are only interested in the relative concentrations of two or more different atomic species in a given material. In this case, the detector constant $K$ and x-ray flux $F$ will simply cancel out, provided the signal intensities of the different species are measured under identical conditions. This gives an expression for the relative concentrations of two species:

$$\frac{C_a}{C_b} = \frac{I_a/\lambda a\sigma_a}{I_b/\lambda b\sigma_b}$$

The photoelectron cross section $\sigma$, also known as the Scofield number, is obtained from theoretical calculations [9], while the mean free path $\lambda$ can be obtained from databases, such as Reference [10].

### 2.5.4 Thin films and multilayer films

The basic analysis in the previous section can also be applied to thin films and films containing multiple layers. It becomes slightly more complex because of an increasing number of terms.

For a film of finite thickness, Equation 2.4 cannot be summed to infinity, but rather over the thickness $t$ of the film:

$$N = \int_{-t}^{0} N_0 Pdz = N_0 \lambda (1 - e^{-t/\lambda \sin \theta})$$

(2.7)
Hence, to determine concentration ratios for a thin film, the thickness of the film must be known. Film thicknesses, particularly those formed during oxidation, are not easy to determine exactly. Fortunately, XPS provides a method of estimating the thickness of a thin film.

Figure 2.10 shows an aluminium film with an oxide layer of thickness \( t \) upon it. The thickness of the aluminium layer is several times greater than the photoelectron mean free path, so Equation 2.4 still applies.

In the absence of an oxide layer, the signal intensity from the aluminium metal layer \( I_{Al, met} \) is given by:

\[
I_{Al, met} = K F \lambda_{Al, met} \sigma_{Al} C_{Al, met} \sin \theta \quad (2.8)
\]

where \( \lambda_{Al, met} \) is the mean free path of an aluminium photoelectron within the aluminium metal layer, \( C_{Al, met} \) is the the concentration of aluminium atoms in the metal layer, and \( \sigma_{Al} \) is the Scofield number for the photoelectron.

When the metal is covered by an oxide layer, this signal intensity is attenuated by an exponential factor:

\[
I_{Al, met} = K F \lambda_{Al, met} \sigma_{Al} C_{Al, met} \sin \theta e^{-t/\lambda_{Al, ox} \sin \theta} \quad (2.9)
\]

\( \lambda_{Al, ox} \) is the mean free path of the aluminium photoelectron within the oxide layer.

The signal from the oxide layer is composed of an aluminium peak and an oxygen peak. The aluminium signal intensity is given by Equation 2.7:

\[
I_{Al, ox} = K F \lambda_{Al, ox} \sigma_{Al} C_{Al, ox} \sin \theta(1 - e^{-t/\lambda_{Al, ox} \sin \theta}) \quad (2.10)
\]

where \( C_{Al, ox} \) is the concentration of aluminium atoms within the oxide.

Figure 2.11 is a high resolution XPS scan of the aluminium 2p region. The high binding energy peak comes from the aluminium within the oxide layer, while
Figure 2.10: Analysis for an aluminium/aluminium oxide film stack.
The low binding energy peak is due to the buried aluminium metal layer. If we compute the relative intensity of the signals from the bottom layer and top layer, the spectrometer constants $K, F$ and the Scofield factors $\sigma_{Al}$ will cancel out, resulting in the following equation:

$$\frac{I_{Al,ox}}{I_{Al,met}} = \frac{\lambda_{Al,ox} C_{Al,ox}(1 - e^{-t/\lambda_{Al,ox} \sin \theta})}{\lambda_{Al,met} C_{Al,met} e^{-t/\lambda_{Al,ox} \sin \theta}}$$  \hspace{1cm} (2.11)

This can be rearranged to obtain an expression for the thickness of the film:

$$t = \lambda_{Al,ox} \sin \theta \ln \left( \frac{\lambda_{Al,met} C_{Al,met}}{\lambda_{Al,ox} C_{Al,ox}} \frac{I_{Al,ox}}{I_{Al,met}} + 1 \right)$$  \hspace{1cm} (2.12)

This expression still contains quantities which cannot be determined from an XPS experiment, such as the photoelectron mean free paths and aluminium atom concentrations in the metal and oxide. The values for these terms can be obtained from databases, and calculation of the film thickness can then be made.

Once the oxide thickness is known, the oxygen/aluminium ratio in the oxide can be obtained from the relative intensities of the oxygen and aluminium signals.
originating from the oxide layer:

$$\frac{C_{O,\text{ox}}}{C_{Al,\text{ox}}} = \frac{I_{O,\text{ox}}}{I_{Al,\text{ox}}} \frac{\lambda_{Al,\text{ox}} \sigma_{Al}(1 - e^{-t/\lambda_{Al}}} \sin \theta)}{\lambda_{O,\text{ox}} \sigma_{O}(1 - e^{-t/\lambda_{O}}} \sin \theta)}$$

(2.13)

As in Equation 2.12, this expression contains quantities (the mean free paths and Scofield factors) which must be obtained from databases or theoretical calculations. Although doing so can give fairly accurate results [5], a better method would be to acquire data from a sample whose stoichiometry is known. For aluminium oxide, sapphire can be used as a reference sample. The term containing the mean free paths and Scofield numbers in Equation 2.13 is then written in terms of the signal intensities $I_{Al,\text{ref}}$ and $I_{O,\text{ref}}$ from the reference sapphire sample:

$$\frac{\lambda_{Al,\text{ref}} \sigma_{Al}}{\lambda_{O,\text{ref}} \sigma_{O}} = \frac{I_{Al,\text{ref}}}{I_{O,\text{ref}}} \frac{C_{O,\text{ref}}}{C_{Al,\text{ref}}} = \frac{3}{2} \frac{I_{Al,\text{ref}}}{I_{O,\text{ref}}}$$

(2.14)

Substituting this equation into Equation 2.13 then gives

$$\frac{C_{O,\text{ox}}}{C_{Al,\text{ox}}} = \frac{I_{O,\text{ox}}}{I_{Al,\text{ox}}} \frac{3I_{Al,\text{ref}}(1 - e^{-t/\lambda_{Al}}} \sin \theta)}{2I_{O,\text{ref}}(1 - e^{-t/\lambda_{O}}} \sin \theta)}$$

(2.15)

One further consideration is the choice of values for the density of the oxide used in calculating the film thickness, as well as the mean free paths of the oxygen and aluminium photoelectrons in the oxide. Often, the corresponding values for sapphire ($\gamma$-Al$_2$O$_3$) are used [4, 11]. This assumption may not be completely valid when studying oxide growth on thin films, where the oxide layer is most likely amorphous and hence having a density which is probably different from that of sapphire. The mean free paths, which depend upon the oxide structure and stoichiometry, may also be different.

One way of getting around this problem is to assume that the oxide density changes as a function of the oxide O/Al ratio. Equations 2.12 and 2.15, together with an equation which models how the oxide density changes with stoichiometry,
are then calculated iteratively until a numerically stable solution is obtained [12]. A similar model for the mean free paths can also be added to the system of equations.
References for Chapter 2


CHAPTER 3
ALUMINIUM OXIDE THIN FILM GROWTH

3.1 Introduction

The quality of a tunnel junction is determined primarily by one feature — the quality of the aluminium oxide barrier layer grown. While there are various different methods of producing this barrier, such as plasma oxidation of aluminium and direct deposition of aluminium oxide, I will focus here only on room temperature thermal oxidation. This is the most straightforward and controllable way of oxidising the film, with the least number of experimental parameters (oxygen purity, oxygen partial pressure and exposure time).

In this chapter, XPS data on aluminium films at various stages during the oxidation process will be presented. From this, we can determine the chemical changes occurring both within the aluminium oxide layer and on the surface of the aluminium oxide. Also, by studying what happens when a metallic electrode is deposited onto the aluminium oxide film, we can gain a better understanding of the interfacial processes which occur when making actual tunnel junction devices, and how these processes are beneficial and/or detrimental to the device quality.

3.2 Aluminium film growth

Although XPS measurements are not particularly sensitive to surface roughness, it may still be important to grow uniform aluminium layers since this duplicates the conditions under which device quality films are made. For device films, particularly those with ultrathin oxide layers, seed layers are required to produce smooth and uniform films [1]. However, for the Al/AlO_x systems investigated in this thesis,
preliminary test scans indicated that their XPS spectra were mostly unaffected by either the presence or absence of seed layers. Hence, as far as the XPS measurements shown in this thesis are concerned, a direct deposition of a thick aluminium layer onto the oxidised silicon substrate is sufficient; no seed layers are required.

Aluminium oxide thin films were initially grown in a separate evaporator and then transferred in air into the XPS chamber. However, it is not possible to study the effect of low oxygen doses on aluminium films with this method. In later experiments, a mobile UHV pump station was used to transfer samples between the evaporation system and the XPS system, without exposing the sample to ambient air.

A brief note on nomenclature — for convenience, samples, particularly multi-layer films, are identified by their components in the following way: A/B/C/etc., where A, B and C refer to either the material deposited or process carried out. For example, the sample produced by depositing 300 Å of gold on a silicon substrate, followed by a deposition of 10 Å of aluminium, which is then further oxidised at a dose of 1 torr·s and finally capped with 5 Å of cobalt, is denoted by 300Å Au/10Å Al/1 torr·s/5Å Co.

### 3.3 XPS spectra analysis

The first step in studying the aluminium oxide system involves the identification and assignment of peaks in the XPS spectra. To do this, we start with the most basic system available - that of a single, unoxidised aluminium film.

This baseline sample is a 300 Å thick layer of aluminium, thermally evaporated onto a clean silicon substrate. The evaporation is done in a UHV chamber with a base pressure of $\sim 2 \times 10^{-10}$ torr. During the evaporation process, the pressure
rises by a factor of 10 to $\sim 2 \times 10^{-9}$ torr. The sample is then transferred into the XPS chamber by means of a mobile pump station whose pressure was maintained at $10^{-9}$ torr.

The transfer process requires about 12 hours to complete. Assuming the partial pressure of the residual oxygen in the pump station is 20% of the total pressure, this results in the sample being exposed to an oxygen dose of about 8 $\mu \text{torr-s}$.

For all the aluminium samples studied in this thesis, the following XPS scans are taken:

1. A low resolution survey scan, 0–1000 eV

2. A high resolution oxygen 1s scan, 525–545 eV

3. A high resolution aluminium 2p scan, 68–88 eV

For samples where the aluminium layer is beneath a metal electrode, a high resolution scan of the metal overlayer is taken as well.

The survey scan (Figure 3.1) provides a quick check on the sample cleanliness. The survey scan of a clean sample would contain only peaks belonging to oxygen, aluminium and carbon; the latter element coming mostly from pump oil, and also from the carbon crucible containing the aluminium source during sample evaporation.

The presence of a strong oxygen line in the scans of the baseline “unoxidised” sample is not unusual — as estimated earlier, the sample receives a dose of around 8 $\mu \text{torr-s}$, more than sufficient to form an oxygen monolayer on the surface [2]. The aluminium 2p spectrum confirms this — two peaks are present, a lower binding energy metal peak at $\sim 73$ eV and a higher binding energy oxide peak at $\sim 75$ eV (Figure 3.2).
Figure 3.1: Survey scan of an unoxidised aluminium sample transferred in vacuum.
**Figure 3.2:** Aluminium 2p spectrum, unoxidised aluminium sample. Even under UHV conditions (~2×10⁻⁹ torr), there is a sufficient amount of oxygen for a thin layer of oxide to form. Hence there is a small oxide peak at around 76 eV, along with the main metal peak at around 73 eV.
Fitting the aluminium 2p spectra is fairly straightforward as the two peaks are well resolved. The metal peak is fitted with an asymmetric 90% Gaussian:10% Lorentzian lineshape (abbreviated as a 10% GL lineshape), while the oxide peak is fitted with a symmetric 10% GL lineshape. A least-squares fit procedure is used to obtain the best fit, and neither the binding energies nor the peak widths (FWHMs) are constrained. Each of the aluminium peaks actually has two peak components - the larger, more intense peak component arising from the 2p\textsubscript{3/2} level, and a smaller one from the 2p\textsubscript{1/2} level. Even at the highest resolution, the spectrometer is unable to resolve the two peak components; hence, for all practical purposes, they may be regarded as a single peak.

Obtaining fits for the oxygen 1s spectrum is more difficult, as this peak is rather broad, indicating closely spaced peak components. In order to fit this spectrum, the following assumptions are made:

1. The spectrum consists of two components. One peak component comes from oxygen within the oxide layer, and the other comes from chemisorbed oxygen on the oxide surface.

2. Although the absolute binding energy positions of the aluminium and oxygen peaks originating from the oxide may shift between different XPS runs due to effects such as sample charging or spectrometer drift, these effects will affect both peaks equally. Hence, the binding energy difference between these two peaks is not affected by calibration drifts.

3. This binding energy difference depends only on the binding state between the aluminium and oxygen atoms in the oxide and therefore has a fixed value which depends on the nature of the oxide. For a thermally grown oxide film,
this value is $457.0 \pm 0.5$ eV [3]. However, this value may change depending on
the nature of the oxide. For the most part, an unconstrained best fit with two
symmetric lineshapes will yield an aluminium-oxygen oxide binding energy
difference of about $457$ eV. In certain cases however, because of experimental
error, this binding energy difference must be constrained to obtain the “true”
peak values.

Fitting the oxygen spectrum according to these assumptions thus gives a lower
binding energy peak (corresponding to the oxygen within the oxide) and a smaller,
higher binding energy peak (corresponding to the chemisorbed oxygen on the sur-
face). Figure 3.3 shows the oxygen spectra and peak fits for the unoxidised alu-
minium sample.

The fitting and analysis procedure thus goes as follows:

1. The aluminium 2p spectrum is fitted with two 10% GL peaks, an asymmet-
ric metal peak and a symmetric oxide peak, using a least-squares method
without any peak constraints.

2. The oxide oxygen peak binding energy is determined from the oxide alu-
minium peak binding energy obtained in step 1.

3. The oxygen 1s spectrum is fitted with two peaks, using a least-squares
method, initially without any peak constraints. If the unconstrained best
fit does not yield an Al–O binding energy difference consistent with the na-
ture of the sample, the Al–O binding energy difference is then fixed to the
value calculated in step 2 and the fit carried out again.

4. The oxide thickness and stoichiometry of the film are calculated using the
iterative method described in Chapter 3.
Figure 3.3: Oxygen 1s spectrum, unoxidised aluminium sample. The large peak around 532 eV is due to the oxide and the smaller peak at around 534 eV is due to the chemisorbed oxygen.
To check for the possibility of x-ray damage to the samples, particularly changes due to sample heating, two consecutive XPS runs were performed on a test sample. The spectra for the two runs were identical (within the limits of the spectrometer), indicating that the data collection process does not noticeably change the chemical composition of the sample.

3.4 Single layer aluminium films

3.4.1 Sample preparation and oxidation

We are now in a position to track the changes in the XPS spectra as the sample is gradually oxidised. Starting with an unoxidised sample as prepared above, a set of XPS runs is performed, with the sample being exposed to an increasingly larger oxygen dose between runs. The oxidation step is carried out at room temperature. The sample is moved from the XPS chamber to the load lock, which is then filled with 99.997% pure dry oxygen to a particular pressure. Once the required amount of oxidation time has elapsed, the load lock is then evacuated and the sample transferred back into the XPS chamber. Unless otherwise specified, the oxygen exposures mentioned in this section refer to the total cumulative dose to which the sample has been subjected.

For small oxygen exposures (50 torr-s or less), the oxygen pressure used was 50 mtorr. Mid ranged exposures (between 50 and 5000 torr-s) were carried out pressures of around 500-600 mtorr, and higher exposures at pressures of 1-2 torr. However, using different oxygen pressures to achieve a particular dose did not seem to produce any noticeable differences (as far as the XPS spectra is concerned). This is consistent with earlier oxidation studies on aluminium oxide based superconduct-
Figure 3.4: Aluminium 2p spectra taken after oxygen exposures of 1, 5, 50 and 300 torr·s.

Figure 3.4 shows the aluminium 2p spectra after four different oxygen exposures (1, 5, 50 and 300 torr·s). The absolute intensity of the metal peak decreases with increasing dose. This attenuation in the metal peak intensity is expected — as the dose increases, so does the thickness of the oxide layer (discussed later in this section). The signal from the metal layer is thus attenuated more as the oxide gets thicker, resulting in a decrease in the absolute intensity of the peak. Paradoxically, the absolute intensity of the oxide peak increases only by a small amount, even though the amount of oxide has increased and hence one would expect a larger increase in the intensity (Figure 3.5).

Equations 2.7 and 2.9 provide the solution to this puzzle. As the oxide grows in thickness, the increased amount of oxide does result in more photoelectrons being produced; however, as the thickness increases, so does the probability that a
**Figure 3.5**: Absolute intensities of the aluminium oxide and metal peaks as a function of oxygen dose. The absolute intensity of the metal peak quickly decreases with increasing oxygen dose (i.e., increasing thickness) while the absolute intensity of the oxide increases more slowly.
photoelectron is scattered. The increase in intensity due to the increased amount of oxide is offset by an increased attenuation factor, thus resulting in only a slight increase in the oxide peak intensity. On the other hand, there is effectively only a constant amount of aluminium metal present, while the attenuation factor increases with oxygen dose. The net result is thus a larger decrease in the absolute intensity of the metal peak.

Figure 3.6 compares the increase in the measured normalised absolute intensity $I/I_0$ of the oxide peak with that predicted by Equation 2.7. The intensity normalisation factor $I_0$ is selected such that the ratio $I/I_0$ is 1 when the oxide thickness is 12 Å. In calculating the expected normalised intensity, the photoelectron mean free paths are assumed to stay constant as the oxide thickness increases. With the exception of the initial data point, the increase in the measured intensity agrees well with the increase expected from Equation 2.7.

Figure 3.7 shows the corresponding comparison for the metal peak intensities. As with the oxide intensities, there is good agreement between the measured data and Equation 2.9. Furthermore, since the metal layer is buried beneath the oxide, this good agreement is also an indicator that the mean free path of the metal photoelectrons does not significantly change as the oxide increases in thickness. A change in the metal photoelectron mean free path with thickness would result in either a faster (or slower) than expected drop in the intensity of the metal peak, neither of which are seen in Figure 3.7.

Both these intensity comparisons assume that the chemisorbed oxygen layer on the oxide surface does not attenuate the signals from the underlying layers. In reality, there will be some attenuation; however, as the chemisorbed layer is believed to be thin and sparse [2, 5], the signals will most likely be attenuated by
Figure 3.6: Measured and expected change in the relative absolute intensity of the oxide peak in the aluminium 2p spectrum for a slowly oxidised 300 Å aluminium sample.
Figure 3.7: Measured and expected change in the relative absolute intensity of the metal peak in the aluminium 2p spectrum for a slowly oxidised 300 Å aluminium sample.
Figure 3.8: Thickness of the aluminium oxide layer as a function of oxygen exposure for a slowly oxidised 300 Å aluminium sample.

only a negligible amount.

3.4.2 Oxide thickness and stoichiometry

The oxide thicknesses at the various exposures are calculated from the relative intensities of the aluminium 2p metal and oxide peaks, according to Equation 2.12. Figure 3.8 shows the increase in the oxide thickness as a function of oxygen exposure. From an initial starting thickness of about 7.0 Å, the thickness increases steadily with the oxygen dose until about $10^4$ torr-s. At this point, the oxide growth rate slows down considerably.
The thicknesses shown here were calculated using the iterative method described in Chapter 2. In this method, the concentration of aluminium atoms in the oxide is assumed to change smoothly with the stoichiometry of the oxide (Figure 3.9). Such a model describes a process whereby the oxide lattice structure “inflates” as more oxygen atoms is pushed into the oxide lattice, increasing its O/Al ratio towards that of stoichiometric Al$_2$O$_3$.

However, the following scenario is also possible: the oxide layer has a lattice structure which is akin to that of sapphire, but with one oxygen site vacant. In this case, the aluminium atom concentration in the oxide would stay constant at
Figure 3.10: Calculated oxide thickness as a function of the aluminium atomic concentration, from the intensity values obtained from a single aluminium thin film oxidised at 1000 torr·s.

A value close to that of Al₂O₃ (for sapphire, this value is 71.2 mol/dm³ [6]).

The calculated oxide thickness thus depends on the value of aluminium atom concentration used. Figure 3.10 shows the range of thickness values possible for a single aluminium film exposed to an oxygen dose of 1000 torr·s.

The uncertainty in the thickness does not significantly affect the calculated stoichiometry, as the thickness dependence in the stoichiometry calculation appears only as a ratio of exponential terms (see Equation 2.15). An uncertainty of 3 Å (the difference in the thickness between the metal and sapphire limits) produces only a change of about 2% in the stoichiometry. This is considerably less than
Figure 3.11: O/Al ratio as function of oxygen dose, for a slowly oxidised 300 Å aluminium sample.

the error due to uncertainties in the intensity measurements and the peak fitting routines.

Figure 3.11 shows the stoichiometry of the oxide film as a function of the oxygen dose. Apart from the starting value and the values at high doses (above $10^4$ torr-s), the oxygen/aluminium ratio stays roughly constant at about 1.0, indicating that the oxide layer is for the most part oxygen deficient.

Scans of different “undosed” aluminium films show a range of stoichiometry values, ranging from 0.9 to 1.3. It is estimated that these films pick up a dose of about 8 $\mu$torr-s during the sample transfer. At these small exposures, the oxide
layer may not be covering the entire film completely; rather, small islands of oxide are present on the surface [7]. Depending on how far the island growth stage has progressed, the measured oxide signal intensities will vary; hence, the calculated thickness and stoichiometry at these low exposures may not have any significance. At oxygen exposures of $10^4$ torr-s and above, the oxygen/aluminium ratio drops to a value below 1.0.

### 3.4.3 Chemisorbed oxygen and the Al/AlO$_x$ system

The above oxidation results were reproduced in other similar aluminium thin film samples. From these results, we can conclude that the oxide formed by the room temperature oxidation process is oxygen deficient, with oxide O/Al ratios typically around 1.0. Oxygen molecules landing on the oxide surface then pick up electrons via a charge transfer mechanism, leaving behind positively charged oxygen vacancy sites within the oxide. These negatively charged oxygen molecules (O$_2^-$) then form a weak chemisorption bond between the positive vacancies in the oxide. This is the source of the chemisorbed oxygen peak observed in the O 1s spectrum.

### 3.4.4 Oxygen 1s peak intensities

Although making direct comparisons of absolute intensity values may be a somewhat risky endeavour (see the previous chapter), such comparisons can offer strong hints about how the sample changes as the oxidation proceeds.

As with the aluminium peaks, we can compare the attenuation in the oxide oxygen intensity with the expected change due to an increasing oxide thickness (Figure 3.12). For intermediate oxygen exposures, the measured intensity follows the expected trend to some degree; however, at high exposures, there is a rapid
Figure 3.12: Measured and expected intensities of the O 1s oxide peak with thickness, for a slowly oxidised 300 Å aluminium sample.

Dropoff in the intensity value. At the same time as the O 1s oxide intensity drops, the chemisorbed oxygen intensity increases (Figure 3.13).

The possibility that the absolute oxide oxygen intensity dropoff is due to a slowly decreasing x-ray flux can be ruled out for several reasons. Firstly, although the oxide oxygen intensity drops, the chemisorbed oxygen intensity rises at the same time. Furthermore, there is no corresponding large drop in the aluminium signal intensities. Secondly, gold calibration scans taken at regular intervals (in particular before and after this aluminium sample was examined) shows peaks of comparable intensities, indicating no significant decrease in the emitted x-ray
Figure 3.13: Absolute intensities of the chemisorbed and oxide oxygen peaks as a function of oxygen exposure, for a slowly oxidised 300 Å Al sample.
flux over time. Finally, further repeated slow oxidation experiments also show the intensity changes displayed here.

One method of smoothing out the smaller fluctuations in the intensity values is to normalise all the intensity values with respect to the metal intensity. Since there is essentially an infinite amount of metal in the system, the absolute metal intensity is affected only by the thickness of the oxide layer above it. Dividing the expected metal intensity by the measured intensity (Figure 3.7) yields a factor for each data point which corrects for variations in the x-ray flux. Applying this factor to the oxide and chemisorbed intensity values then results in normalised absolute intensity curves, from which trends can be more easily observed (Figures 3.14 and 3.15).

The onset of this rise/drop in the oxygen intensities does not appear to depend on the oxygen dose, but rather on the thickness of the oxide. Among the four slowly oxidised aluminium samples studied, this onset occurred when the oxide thickness was between 13–14 Å.

From the calculated stoichiometry values, it appears that, at this thickness, the oxide begins to lose oxygen when exposed to a dose. This lost oxygen does not leave the sample completely, but rather returns to the chemisorbed state. The mechanism for this process is not yet fully understood.

### 3.4.5 Binding energy

Figure 3.16 shows the binding energy difference between the oxide and metal peaks as a function of the oxygen exposure. Apart from the initial starting point, the binding energy difference decreases as the oxygen dose increases (i.e., as the thickness of the oxide increases).
**Figure 3.14:** Normalised absolute intensities of the O 1s chemisorbed and oxide peaks as a function of oxygen exposure, for a slowly oxidised 300 Å Al sample.
**Figure 3.15:** Normalised absolute intensities of the metal and oxide Al peaks as a function of oxygen exposure, for a slowly oxidised 300 Å Al sample.
Figure 3.16: The binding energy difference between the oxide and metal peak in the aluminium 2p spectra as a function of oxygen exposure. This difference decreases with increasing oxygen exposures.

Repeating the experiment with smaller exposure steps shows initially an increase in the binding energy difference which levels off around 1–10 torr-s, and a decrease after that (Figures 3.16 and 3.17).

Such changes in the binding energy with increasing oxide thickness are not unusual; they have been observed in other oxide systems such as silicon dioxide [8]. In these systems, the binding energy shift can be well explained using an image charge model [8, 9]. In this model, the positive vacancies left behind in the oxide when photoelectrons are emitted set up negative image charges in the metal and vacuum. The net effect of the resultant potential is a slight increase in the binding
Figure 3.17: The binding energy difference between the oxide and metal peak in the aluminium 2p spectra as a function of oxygen exposure. This difference rises at low oxygen exposures, but drops after exposures of 10 torr-s.
energy of the oxide peak.

Additionally, in the oxidation model postulated in the previous section, oxygen vacancies in the oxygen-deficient oxide layer produce regions of positive charge within the oxide. As with image charges, the potential set up by these positively charged regions will produce an upward shift in the binding energy of the oxide peak.

In the aluminium oxide system, there is an initial increase in the binding energy difference between 0 and 1 torr-s; but subsequently, the binding energy difference starts dropping monotonically. This is in the opposite direction to that observed in the silicon/silicon dioxide system. Hence, another mechanism must be responsible for the downward shift observed.

The most likely explanation is that a Cabrera-Mott capacitor is set up across the oxide [10]. A negative surface charge together with its corresponding positive charge in the metal sets up a potential across the oxide (Figure 3.18(a)). As a result of this potential, photoelectrons generated within the oxide will have a lower binding energy than photoelectrons coming from the interface. The magnitude of this shift depends on the depth of the photoelectrons from the oxide surface. By summing up the shift contributions from different layers within the oxide, a lower binding energy peak is obtained (Figure 3.18(b)).

The magnitude of the overall binding energy shift observed is only about 0.1 eV; this is lower than the observed shift due to either the image charge or Mott potential. It is likely that a combination of different processes is happening. At low oxygen exposures (less than 1 torr-s), the oxide surface has only a low density of chemisorbed oxygen; hence the shifts due to image charge effects and oxide oxygen vacancies dominate. At higher exposures, the shift due to the Mott poten-
Figure 3.18: (a) Schematic of the Al/AlO\textsubscript{x} bilayer sample. The negatively charged chemisorbed layer and associated positive charge in the metal produce a voltage $V$ across the oxide. (b) Bottom - In the absence of a potential across the oxide, the signal components arising from different depths within the oxide have the same binding energy. Top - When there is a Mott potential of 0.6V across the oxide, the signal components will have different binding shifts, depending on their depth within the oxide. The sum of the components result in an oxide peak which is shifted to a lower binding energy. Figure taken from Reference [10].
tial dominates, resulting in an overall downward shift in the binding energy with thickness.

### 3.4.6 Air oxidation

Aluminium samples transferred in air into the XPS system also display the same peaks as the vacuum transferred samples. Transferring the sample in air between the evaporation and XPS systems typically takes about 10 minutes; this is equivalent to a dose of about $6 \times 10^5$ torr-s. The air-transferred oxide films are also oxygen deficient, with an O/Al ratio of around 1.0, while their thickness is comparable to a vacuum-transferred film exposed to an equivalent dose of oxygen.

The main difference is in the intensity of the chemisorbed peak. This intensity is higher compared to an equivalent vacuum-transferred oxide (Figure 3.19). The difference in intensity is most likely due to the presence of O–H groups; either in the form of water adsorbed onto the sample surface, or in the aluminium hydroxide formed when water vapour reacts with the oxide [11]. As the binding energy of the O–H peak is extremely close to that of the chemisorbed oxygen peak, the two individual peaks cannot be uniquely resolved. When the sample is left in vacuum over a few days however, the surface water molecules quickly desorb. Furthermore, the reaction of water with aluminium oxide to form aluminium hydroxide is reversible\(^1\):

$$\text{Al}_2\text{O}_3(\text{s}) + \text{H}_2\text{O}(\text{g}) \leftrightarrow \text{Al(OH)}_3(\text{s})$$  \hspace{1cm} (3.1)

In vacuum, the equilibrium of this reaction shifts towards the left, and the alu-

\(^1\)Although this chemical reaction involves stoichiometric aluminium oxide, it still holds for the nonstoichiometric oxide formed on the air oxidised samples.
Figure 3.19: Oxygen 1s spectra of two aluminium samples. The vacuum-transferred sample has been exposed to $3 \times 10^5$ torr$\cdot$s of oxygen, roughly equivalent to the total oxygen dose received during an air transfer.
Figure 3.20: Two oxygen 1s spectra of an air-transferred aluminium film, taken 6 days apart. As the surface water desorbs from the film in UHV, the high binding energy component of the peak reduces in intensity. This results in an overall shift in the peak maximum towards a lower binding energy.

The amount of aluminium hydroxide formed during the sample transfer reverts back to aluminium oxide as the water is pumped away. Figure 3.20 shows two sets of oxygen spectra for an aluminium thin film, the first taken immediately after the sample was transferred in air into the XPS system, and the second taken after the sample had been in the XPS system for 6 days. There is a slight decrease in the size of the high binding energy shoulder; at the same time, the main oxide peak intensity shows a slight increase. The intensities of both peaks are plotted as a function of time in vacuum in Figure 3.21.
Figure 3.21: Intensities of the oxide and chemisorbed peaks in the O 1s spectra over time (in UHV) for an air transferred aluminium sample. After about 5 days, the intensities finally reach stable values.
After 4–6 days in vacuum, no further change in the oxygen spectrum is observed; what remains on the high binding energy side of the peak is the chemisorbed oxygen. At this point, the ratio of the peak intensities becomes comparable to that of a vacuum transferred sample that has been given an equivalent oxygen dose ($\sim 3 \times 10^5$ torr-s).

Further evidence of the presence of water can be seen in Figure 3.22, which shows the relative intensities of the oxygen 1s chemisorbed and oxide peaks of samples grown at different times of the year and transferred in air to the XPS system. The intensity of the chemisorbed oxygen peak reaches a maximum during the humid summer months, and is a minimum during winter, when the ambient air becomes much drier.

### 3.5 Multilayer films

For magnetic tunnel junctions, it is desirable to make the oxide barrier as thin as possible. As to be expected, several difficulties arise as the oxide layer gets thinner.

First and foremost is the problem of achieving a complete, pinhole free oxide layer. If room temperature thermal oxidation is used to form the oxide, a minimum amount of aluminium must be deposited in order to achieve a fully formed, pinhole free barrier [12]. In addition, a minimum dose of oxygen is required as well [13].

The problem with having a such thin starting layer of aluminium is that, at the oxygen doses employed for device quality films (typically around 100–200 torr-s), the underlying electrode material is likely to oxidise as well. The presence of the electrode oxide layer at the barrier interface then leads to a degradation in the quality of the tunnel junction [14]. Hence, it is desirable to find methods of growing a thin, complete aluminium oxide layer which do not produce significant
Figure 3.22: Relative intensities of the O 1s oxide and chemisorbed peaks of air transferred samples over the course of 15 months. There is a slight but noticeable change in the relative intensities due to the air humidity at different times of the year.
detrimental effects on the base electrode. This problem will be addressed in the next chapter.

For superconducting tunnel junctions, the thickness of the starting layer of deposited aluminium is not so much an issue, as long as it is smaller than the coherence length of the superconductor (which, for Type I superconductors, is usually a few hundred Å).

In both types of junctions however, another question arises — what happens to the chemisorbed oxygen on the oxide surface as the top electrode is deposited? There are two possibilities; first, the chemisorbed oxygen is simply knocked off the oxide surface; second, the chemisorbed oxygen stays on the oxide surface. In the latter case, it would naturally be pertinent to investigate if and how the chemisorbed oxygen affects the junction quality.

3.5.1 Experimental details and XPS analysis

When studying multilayer films, the sample depth into which the XPS probes becomes an important consideration. Previously, for single layer aluminium films, the thicknesses of the oxide layers were no larger than 15 Å — well below the attenuation length of the aluminium and oxygen photoelectrons. For these samples, the entire oxide film as well as part of the underlying metal can be seen by XPS.

Adding a top layer to the metal results in more attenuation of the underlying signal. When the total thickness of the overlayers become comparable to the mean free path of the photoelectrons, there is a risk of probing only part of the buried layer (Figure 3.23). Furthermore, as the mean free path is somewhat shorter for O 1s photoelectrons compared to Al 2p photoelectrons, measured quantities such as the stoichiometry would not reflect the true stoichiometry when only part of
the oxide layer is probed.

Hence, it is necessary to ensure that overlayers are thin enough that the entire region of interest can be studied with XPS, but at the same time thick enough to completely cover the oxide surface.

Fitting the oxygen 1s peak is also more problematic when multilayers are involved. In addition to the aluminium oxide peak, peaks from the oxides of the overlayer will also be present. In many cases, further additional peaks, believed to be due to adsorbed oxygen on the overlayer surface, are also observed. As the peaks of the various oxides and chemisorbed peaks are so closely spaced, there is more uncertainty in fitting the peaks, and as a result, more uncertainty in the aluminium oxide stoichiometry calculations.

### 3.5.2 Metal XPS scans

Reference XPS scans of the metal overlayer material are first carried out. From these scans, the peak positions of the metal as well as its associated oxide can be determined. This serves two purposes. Firstly, we can check if any of the metal peaks will potentially overlap with the peaks from the aluminium layer. Secondly, and perhaps more importantly, we can identify the metal oxide peak, which allows us to better resolve the oxygen spectrum of a multilayer film. The three metals studied were cobalt, niobium and yttrium; these are the metal layers used in the multilayer samples.

#### Cobalt

Cobalt is known to form two different oxides at room temperature, CoO and Co$_3$O$_4$. From the oxygen spectrum alone, it is not possible to distinguish the two. However,
Figure 3.23: (a) A large fraction of photoelectrons originating at (1) and (2) can exit the sample without being scattered since their mean free paths (dashed ellipse) are greater than the depths at which they originate. Photoelectrons at (3) have very small probability of exiting the surface without scattering, and hence they will not contribute much to the signal. For this sample, the entire oxide depth can be observed, hence reliable information about the oxide can be obtained. (b) When a top layer is added, photoelectrons originating from the lower layers of the oxide will have a hard time reaching the sample surface, while photoelectrons originating above them will not. The entire oxide depth in this case cannot be observed. Calculated oxide quantities such as the stoichiometry might therefore not be accurate, particularly since the photoelectron mean free paths for different chemical species differ slightly. (c) Table of mean free path values, in Å, for aluminium 2p and oxygen 1s photoelectrons in various materials. From Reference [15].
**Figure 3.24:** Cobalt 2p spectra of two cobalt films, one unoxidised and the other oxidised in air. The two shake-up peaks in the air oxidised cobalt sample indicate the presence of CoO.

they can be distinguished by the intensity of the satellite “shake-up” peaks in the cobalt 2p spectra (Figure 3.24). CoO has a much higher intensity of shake up peaks than Co$_3$O$_4$ [16].

Figure 3.25(a) shows the oxygen spectrum of a 300 Å thick cobalt film which has been oxidised in air. The lower binding energy peak at $\sim$530.5 eV corresponds to cobalt oxide. Interestingly enough, a secondary peak at a higher binding energy is also seen. Several groups have also observed this higher binding energy peak in the XPS spectra of cobalt oxide, and have assigned this peak to adsorbed oxygen on the cobalt surface [16, 17]. Further evidence for this is shown in Figure 3.25(b), a scan
Figure 3.25: Oxygen 1s spectra of a cobalt film (a) immediately after film growth, and (b) after a 250°C, 1 hour anneal in UHV. During the anneal, some of the adsorbed oxygen reacts further with the cobalt to produce more cobalt oxide.

taken after the cobalt film has been annealed at 250°C for an hour. The intensity of the cobalt oxide peak has increased while the chemisorbed peak intensity has decreased, indicating that the anneal has caused some of the chemisorbed oxygen to react further, either producing more cobalt oxide, and/or converting the existing CoO into the more oxygen rich Co₃O₄.

The relative intensities of the chemisorbed and oxide peaks are very different in aluminium and cobalt. It is not possible to tell if this difference is due to different amounts of chemisorbed oxygen, or different amounts of oxide. Unlike aluminium, the cobalt spectrum does not have two easily resolvable peaks corresponding to a
metal and oxide, hence the cobalt oxide thickness cannot be calculated. However, given that cobalt is less reactive to oxygen than aluminium, it is more likely that the relative intensity difference is due to less cobalt oxide.

The cobalt oxide oxygen peak appears far below any of the oxygen peaks in aluminium oxide, so it can be easily separated out. Unfortunately, the chemisorbed peak appears at the same energy location as that of an aluminium oxide peak. This makes the peak identification in an aluminium/cobalt bilayer film much more difficult.

**Niobium**

Figure 3.26 shows the niobium 3d spectrum of an air transferred 300 Å niobium film. Although the metal peaks can be readily distinguished from the oxide peaks, there is more uncertainty in fitting the NbO and Nb$_2$O$_5$ peaks, particularly when only a small amount of oxide is present.

Again, two peaks are seen in the oxygen 1s spectrum (Figure 3.27). As with cobalt, only one oxide peak is seen in the O 1s spectrum; the two types of niobium oxide, NbO and Nb$_2$O$_5$, cannot be individually resolved.

**Yttrium**

Figure 3.28 shows the oxygen 1s spectrum of a 300 Å thick yttrium film, transferred in vacuum. Even though the film has not been exposed to any controlled oxygen dose, a large oxide peak is still present, accompanied by a smaller high binding energy peak, which is again assigned to adsorbed oxygen on the yttrium surface.

Large oxide peaks are also present in the yttrium 3d spectrum (Figure 3.29, together with smaller metal peaks. The large attenuation of the metal signal
Figure 3.26: Niobium 3d spectrum, 300 Å niobium sample, air transferred, showing metal and oxide peaks. The niobium 3d peak is a doublet, reflecting the spin-orbit splitting of the 3d core level in niobium.
**Figure 3.27:** Oxygen 1s spectrum of a 300 Å niobium sample, air transferred. The low binding energy peak at \(~530.8\) eV arises from niobium oxide, and the high binding energy peak is due to adsorbed oxygen on the surface.
**Figure 3.28:** Yttrium 3d spectrum of a 300 Å yttrium sample, vacuum transferred. From the relative intensities of the oxide and metal peaks, it appears that the top layer of the sample is mostly oxide. As with niobium, the Y 3d level also show spin-orbit splitting.
Figure 3.29: Oxygen 1s spectrum of a 300 Å yttrium sample, vacuum transferred. The yttrium oxide peak is at ~531.4 eV. The high binding energy peak is again attributed to adsorbed surface oxygen.

indicates that a relatively thick oxide layer has formed.

3.5.3 Metal/Aluminium bilayer films

In the experiments with a single layer of aluminium, there is essentially an infinite reservoir of aluminium metal, whereas in thin films, the aluminium metal becomes the “limiting reagent” in the oxidation process. As thin films (30 Å or less) are used in actual devices, it is necessary to investigate how the oxidation process differs, if at all, from the case of a thick, single layer aluminium film.

For a multilayer film, obtaining quantitative information becomes more diffi-
cult. More assumptions and estimates are required, and this in turn raises the uncertainty in the figures obtained. For instance, the thickness calculation (Equation 2.12) assumes that there is an infinite amount of metal below the oxide; for a multilayer film, this is no longer true. An estimate must be made for the thickness of metal remaining after the oxidation. As a result, the oxide thickness can only be estimated as well. There is less uncertainty in the calculated stoichiometry, as this value depends only weakly on the thickness of the oxide layer (Equation 2.13).

To investigate the effect of a bottom electrode on an aluminium film, bilayer film samples are used. These samples are grown by depositing a thick bottom metal layer onto a silicon substrate, followed by a thinner layer of aluminium. The aluminium layer is then oxidised, and the sample is transferred into the XPS system.

### 3.5.4 Binding energy shifts

Initial bilayer samples consisted of a 300 Å thick metal base layer and 30 Å thick aluminium layer. The most striking difference between these samples and the single layer aluminium films lies in the binding energy shifts of aluminium oxide peaks. This effect is most dramatic for aluminium layers grown on gold.

Figure 3.30 compares the aluminium 2p spectra of an Au/Al film and an Al film. The energy scale in both scans is calibrated against a separate gold thin film sample. In both samples, the metal peaks are around 72.9 eV, while the oxide peak in the Au/Al film has been shifted by about 1.3 eV towards a lower binding energy. The binding energies of the oxygen peaks are similarly affected (Figure 3.31). The binding energy difference between the oxide oxygen and aluminium peaks is still about 457 eV, indicating that there is no change in the nature of the oxide O–Al
Figure 3.30: Comparing the aluminium 2p spectra of a single layer aluminium film, to a gold/aluminium bilayer film. The energy calibration for both data sets were done on a separate gold film. For the gold/aluminium sample, there is no shift in the metal peak position, but the oxide peak shifts downwards by about 1.3 eV, compared to the single layer aluminium film.

For other metals such as cobalt, niobium and tantalum, similar binding energy shifts are also observed. The magnitude of the shift is typically around 0.2–0.3 eV, which is much less than that observed with gold.
Figure 3.31: Oxygen 1s spectra of a single layer aluminium film and a gold/aluminium bilayer film. As with the aluminium 2p spectra, the peaks are shifted downwards, this time by about 1.0 eV.
3.5.5 Aluminium layer thickness

Apart from the shift in the binding energies, the XPS spectra for the metal/aluminium bilayer films appear identical in all other respects to a single aluminium layer film. Even at high oxygen doses (i.e., air oxidised), an aluminium metal peak can still be observed; furthermore, no oxides of the base metal layer were seen. Hence, for this starting aluminium thickness, a limiting oxide thickness is quickly reached. This oxide is a passivating layer which prevents the deeper aluminium and electrode layers from being oxidised.

As the deposited aluminium gets thinner, there is naturally less metal remaining after the oxidation. This is illustrated in Figure 3.32 — for an air oxidised sample composed of 20 Å of aluminium on 300 Å of tantalum, there is still aluminium metal left; when the starting aluminium layer drops to 10 Å, it becomes fully oxidised and no metal peak is seen. Figure 3.33 shows the corresponding oxygen 1s spectra. Although the individual peaks cannot be unambiguously resolved, there is a clear shift of the peak towards the lower binding energy, where the tantalum oxide peak is located. This downward shift thus indicates an increase in the intensity of the tantalum oxide peak.

3.5.6 Overlayers

In tunnel junctions, the aluminium oxide barrier never appears on its own, but always sandwiched between two electrodes. Two questions naturally arise: first, what happens to the chemisorbed oxygen on the aluminium oxide surface? Second, are there any interactions between the aluminium oxide layer and the top deposited electrode?

As in the previous section, bilayer samples are studied. A thick (300 Å) layer of
Figure 3.32: Aluminium 2p spectra of tantalum/aluminium bilayers, with different starting thicknesses of aluminium. Starting aluminium thicknesses of 15 Å and 20 Å will have some metal left upon oxidation, as the smaller metal peak at \( \sim 73 \) eV shows. When the starting aluminium thickness drops to 10 Å, the entire aluminium layer is oxidised, hence no metal peak is seen.
Figure 3.33: Oxygen 1s spectra of tantalum/aluminium bilayer samples, with different starting thicknesses of aluminium. As the starting aluminium layer becomes thinner, the oxygen peak shifts towards a lower binding energy due to the increasing tantalum oxide peak intensity at $\sim 531.5$ eV (not shown).
aluminium is first deposited onto a silicon substrate and given a controlled dose of oxygen. A thin (~10 Å) layer of metal is then deposited on top of the oxide film. This thickness of metal is sufficient to completely cover the underlying aluminium layer [2].

The bilayer samples are transferred to the XPS system under vacuum to minimise oxidation of the top metal layer; however, as the XPS scans of the pure metals show (see previous section), a small amount of oxide and chemisorbed oxygen is inevitably present. Separating out the aluminium oxide peak from the other oxygen peaks becomes a difficult task, resulting in considerable uncertainty in the peak intensity, as well as the oxide stoichiometry.

As there are no overlaps between the aluminium 2p region and the peaks from any of the other electrode materials used, unambiguous fits for this region can be obtained. The thickness calculation proceeds in the same way as that of a single layer aluminium film (Equation 2.12). The attenuation factors for the metal and oxide peak due to the overlayer differ by less than 10%, and since the thickness calculation relies only on the relative intensities of the peaks, the correction factor due to the overlayer becomes insignificant compared to other uncertainties in the thickness. Hence, the thickness can be calculated using Equation 2.12 without having to first correct the intensities for any overlayer attenuation.

### 3.5.7 Aluminium/cobalt films, XPS spectra

Figures 3.34 and 3.35 shows the aluminium 2p and oxygen 1s spectra of a sample consisting of 300 Å of aluminium, oxidised at 1 torr·s, and then capped with 10 Å of cobalt.

From the aluminium 2p peak intensities (Figure 3.34), the thickness of the
Figure 3.34: Aluminium 2p spectra of two films, 300Å Al/1 torr-s and 300Å Al/1 torr-s/10Å Co. The larger attenuation of the metal peak in the Al/Co sample indicates a thicker aluminium oxide layer.
Figure 3.35: Oxygen 1s spectra of a 300Å Al/1 torr·s film and a 300Å Al/1 torr·s/10Å Co film. The bilayer film spectrum shows no chemisorbed peak, and a small cobalt oxide peak.
buried aluminium oxide layer was calculated to be about 17 Å.

The oxygen spectrum is still primarily composed of two peaks, and looks almost identical to that of pure cobalt (Figure 3.25). However, in the bilayer oxygen spectrum, the intensity of the peak at \( \sim 532.3 \) eV is much larger relative to the cobalt oxide peak. This additional increase in the peak intensity is most likely due to the aluminium oxide below the cobalt layer. Also, comparing this oxygen spectrum with that of pure aluminium, it is observed that the chemisorbed oxygen peak at \( \sim 534.0 \) eV is almost non-existent. As the main peak component of the spectrum is already fairly symmetric, fitting the spectra uniquely to three peaks (cobalt oxide, aluminium oxide and chemisorbed oxygen) is not possible without constraining the positions and/or widths of the individual components.

It thus appears that, when a cobalt layer is deposited on top of the aluminium oxide, the chemisorbed oxygen on the oxide either desorbs or reacts with the cobalt and/or aluminium layer. Given the large increase in the aluminium oxide layer thickness, the latter explanation is more likely — i.e., a significant portion of the chemisorbed oxygen reacts further with the aluminium layer to produce more aluminium oxide. Assuming that the main peak in the oxygen 1s spectra is completely due to aluminium oxide, the oxide stoichiometry is estimated to be about 2.0.

From the oxygen 1s spectrum of this sample, it is not possible to determine if the cobalt oxide peak observed is due to surface oxidation of the top cobalt layer, or to interactions at the aluminium oxide/cobalt interface.

### 3.5.8 Aluminium/niobium films, XPS spectra

Figures 3.36 and 3.37 show the aluminium 2p and oxygen 1s spectra of a 300 Å aluminium film, oxidised at 1 torr-s and overcoated with 10 Å of niobium. As with
Figure 3.36: Aluminium 2p spectra of a 300Å Al/1 torr-s and a 300Å Al/1 torr-s/10Å Nb film. Compared to the Al/Co film, the aluminium oxide layer in the Al/Nb film is not as thick.

The cobalt overlayer, the oxide thickness increases to around 11 Å. This is much less than the increase in the case of the cobalt layer. The chemisorbed oxygen peak is again almost absent in the oxygen 1s spectrum, but a niobium oxide peak is clearly observed, indicating that the chemisorbed oxygen has either reacted with the aluminium oxide and/or the niobium layers. Again, assuming that the main oxygen peak is completely due to aluminium oxide, the stoichiometry of the oxide layer is estimated to be around 1.8.

One method to determine if the niobium oxide observed is due to surface or interface oxidation is to deposit a third layer of material onto the niobium layer.
Figure 3.37: Oxygen 1s spectra of a 300Å Al/1 torr-s and a 300Å Al/1 torr-s/10Å Nb film. Again, there is no visible chemisorbed oxygen peak in the Al/Nb sample, but niobium oxide is observed.
While this layer must be thick enough to completely cap off the niobium layer and protect it from surface oxidation, it also must be thin enough so that the entire niobium layer can be observed, without significant attenuation of the signals originating from the niobium/aluminium oxide interface. A sample with a composition of 300Å Al/1000 torr·s/5Å Nb/10Å Al satisfies this condition; the 10 Å capping layer of aluminium completely covers the niobium surface, but the entire 5 Å layer of niobium can be seen. The niobium 3d spectrum for this sample is depicted in Figure 3.38. Both niobium metal and niobium oxide peaks are present. Since there is very little possibility of surface oxidation of the niobium, the niobium oxide observed here must therefore originate from the aluminium oxide/niobium interface.

### 3.5.9 Aluminium/yttrium films, XPS spectra

Figures 3.39 and 3.40 show the aluminium 2p and oxygen 1s spectra of a 300 Å Al film oxidised at 1 torr·s which is then coated with 10 Å of yttrium. This Al/Y sample behaves rather differently from the cobalt and niobium overlayer samples. First, the oxygen 1s peak is fairly broad — much broader than any of the samples studied previously. A three peak fit is used; one peak corresponding to yttrium oxide (identified using scans of the pure yttrium sample), the second corresponding to aluminium oxide, and the final one to chemisorbed oxygen. Judging from the relative intensities of the peaks in the oxygen 1s spectrum of pure yttrium, the chemisorbed peak appearing here cannot be solely due to adsorbed oxygen on the yttrium surface. Rather, it is a combination of both this adsorbed oxygen, as well as oxygen chemisorbed onto the aluminium oxide surface, and buried beneath the yttrium layer.
Figure 3.38: Niobium 3d spectrum of a 300Å Al/1000 torr-s/5Å Nb/10Å Al film. The spectrum can be resolved into a set of niobium metal and niobium oxide doublet peaks.
Figure 3.39: Aluminium 2p spectra of a 300Å Al/1 torr-s and a 300Å Al/1 torr-s/10Å Y film. The relative intensities of the oxide and metal peaks are identical in both spectra, which implies that the aluminium oxide thickness is the same in both cases.
**Figure 3.40:** Oxygen 1s spectra of a 300Å Al/1 torr·s and a 300Å Al/1 torr·s/10Å Y film. The peak for the Al/Y sample is fairly broad, but a tentative fit using three peaks can be made — the yttrium oxide peak, the aluminium oxide peak and the chemisorbed peak.
The aluminium 2p spectrum of the Al/Y sample is practically the same as that obtained for a pure aluminium sample. Depositing the yttrium layer produces no increase in thickness; the aluminium oxide thickness for the Al/Y sample is about 9 Å, well within the error limits for the measured thickness of a single layer aluminium sample exposed to an equivalent dose of oxygen. The stoichiometry of the oxide layer is estimated to be about 1.37.

3.5.10 Overlayers — conclusions

Naturally, it would be impractical to test the effect of every possible metallic electrode material on aluminium oxide systems. However, from the collected data on cobalt, niobium and yttrium layers, it is possible to draw some general conclusions.

As with the thick metal/thin aluminium bilayer films studied in the previous section, small shifts in the binding energies of the aluminium oxide peaks were observed. The magnitudes of these shifts are around a few tenths of an eV, and appears to depend again on the work function of the metal overlayer.

In all the three cases studied above, XPS scans of the oxygen spectral 1s region indicate an absence of the chemisorbed oxygen peak observed in single layer aluminium films. Depositing a cobalt or niobium top layer caused the aluminium oxide thickness to increase from its nominal value (at a dose of 1 torr-s) of about 9 Å to a significantly higher value. However, depositing an overlayer of yttrium did not produce a thickness increase. With a niobium or yttrium overlayer, niobium oxide and yttrium oxide were respectively observed in the XPS spectra; no cobalt oxide was observed when a cobalt overlayer was deposited.

From these observations, it can be concluded that the chemisorbed oxygen on the aluminium oxide surface does not leave the surface when a top layer is
deposited\textsuperscript{2}. Rather, the chemisorbed oxygen reacts further with the aluminium and aluminium oxide layers, as well as with the deposited top layer.

The extent of both reactions seems to be governed by the work function of the metal overlayer relative to that of aluminium. Figure 3.41 is a plot of the aluminium oxide thickness against the work function of the metal used in the overlayer. Among the three metals used, cobalt has the highest work function, and results in the largest thickness increase in the aluminium oxide layer. The work function of yttrium lies below that of aluminium, and there is no change in the aluminium oxide thickness. Extrapolating a line through the Co and Nb points to the nominal aluminium thickness region yields a work function value of \(\sim 4.0\ \text{eV}\), close to the work function value for aluminium (4.08 eV).

As there is only a finite amount of chemisorbed oxygen present on the aluminium oxide surface, there is naturally a correlation between the aluminium oxide thickness increase and the amount of oxide formed at the interface with the overlayer. A thicker aluminium oxide layer would mean that most of the chemisorbed oxygen had reacted with the aluminium/aluminium oxide, leaving only a small amount (if at all) to react with the overlayer. For instance, the samples with the cobalt overlayer do not show any cobalt oxide at all, since almost all the chemisorbed oxygen has gone into producing a thicker aluminium oxide layer. In contrast, when an yttrium overlayer is deposited, it is more favourable for the chemisorbed oxygen to react with the overlayer rather than producing more aluminium oxide; hence, virtually all the deposited yttrium was oxidised.

The estimates obtained for the oxide O/Al ratio are all much higher than the ratios for uncovered aluminium films. In the case of cobalt and niobium, the

\textsuperscript{2}At least, most of the chemisorbed oxygen do not.
Figure 3.41: Thicknesses of the buried aluminium oxide layers for three different overlayer metals. The overlayer samples were composed of a 300 Å thick base layer of aluminium, oxidised at 1 torr·s, followed by the deposition of 10 Å thick metal overlayer. The dashed lines indicate the nominal thickness for an uncovered aluminium film oxidised at 1 torr·s.
ratios are higher than 1.5 (i.e., for stoichiometric Al\textsubscript{2}O\textsubscript{3}). While aluminium oxide films with high O/Al ratios are possible, particularly in highly stressed films [18], a further explanation may be that not all of the chemisorbed oxygen has reacted with the oxide layer. Instead, a small amount of chemisorbed oxygen remains trapped at the interface between the oxide layer and top electrode; a recent study [19] shows a higher concentration of oxygen at the oxide/top electrode interface. In this case, the chemisorbed oxygen peak will still be present in the oxygen 1s spectrum, but as a result of the binding energy shift due to the higher work function of the overlayer, the chemisorbed peak is shifted downward in binding energy and overlaps with the oxide peak. The chemisorbed peak cannot be uniquely separated from the oxide peak, hence a calculation based on the assumption of only a single oxide peak will lead to an artifically high O/Al ratio for the oxide. Unless the oxygen spectra can be uniquely and unambiguously resolved into its individual components, obtaining a more accurate estimate for the oxide O/Al ratio is not possible.
References for Chapter 3


CHAPTER 4

POST OXIDATION MODIFICATION OF ALUMINIUM OXIDE
THIN FILMS

4.1 Introduction

As the previous chapter has shown, room temperature oxidation of aluminium films produces oxide layers which are almost always oxygen deficient, at least over the range of pressures and times investigated. Even so, fairly high quality junctions can be reproducibly fabricated with such oxide layers [1]. For aluminium-based Josephson junction qubits, one of the main goals is to reduce low frequency resistance noise, the source of which is often attributed to defect sites in the oxide [2].

Given the XPS results thus far, it is therefore reasonable to expect that raising the stoichiometry of the as-formed oxide layer towards 1.5 (i.e., Al$_2$O$_3$) would result in a better structured film containing fewer defect sites, leading to lower noise devices.

This chapter investigates two methods of post-oxidation film modification — thermal annealing and electron bombardment. The relative merits and disadvantages of both methods will be discussed, as well as their implications for tunnel junction device fabrication.

4.2 Annealing

Annealing is a common technique used to improve the crystallinity of materials, both for bulk and thin film samples. Many different anneal “recipes” exist for aluminium oxide; some involve heating the aluminium sample during the oxidation process [3], others involve heating the sample after the oxide has formed [4]. The
anneals used here are of the second type since we are primarily interested in seeing how the chemisorbed oxygen left on the surface after oxidation reacts, rather than growing a thicker oxide.

For these aluminium samples, two methods of annealing are used. The first method relies on a quartz halogen bulb mounted in the XPS system. Unfortunately, due to the system geometry, there is a considerable distance between the sample surface and the bulb. This limits the maximum sample surface temperature to about 250°C.

The second anneal method is done with a small oven setup in the sample preparation chamber. This oven allows samples to be annealed to temperatures of up to 500°C after growth. The oven is a resistive heater in the form of a tungsten wire cage. The drawback of this method is that a large region around the oven also heats up rapidly.

4.2.1 Annealing related problems

Regardless of the choice of anneal method, the cleanliness of the heating unit and the surrounding area is important, as does the type of material from which the heating unit is constructed. Since the temperature of the heating unit reaches 500°C or higher during the anneal, materials with higher vapour pressures can easily deposit onto the sample; copper, for instance, or components in stainless steel like manganese and nickel.

Figure 4.1 shows survey scans of an aluminium film taken before and after an anneal with the bulb heating method. Large manganese and nickel peaks are observed in the postanneal survey scan; the most likely source of these impurities would be the stainless steel heat reflectors and baffles placed around the heater.
**Figure 4.1**: Survey scans of a vacuum-transferred 300 Å aluminium film oxidised at 300 torr-s, before and after a 250°C, 1 hour anneal. After the anneal, several more peaks (Mn, Ni, etc) appear; there is also an increase in the intensity of the carbon peak.

Deposited impurities are also observed in anneals with the tungsten cage oven. In particular, large copper peaks are observed; these come from the copper supports in the original tungsten cage design.

As the previous chapter has shown, metal deposition onto aluminium oxide films can significantly alter its composition. Hence, the value of XPS data for these “contaminated” samples is extremely dubious, since there is no way of distinguishing between effects due to the anneal and effects due to the impurity overlayer.
Figure 4.2: Survey scans of two vacuum-transferred 85Å Au/12Å Cu/12Å Co/30Å Al/300 torr-s films, one as grown and the second annealed at 375°C for 1 hour. The relative intensities of the gold peaks are much higher in the annealed sample.

A further problem with annealing is the interdiffusion of material across different layers in a multilayer stack. Figure 4.2 shows the survey scan of a multilayer stack consisting of 85Å Au/12Å Cu/12Å Co/30Å Al, oxidised at 300 torr-s and transferred in vacuum to the XPS system. Before annealing, the strongest signals come from the aluminium layer, with less intense peaks from the Au, Cu and Co layers. After an anneal at 375°C for 3 min, the intensities of the gold peaks increase significantly, indicating a larger concentration of gold in the XPS depth being probed.
Figure 4.3: Aluminium 2p spectra of two vacuum-transferred 85Å Au/12Å Cu/12Å Co/30Å Al/300 torr-s films, one as grown and the second annealed at 250°C for 1 hour. The oxide peak position shifts towards a lower binding energy after the anneal.

Further evidence of the gold diffusing towards the surface can be seen in Figure 4.3. Before the anneal, the separation between the aluminium metal and oxide peaks is about 2.3 eV, identical to that observed in an oxidised Co/Al bilayer sample. After the anneal, the binding energy difference drops to that observed in Au/Al bilayer samples. This demonstrates that much of the gold is now in contact with the aluminium layer, bringing about the oxide binding energy shift observed in the spectrum.

As the previous scans indicate, annealing an aluminium oxide layer “cleanly”
at the temperatures required is not a trivial task. A second tungsten cage oven was therefore constructed; all the support material of the cage was built from molybdenum (a refractory metal) and ceramics. With this oven construction, no contaminant deposition was observed during anneals.

### 4.2.2 XPS scans of annealed films

Figures 4.4 and 4.5 show the aluminium 2p and oxygen 1s spectra for three 300 Å aluminium films, each oxidised at 300 torr-s. One sample is unannealed, the second annealed at 375°C for 3 mins (with the old oven) and the final sample annealed at 500°C for 1 hour (with the new oven). All three samples are subsequently transferred in air into the XPS system.

For the sample annealed at 375°C, re-exposure to air after the anneal appears to revert the oxide back into its original state. The thickness of the oxide is 12.3 Å while its O/Al ratio is ~1; essentially the same as the unannealed sample (thickness 12.4 Å, O/Al ratio ~1). Furthermore the O 1s spectrum of the annealed oxide shows an intensity ratio of chemisorbed oxygen to oxide oxygen almost identical to that of the unannealed sample. Hence, even if such an anneal results in a reaction between the chemisorbed oxygen and the oxide layer, the effects of the anneal are not permanent.

In the case of the 500°C anneal and subsequent re-exposure to air, the large attenuation in the aluminium metal peak intensity shows that a significant increase in the oxide thickness has occurred. The thickness calculated from the aluminium peak fits is 18.2 Å, about 6 Å thicker than the unannealed sample. The chemisorbed oxygen intensity is also reduced by a considerable amount, but does not disappear completely. However, the oxide stoichiometry is still ~1, comparable to that of
Figure 4.4: Aluminium 2p spectra of two air-transferred 300 Å aluminium films, one unannealed and the other annealed at 500°C for 1 hour. The relative intensity of the oxide peak is higher in the 500°C annealed sample, indicating a thicker oxide layer.
Figure 4.5: Oxygen 1s spectra of two air-transferred 300 Å aluminium films, one unannealed and the other annealed at 500°C for 1 hour. The 500°C annealed sample has a lower chemisorbed oxygen peak intensity.
Figure 4.6: Oxygen 1s spectra of three vacuum-transferred 200Å Co/10Å Al/10 torr-s films, one unannealed, the second annealed at 300°C for 3 mins and the third annealed at 500°C for 3 mins. The intensity of the chemisorbed peak decreases with increasing anneal temperature.

The annealing experiments are repeated for a set of bilayer films consisting of a 200 Å thick base layer of cobalt on which 10 Å of aluminium is deposited. The films are initially oxidised at 10 torr-s. One such bilayer sample is then annealed at 300°C for 3 mins, and another at 500°C for 3 mins. The annealed films are then transferred in vacuum to the XPS system. Figure 4.6 shows the oxygen 1s spectra of these two annealed sample, along with an unannealed sample for comparison. The 300°C anneal is sufficient to bring about a significant reduction in the intensity
of the chemisorbed peak. Increasing the anneal temperature to 500°C reduces the peak intensity slightly further, but does not completely eliminate the peak. In both cases, the oxide peak intensity increases.

Although the thickness of the aluminium oxide layer cannot be calculated using Equation 2.12 for such a bilayer sample, an rough estimate can be made by comparing the oxide Al 2p peak intensities. For the unannealed sample, the oxide layer thickness is estimated at \( \sim 11.0 \, \text{Å} \). This increased to \( \sim 11.4 \, \text{Å} \) and \( \sim 12.8 \, \text{Å} \) respectively for the 300°C and 500°C annealed samples. The O/Al ratios for the annealed samples, however, remained at \( \sim 1.0 \), essentially unchanged from that of the unannealed sample.

### 4.2.3 Conclusions

Annealing at temperatures between 300°C and 500°C appears to cause the chemisorbed oxygen on the surface to react further, at least partially, with the underlying aluminium metal layer to form a thicker oxide. However, the resulting films are still oxygen deficient, even at high anneal temperatures and anneal times of around an hour. Re-exposing annealed films to oxygen causes the chemisorbed oxygen peak to reappear, although its intensity is smaller than that of unannealed films.

For ultrathin oxide layers (less than 10 Å), the problem of interfacial diffusion may wipe out any benefits brought about by the anneal. The preliminary data shown above indicates that fairly high temperatures (greater than 300°C) are required to bring about changes in the oxide structure; unfortunately having such high temperatures also enhances the diffusion rate. Hence, carefully timed and controlled annealing processes would have to be developed to make this a viable technique for oxide improvement.
4.3 Floodgun experiments

Since aluminium oxide is insulating, there is always a possibility that charging effects (see Chapter 3) may cause shifts in the measured binding energies, particularly when the oxide is thick [5].

No binding energy shift was seen in the samples studied here, indicating a lack of charging within the oxide. However, an interesting side effect was observed: after exposing the sample to the floodgun for a short interval, changes occur in the oxygen and aluminium peak intensities. These changes remain even after the floodgun had been turned off. This suggests that the low energy electron bombardment from the floodgun had somehow resulted in a reaction in the oxide.

The possibility that the electron beam is merely heating the sample and merely annealing the sample can be ruled out for a variety of reasons. A thermocouple placed near the sample surface showed no large increase in the surface temperature. Even after leaving the floodgun running continuously for about 12 hours, the surface temperature only reached around 80°C. More compelling is that no diffusion of the bottom layers was observed in multilayer samples which were electron bombarded, unlike the annealed multilayer samples described in the previous chapter.

Such electron bombardment (also called “electron irradiation”) processes are not uncommon; mid to high energy (keV range) electron irradiation processes are routinely used to modify material surfaces, for example, in electron beam lithography.

Electron bombardment at energies of 50–200 eV have also been used to successfully enhance the oxidation rate of aluminium [6]. In these experiments, the aluminium films were electron bombarded in the presence of oxygen. The elec-
Figure 4.7: Aluminium 2p spectra of an air-transferred 300 Å aluminium film, as grown and after a 10 eV, 15 hour floodgun exposure. The thickness of the oxide increases somewhat after the floodgun exposure.
Figure 4.8: Oxygen 1s spectra of an air-transferred 300 Å aluminium film, as grown and after a 10 eV, 15 hour floodgun exposure. After the floodgun exposure, the chemisorbed peak intensity decreases significantly while the oxide peak intensity increases.
tron bombardment produces a dissociation of the adsorbed oxygen molecules into \( O^- \) ions. These ions are more reactive and therefore the oxidation rate of the aluminium film increases.

### 4.3.1 10 eV floodgun experiments

**Heavily oxidised aluminium film**

Preliminary experiments established that a floodgun energy of 10 eV would bring about observable changes in a reasonable amount of time (i.e., after about an hour). The electron emission current is estimated to be about 10 \( \mu \text{A/cm}^2 \).

Figures 4.9 and 4.10 show the Al 2p and O 1s spectra of an air-transferred, 300 Å thick aluminium sample, before and after being exposed to the floodgun at 10 eV for 85 minutes. There is only a slight change in the aluminium 2p spectrum; in contrast, the chemisorbed oxygen component of the oxygen 1s spectrum decreases down by a significant amount. This is accompanied by a corresponding increase in the oxide component. Furthermore, the binding energy difference between the oxide oxygen and aluminium peaks increases from about 456.9 eV to 457.1 eV, reflecting a possible increase in the O–Al bond strength within the oxide.

Peak fits to the aluminium spectrum show that the thickness of the film from 12.1 Å to 12.8 Å as a result of the floodgun exposure. Of more interest is the change in the oxide stoichiometry, which increases from its initial value of 1.0 to a value of 1.3 after the floodgun exposure.

The electron bombarded aluminium sample appears to be stable when left in a UHV environment. Scans of the oxide taken a full day after the electron bombardment process show no change in the peak intensities, improved oxide stoichiometry or thickness.
Figure 4.9: Aluminium 2p spectra of an air-transferred 300 Å aluminium film, as grown and after a 10 eV, 85 min floodgun exposure.
Figure 4.10: Oxygen 1s spectra of an air-transferred 300 Å aluminium film, as grown and after a 10 eV, 85 min floodgun exposure.
To check if the floodgun induced changes are permanent, the aluminium sample is then exposed to 300 torr·s of oxygen. Again, only a small change is observed in the aluminium spectrum, but the oxygen spectrum shows a reversal — a drop in the oxide peak intensity with a corresponding increase in the chemisorbed oxygen peak intensity. A comparison to the O 1s spectrum of the as-grown film in Figure 4.10 however reveals that the oxygen peaks do not return to their original intensities, but instead to a state with a slightly higher oxide intensity and a slightly lower chemisorbed oxygen intensity. This is supported by the calculated oxide stoichiometry and thickness values of 1.1 and 12.5 Å respectively, both still higher than their as-grown values of 1.0 and 12.1 Å. A subsequent floodgun exposure again brings the chemisorbed peak intensity down and the oxide stoichiometry back to a high value (Figure 4.12).

The oscillatory behaviour of the oxide stoichiometry is repeated upon further electron bombardment/re-oxidation cycles (Figure 4.13). However, with each cycle, the magnitude of the change in the oxide stoichiometry decreases. The oxide stoichiometry appears to eventually tend towards a stable value of $\sim$1.25. The amount of chemisorbed oxygen picked up at each re-oxidation step also decreases with each cycle (Figure 4.14). The oxide thickness also shows an increase with each floodgun step (Figure 4.15), but unlike the oxide stoichiometry, it is not known if the thickness continues to increase with further cycles, or if it tends towards a limiting value.

**Lightly oxidised aluminium films**

The 10 eV floodgun experiments carried out in the previous section utilised a heavily oxidised and therefore thick, aluminium thin film. If a lightly oxidised alu-
**Figure 4.11:** Oxygen 1s spectra of an air-transferred 300 Å aluminium film, after a 10 eV, 85 min floodgun exposure and after a 300 torr-s oxygen dose.
Figure 4.12: Oxygen 1s spectra of an air-transferred 300 Å aluminium film, after a 300 torr-s oxygen dose and after a 10 eV floodgun, 75 min exposure.
**Figure 4.13:** Air-oxidised aluminium film, 10 eV, 1 hour floodgun exposure and 300 torr·s re-oxidation cycles. This graph shows the oxide stoichiometry after each process step.
Figure 4.14: Air-oxidised aluminium film, 10 eV, 1 hour floodgun exposure and 300 torr-s re-oxidation cycles. The chemisorbed oxygen peak intensity after each process step, normalised to its initial value, is shown here.
**Figure 4.15:** Air-oxidised aluminium film, 10 eV, 1 hour floodgun exposure and 300 torr·s re-oxidation cycles. This graph shows the oxide thickness after each process step.
Figure 4.16: Vacuum-transferred aluminium film, initially oxidised at 1 torr·s, exposed to a series of 10 eV, 1 hour floodgun exposure and 300 torr·s re-oxidation cycles. This graph shows the oxide stoichiometry after each process step.

As grown, 300Å Al, 1 torr·s
Oxidation Step, 400 mtorr·s
Floodgun Step, 10 eV, 1hr

Aluminium sample is used instead, how would its behaviour differ under the floodgun and re-oxidation treatment?

To answer this question, a 300 Å thick aluminium film is grown and oxidised at 1 torr·s, and then vacuum-transferred to the XPS system. A number of floodgun exposures (10 eV, 1 hour) and re-oxidation (400 mtorr·s) cycles are then carried out. Figures 4.16, 4.17 and 4.18 show the changes in the oxide stoichiometry, thickness and normalised chemisorbed oxygen intensity at each process step.

Interestingly, the behaviour of this sample is initially very different from the heavily oxidised sample. Although there is still a general trend towards lower
Figure 4.17: Vacuum-transferred aluminium film, initially oxidised at 1 torr·s, exposed to a series of 10 eV, 1 hour floodgun exposure and 300 torr·s re-oxidation cycles. This graph shows the oxide thickness after each process step.
Figure 4.18: Vacuum-transferred aluminium film, initially oxidised at 1 torr·s, exposed to a series of 10 eV, 1 hour floodgun exposure and 300 torr·s re-oxidation cycles. This graph shows the chemisorbed oxygen intensity normalised to its initial value (at step 1) after each process step.
chemisorbed oxygen intensities and higher O/Al ratios and thicknesses, the correlation between the process steps and these quantities is not as clear. One probable explanation for this is that unlike the heavily-oxidised sample, this sample, as grown, has not reached the stage where oxide growth slows down or stops completely. As a result, in addition to partly reversing the floodgun-induced changes, the early re-oxidation steps also oxidise more of the underlying aluminium, forming a thicker oxide. Only when the oxide thickness exceeds about 11 Å does its behaviour begin to resemble that of the heavily-oxidised sample.

4.3.2 Higher floodgun voltages

One possible explanation for the floodgun-induced changes is an accumulation of negative charge on the oxide surface, producing a potential difference across the oxide, causing it to grow in thickness further. If this is the case, a higher floodgun voltage bias would lead to a greater potential difference across the oxide, resulting in more chemisorbed oxygen reacting to produce an even thicker oxide.

The data shown in Figures 4.19 and 4.20 confirm this prediction. After exposing an unoxidised aluminium film for an hour to the floodgun set at 20 eV, the oxide oxygen peak intensity increases greatly, while the chemisorbed oxygen peak is almost reduced to zero. The oxide thickness also increases by almost 4 Å, about four times as much as that observed for films exposed to a 10 eV floodgun electron bombardment after an equivalent amount of time. Interestingly though, the oxide O/Al ratio still reaches only \(\sim 1.2\), the same as that observed with a 10 eV floodgun exposure. Re-oxidation of the film again results in the reappearance of the chemisorbed oxygen peak, together with a decrease in the oxide O/Al ratio. Repeated floodgun and oxidation cycles produce the same type of oscillatory be-
\textbf{Figure 4.19:} Aluminium 2p spectra of a 5 mtorr-s, vacuum-transferred aluminium thin film, as grown and after a 20 eV, 1 hour floodgun exposure.
Figure 4.20: Oxygen 1s spectra of a 5 mtorr-s, vacuum-transferred aluminium thin film, as grown and after a 20 eV, 1 hour floodgun exposure.
Figure 4.21: Vacuum-transferred 300 Å thick aluminium film, initially oxidised at 5 mtorr·s and subsequently exposed to two 20 eV floodgun/oxidation cycles. The chemisorbed oxygen peak intensity is shown at each process step, normalised relative to its initial value. At every 20 eV floodgun step, the peak intensity is close to zero, indicating an almost complete absence of chemisorbed oxygen on the oxide surface.

haviour in the normalised chemisorbed oxygen intensity and oxide stoichiometry as seen in the previous 10 eV electron bombarded samples (Figures 4.21 and 4.23) but not in the oxide thickness (Figure 4.22).

4.4 Floodgun experiments — conclusions

In the Mott-Cabrera model, oxide growth occurs as a result of the electric field across the oxide. Exposing the oxide surface to an electron beam causes surface
Figure 4.22: Vacuum-transferred 300 Å thick aluminium film, initially oxidised at 5 mtorr-s and subsequently exposed to two 20 eV floodgun/oxidation cycles. The oxide thickness is plotted at each process step.
Figure 4.23: Vacuum-transferred 300 Å thick aluminium film, initially oxidised at 5 mtorr·s and subsequently exposed to two 20 eV floodgun/oxidation cycles. At each floodgun process step, the oxide O/Al reached ~1.2 but dropped to about ~1 upon re-oxidation.
charge to accumulate, resulting in a larger potential difference across the oxide. This in turn drives the oxide growth further, thus producing a thicker oxide [7].

However, the increased potential difference across the oxide cannot explain the increase in oxide stoichiometry; i.e., the increased electric field could just as well have promoted the growth of oxygen-deficient oxide instead. The electron bombardment must therefore have an additional effect on either the chemisorbed oxygen or the vacancy sites. One possibility is that the electron bombardment promotes the dissociation of the chemisorbed oxygen ($O_2^-$) into oxygen ions ($O^-$), which is driven into the oxide, filling up the vacancies. Since these ions are not very energetic, only the vacancies near the oxide surface are filled. This may account for the oxide stoichiometry reaching only $\sim 1.2$ — although the oxide region near the surface might have attained an O/Al ratio of 1.5, regions deeper down still contain oxygen-deficient oxide. As XPS probes the entire oxide layer, the oxide stoichiometry calculated from the peak fits is just an average of the stoichiometries at various depths in the oxide.

In our model for the Al/AlO$_x$/Al system, the negatively charged chemisorbed oxygen molecules are bound to the surface by the positively charged oxygen vacancies in the oxide. This implies that there should be a relationship between the amount of chemisorbed oxygen and the oxide stoichiometry — as the oxide stoichiometry increases towards 1.5, the amount of chemisorbed oxygen should decrease. For the samples which have been electron bombarded at 10 eV and 20 eV, a weak correlation is observed between these two quantities (Figure 4.24).

On the other hand, the changes in the oxide thickness do not appear to follow a distinct trend. Although the samples exposed to the floodgun at 10 eV show either a decrease in thickness or no change at all upon re-oxidation, the 20 eV
Figure 4.24: Chemisorbed oxygen peak intensity plotted as a function of the oxide stoichiometry for two aluminium samples subjected to a series of floodgun/re-oxidation cycles, one at 10 eV and the other at 20 eV.
floodgun samples show the opposite behaviour. The unpredictability of the oxide thickness behaviour might in part be due to the way thicknesses are calculated. As mentioned in Chapter 4, the thickness calculation relies on the oxide density, which in turn is calculated from the oxide stoichiometry using a simple model. Hence, using an oxide density value which is different from its true value can result in thickness differences of about 1–2 Å. Since there is no good way of determining the true oxide density in XPS, apparent thickness changes due to changing oxide densities cannot be distinguished from actual oxide thickness changes. It is also likely that the floodgun is forming both a denser and thicker oxide at the same time; however XPS cannot provide enough information to be able to distinguish between the two possibilities.

4.4.1 Other oxide systems

In the previous chapter, it is shown that surface adsorbed oxygen is observed not only on oxidised aluminium surfaces, but also on the surfaces of other metals such as cobalt and niobium. It is thus natural to ask if the electron bombardment process will bring about a similar change in these metals as well.

To test this, a 300 Å thick cobalt film is grown and transferred in air into the XPS system. A series of 20 eV floodgun exposures and reoxidation steps are then carried out, in a similar fashion to the aluminium films.

Figure 4.25 shows the oxygen 1s spectrum before and after the first 20 eV, 1 hour floodgun exposure. The chemisorbed peak intensity drops to about half its initial value while no significant change in the cobalt oxide peak is observed. A subsequent 1000 torr-s oxygen exposure also does not bring about any noticeable change in either peak intensity. However, a larger oxygen dose (≈ 10^5 torr-s) results
Figure 4.25: Oxygen 1s spectra of a 300 Å air-transferred cobalt film (a) as grown, and (b) after a 20 eV floodgun exposure for 1 hour. A large decrease in the chemisorbed peak is again observed.

in a slight increase in chemisorbed oxygen peak. This is shown in Figure 4.26. Re-exposing the sample to the 20 eV floodgun at this stage again produces a decrease in the chemisorbed oxygen peak.

The above changes in the oxygen 1s spectrum therefore strongly suggests that the cobalt oxide and its chemisorbed oxygen layer behave in a similar fashion to that of aluminium oxide. It is perhaps unfortunate that obtaining accurate quantitative data such as oxide stoichiometries and thickness for the cobalt oxide system is not practical, due to the complexity of the cobalt spectra (see Chapter 4).

One significant difference between the cobalt oxide system and the aluminium
Figure 4.26: Oxygen 1s spectra of a 300 Å air-transferred cobalt film (a) after a 20 eV floodgun exposure for 2 hours, and (b) re-exposure to oxygen at 1 atmosphere for 2 minutes ($\sim 10^5$ torr·s). The intensity of the chemisorbed peak increases slightly.
Figure 4.27: Relative intensities (expressed as a fraction of the total oxygen intensity) of the chemisorbed and cobalt oxide peak, plotted against floodgun exposure time. After about 3–4 hours of floodgun exposure at 20 eV, the relative intensities remain constant.

oxide system is the extent to which the electron bombardment reduces the chemisorbed peak intensity. For the aluminium oxide system, a 1 hour, 20 eV floodgun exposure is sufficient to almost completely remove the chemisorbed peak (Figure 4.25). In the case of cobalt oxide, there is still a large chemisorbed peak remaining after a similar floodgun exposure. In fact, it requires about 3–4 hours of 20 eV floodgun exposure to bring the chemisorbed intensity to a constant value; even so, the chemisorbed peak is never completely removed (Figure 4.27).

The aluminium oxide floodgun experiments described in the previous sections
suggest that the effectiveness of the floodgun (regarding chemisorbed peak intensity reduction) depends on the voltage bias. The results from the cobalt oxide experiments require this postulate to be amended slightly, i.e., that the floodgun effectiveness depends on the voltage bias relative to the work function of the metal being oxidised. Since cobalt has a much higher work function than aluminium, a larger floodgun bias will be necessary to force the chemisorbed oxygen to react completely\(^1\).

\(^1\)As the XPS floodgun has a maximum bias of 20 V, the validity of this statement cannot currently be tested.
References for Chapter 4


CHAPTER 5
ALUMINIUM OXIDE TUNNEL JUNCTIONS

5.1 Introduction

While the XPS results presented in the previous chapter are interesting and demonstrate an improvement in the stoichiometry of electron-bombarded aluminium oxide layers, the true test would be to fabricate tunnel junctions incorporating these treated oxide layers and then check if there would be a corresponding enhancement in the electrical properties of the junctions.

The aluminium oxide tunnel junctions are typically fabricated using a top-down approach, beginning with the deposition of layers of material onto a suitable substrate. Through a series of lithography and etching processes, the tunnel junction is carved out from this multilayer stack.

Aluminium is chosen as the electrode material; such Al/AlO$_x$/Al junctions are of considerable current interest due to their potential for use as quantum bits [1]. Measuring their superconducting properties however requires a millikelvin cryostat which was not readily available. Nevertheless, a measure of the junction quality can still be obtained by studying the noise characteristics of the junction between 350 K and 4.2 K.

The Al/AlO$_x$/Al junctions described in this chapter are fabricated using the tried and tested micropillar process developed originally for magnetic tunnel junctions [2]. Junctions whose sizes ranged between 1.5 $\mu$m$^2$ and 5.0 $\mu$m$^2$ can be reliably made with this process.
5.2 Junction fabrication

5.2.1 Trilayer deposition and oxide formation

The micropillar process is a top-down subtractive process, which means that the various layers of the junction are first deposited onto a wafer before large chunks are selectively removed to define the junction area. In this case, the starting point is a trilayer of Al/AlO$_x$/Al. The junctions are fabricated on a (100) silicon substrate, on which a thick layer of thermal silicon oxide has been grown. As the junction resistances will be very high, this insulating SiO$_2$ layer is necessary to prevent any leakage currents through the silicon substrate (which would short out the junction).

Ideally, all the deposition and oxidation steps for the trilayer stack construction should be done entirely under UHV conditions, in order to have a controllable process as well as to minimise contamination. However, as the evaporation system does not have a floodgun, it is necessary to transfer the wafer to the XPS system where the floodgun is located, run the electron bombardment process, and then transfer the wafer back into the evaporation system to deposit the final top aluminium layer$^1$. One unfortunate disadvantage of this is that ultrathin (10 Å or less) oxide barrier layers cannot be produced — the subsequent air transfer step will always produce a thicker oxide.

The aluminium electrode layers are deposited using electron beam evaporation in the CHA evaporator. The system base pressure is $\sim 7 \times 10^{-7}$ torr and rises to $\sim 1 \times 10^{-6}$ torr during evaporation. A 99.997% pure aluminium source is used. A

$^1$Due to hardware incompatibilities between the evaporation system and XPS system, the mobile pump station described in Chapter 3 cannot be used to do this transfer.
thick (1000 Å) base layer of aluminium is first deposited onto the oxidised silicon substrate. The aluminium layer is then transferred in air to the XPS system and subjected to five 10 eV, 1 hour floodgun/300 torr·s oxidation cycles before being transferred back into the evaporator. A 200 Å top layer of aluminium is then deposited, completing the trilayer stack.

5.2.2 Fabrication considerations

As the trilayer stack will be subjected to various wet and dry chemical processes during fabrication, it is important to choose fabrication methods which are compatible with the junction material. Fortunately, this is not too difficult — microfabrication is a well-established artform [3] with a variety of different recipes for several different materials, many of which have been exhaustively characterised in one form or other. All that needs to be done is some fine tuning to suit the particular device being worked on\(^2\).

5.2.3 Photolithography

The various device areas are defined on the trilayer stack using photoresist stencil masks. Shipley 1813 resist, a positive tone\(^3\) photoresist, is used for most steps in the micropillar fabrication process. This photoresist adheres well to the aluminium trilayer stack, so there is no need for a primer layer. There is no evidence of any chemical reaction between the photoresist and the trilayer stack; neither does the 115°C solvent removal bake appear to produce any adverse effects.

\(^2\)Fine tuning a process can take either a few minutes or few months.

\(^3\)A positive tone resist is one where the UV-exposed areas are washed away during development. The unexposed resist areas remain, corresponding to the dark areas on the glass mask — hence producing a positive image of the glass mask on the resist.
For the micron-sized pillar fabrication step, a resist bilayer consisting of a liftoff resist (Microposit LOR3a) and Shipley 1805 resist is used. This bilayer results in an undercut profile which is required for a subsequent silicon dioxide deposition and liftoff step.

Development of the photoresist is done using 300 MIF, a water-based developer containing tetramethylammonium hydroxide (TMAH). Although the trilayer aluminium oxide stack is enclosed by a passivating native oxide layer, this passivating layer only protects the underlying aluminium metal from further reactions with water. Aluminium oxide, being an amphoteric oxide, will react with the TMAH in the developer. If left in the developer for a long enough period of time, significant portions of the trilayer stack will eventually be etched away. However, since the development times are only a few minutes long and the developer TMAH concentration is rather low, only some pitting of the trilayer stack surface is observed. Such pitting does not appear to be serious enough to produce any noticeable degradation of the junctions.

5.2.4 Reactive ion etching and ion milling

After the photolithography step, unmasked areas of the trilayer stack are etched away, thus transferring the pattern on the mask onto the trilayer. There are many ways of doing an etch; for the micropillar fabrication process, two methods are used: reactive ion etching and ion milling.

In reactive ion etching, a gas such as O₂ or Cl₂ is introduced between two high voltage electrodes, setting up a plasma. A fraction of the gas molecules are further broken down into reactive radical species. These radical species then diffuse to the sample surface where they react to form gaseous byproducts which are then
pumped away. In this fashion, the surface of the sample is etched away. This etch can be anisotropic, depending on the configuration of the etching system.

For aluminium and aluminium oxide, a gas mixture of Cl₂ and BCl₃ is used. Aluminium etches at a fast rate (a few hundred Å per minute) while the aluminium oxide etch rate is much slower (less than one Å per second). The etch rate of the aluminium oxide depends strongly on the etch conditions (e.g., pressure, gas flow rate), making a consistent etch rate difficult to achieve. As a result, it is difficult to precisely etch the trilayer stack to a given depth. One further drawback is that the chlorine based etch gas mixture also reacts with the photoresist, causing an erosion of the resist profile. This may make subsequent liftoff procedures harder to complete cleanly.

Hence, although reactive ion etching of the aluminium trilayer stack is fast and relatively clean, the last two problems make this process suitable only for very coarse features (for instance, the first step in the micropillar fabrication process).

For small features and better control of the etch depth, the ion milling process is used. This etch method is the microfabrication equivalent of sandblasting: a stream of argon ions is accelerated towards the sample, where the highly energetic ions physically knock material off the surface. Etch rates are slower than in a reactive ion etch, which is an advantage as the etch depth can be controlled very precisely.

Ion milling is not without its problems. The highly energetic ion beam naturally results in significant sample heating, particularly of the topmost resist layer. Overheating the resist can cause it to harden, making it particularly hard to remove. To prevent this, the sample is not ion milled continuously, but only for 15–20 s at a time, with a 30–45 s cooling interval between them. When the ion milling
**Figure 5.1:** Sidewall shorting during ion milling. (a) During ion milling, material sputtered off the lower metal electrode surface can accumulate along the side of the junction stack. (b) When this happens, there is a current path across the oxide barrier which shorts out the junction.

The process is carried out this way, together with adequate sample stage cooling, resist heating can be minimised.

Redeposition is another possible problem during ion milling. The ion milling process is essentially a sputtering process where the etched-away material is thrown outwards from the sample surface. Some of this material can accumulate on the sample, particularly along the sidewalls of tall structures, and can potentially short out tunnel junctions (Figure 5.1). Fortunately, this is not a problem for the aluminium trilayer junctions — when milling past the barrier layer, an argon/oxygen gas mixture can be used. The oxygen in this mixture will quickly oxidise any redeposited aluminium along the sidewalls.

### 5.3 Fabrication sequence

After sacrificing several wafers to determine the optimum processing parameters and conditions, a working process is finally obtained. This is shown schematically in Figures 5.2–5.5. Since each step in the fabrication process is time-consuming and
expensive, it is a good practice to characterise the wafer after each step to make sure that the wafer has been processed correctly at that step. This is done mostly with optical microscopy (for checking photolithography quality), step profilometry (for checking if specific etch depths have been reached), scanning electron microscopy and atomic force microscopy (e.g., for checking the overall three-dimensional device profile and cleanliness after liftoff procedures).

5.3.1 Electrode areas

The first photolithography step defines the top and bottom electrode areas and contact pads of the device. Since these areas are large (50 \( \mu \text{m}^2 \) and larger) and most of the material needs to be removed down to the substrate, a \( \text{Cl}_2/\text{BCl}_3 \) reactive ion etch is used in this step (Figure 5.2).

5.3.2 Junction areas

In this step, the micropillar junctions are defined, using the bilayer resist described earlier. The trilayer stack is milled down to about 200 Å below the aluminium oxide layer (Figure 5.3). A number of different junctions are patterned, whose areas range from 1 \( \mu \text{m}^2 \) to 5 \( \mu \text{m}^2 \). To protect the exposed micropillars from sidewall shorting, a thick layer of silicon dioxide is evaporated onto the wafer immediately after the junction etch step. The silicon dioxide layer is then lifted off, leaving behind junctions well-surrounded by insulating oxide. (Figure 5.4).

This silicon dioxide insulation step is where most devices fail to be fabricated correctly. To obtain good coverage of the junction sidewalls, it is necessary to rotate the wafer at an angle during the silicon dioxide evaporation. Unfortunately, this also means that the resist sidewalls, particularly around the resist/wafer interface,
are coated as well. This makes the liftoff process extremely difficult since there is no break in the silicon oxide layer where the lifting-off process can begin. With ultrasonic agitation, the larger micropillars (2–5 μm²) can be uncovered, but not the smaller micropillars whose areas are less than 2 μm².

An additional silicon dioxide deposition and liftoff step is done after this step, to ensure that all the step edges are adequately insulated.

5.3.3 Top lead definition

The final step in the fabrication is to form the top leads to the device, so that electrical contact across the device can be made. This is done by exposing a top lead pattern, then evaporating and lifting off a thick (~200 Å) copper layer to connect the top of the junction to the contact pads (Figure 5.5). Before the copper deposition is done, the sample is briefly ion milled in-situ. This removes the native aluminium oxide layer on the surface so that there is good electrical contact between the copper leads and the top aluminium electrode layer.

5.3.4 Initial junction testing and wirebonding

The finished junctions are very susceptible to electrostatic shock, so handling them requires the usual precautions of grounding and shorting out leads. The four point junction resistances are checked with an electrical probe station. For junctions of this size and barrier thickness, the typical resistance range is around 2–10 kΩ. A lower resistance (less than 1 kΩ) usually indicates a shorted junction — either due to fabrication problems, or the junction was inadvertently damaged by an electrostatic discharge.

Once viable junctions have been identified with the probe station, they are
**Figure 5.2:** The first fabrication step involves masking off the entire junction area. The uncovered trilayer areas are removed by reactive ion etching or ion milling.
Figure 5.3: This step defines the junction area. A small circular or elliptical area (between 1 and 5 μm²) and the contact pad areas are masked off. The uncovered layers are etched away by ion milling. The etch is stopped just below the aluminium oxide layer.
Figure 5.4: After the junction area has been etched, a thick layer of silicon dioxide is deposited to prevent sidewall shorting of the junction.
Figure 5.5: The final step involves depositing a thick layer of copper to connect the top of the junction to the contact pads.
carefully cleaved from the wafer and mounted onto a chip carrier. The terminals of the junctions are wirebonded onto corresponding terminals of the chip carrier, which is then be mounted on a dipstick [4]. Although this requires more time to set up than a probe station, the dipstick arrangement allows electrical measurements to be made at different temperatures, from 4.2 K to about 350 K.

Slight variances in the fabrication environment will often produce minor differences between what is intended and what is actually fabricated. The actual junction areas are often somewhat different from their intended areas. Since the junction areas are needed in the noise calculations, it is necessary to obtain accurate measurements of the true junction areas. This can be achieved with an optical microscope; the junctions are large enough to be seen at magnifications of 50–100x.

5.4 1/f noise in Al/AlO$_x$/Al junctions

One factor which limits the performance of superconducting Josephson junction qubits is the decoherence time; i.e., how long information can be stored in a qubit before it is irreversibly lost due to interactions between the qubit and the environment. This dissipation comes from many sources [5], e.g. fluctuations of charge in the substrate or vortex motion in the superconductors. Suppressing such charge and flux noise is currently one of the major goals of qubit research.

In aluminium oxide-based tunnel junctions, one major source of these charge fluctuations are defect sites within the oxide barrier. Charge trapping can occur at the defect sites, the result of which is 1/f–like noise in the measured voltage [6, 7] when the junction is DC biased. The XPS results presented in Chapter 4 suggest that these defect sites are most likely the oxygen vacancies produced during the
thermal oxidation of the initial aluminium layer. Thus, reducing the number of
oxygen vacancies within the oxide, either by annealing or electron bombardment,
may result in lower noise across the junction.

5.4.1 Experimental setup

The voltage noise is measured by applying a DC bias across the junction, and
recording the voltage fluctuations with a spectrum analyser. Figure 5.6 is a
schematic of the noise measurement setup. To minimise any 60 Hz line noise,
a 6 V battery is used as the current source. The power spectra density is measured
at different current bias values with an Agilent 35670A spectrum analyser. Since
we are primarily interested in the low frequency (1 kHz and less) noise, several low
pass filters were added to the circuit to cut out high frequency noise interference.

Since the absolute value of the noise depends on the junction cross-sectional
area, an area-independent noise value must be computed to allow a comparison of
noise levels between different junctions. This noise figure is computed using the
following expression:

\[
\frac{S_V}{V^2 A}
\]  

(5.1)

where \( S_V \) is the power spectral density at 10 Hz, \( V \) the voltage across the junc-
tion and \( A \) the cross-sectional area of the junction. A derivation of this expression
can be found in Reference [6].

The noise spectra of two sets of Al/AlO_x/Al tunnel junctions are collected
at various temperatures between 350 K and 4.2 K. In one set of junctions (the
floodgun junctions), the aluminium oxide layer went through 5 cycles of electron
bombardment (10 eV for one hour) and re-oxidation (300 torr-s). The second set
Figure 5.6: A schematic of the DC noise measurement setup.
(the control junctions) did not receive any electron bombardment at all.

5.4.2 Noise measurement results

Figure 5.7 shows the low frequency noise spectrum for a control junction at room temperature. For such metal-insulator-metal junctions, the observed noise is believed to be due to several individual noise sources, each of which has a characteristic frequency. The sum of all the individual noise sources then produces the 1/f-like noise spectrum observed in Figure 5.7. A more detailed explanation of such noise structure can be found in References [6, 7]. The floodgun junctions also display similar noise spectra, but with lower noise values.

The noise spectra of the junctions are then recorded as a function of temperature. As the junction cools, its resistance increases, while its resistance noise drops. The decrease in noise can be attributed to the charge trapping sites in the oxide slowly “freezing out” — for charge to move into/out of the trap requires a certain activation energy, and as the temperature of the system decreases, so does the probability that such charge hopping occurs. As a result, the resistance noise of the system decreases when the junction temperature decreases.

Figure 5.8 shows the 10 Hz noise figures, measured between 4.2 K and 350 K, for both a control junction and a floodgun junction. Although the noise level for the control junction decreases faster with temperature initially, it eventually levels off at a higher value compared to the floodgun junction at lower temperatures.

The 10 Hz noise figures at 4.2 K for the two sets of junctions are shown in Figure 5.9. The electron bombarded junctions are less noisy than the control junctions by about a factor of 10. Furthermore, the spread in noise figures is also smaller for the electron bombarded junctions.
Figure 5.7: Low frequency noise spectrum of a control junction at room temperature. The small peak at 60 Hz is due to line noise.
Figure 5.8: Noise figure (at 10 Hz) as a function of temperature for a control junction and a floodgun junction.
Figure 5.9: 10 Hz noise figures measured at 4.2 K for several control and electron bombarded junctions. The electron bombarded junction noise figures are more tightly clustered around a lower value.
In conclusion, the tunnel junction measurements indicate that electron bombardment of the aluminium oxide tunnel barrier does lead to a significant reduction in the junction resistance noise, particularly at low temperatures. This is a somewhat surprising result, given the crudeness of the Al-AlO$_x$-Al trilayer stack deposition, particularly the uncontrolled oxidation of the barrier layer. It will be interesting to find out the extent of the noise improvement for junctions starting from carefully grown trilayer stacks; i.e., where the barrier is grown with a controlled dose of oxygen, the stack deposition, oxidation and electron bombardment processes are all done in-situ, and seed layers are used to produce smooth films.
References for Chapter 5


CHAPTER 6
CONCLUSIONS AND OUTLOOK

This chapter is a summary of the main results of the XPS investigations. As is the nature of research, many more questions are raised for every one answered, so these will be discussed here as well.

6.1 Aluminium oxidation and clusters

The XPS oxygen 1s spectrum of aluminium oxide formed by the thermal evaporation of thin aluminium layers is resolvable into two peaks. The lower binding energy peak is due to the oxide while the higher binding energy peak arises from chemisorbed oxygen on the surface. This is corroborated by the electron bombardment and re-oxidation experiments — the changes in the peak intensity are consistent with the electron bombardment process driving chemisorbed oxygen into the oxide, and the re-oxidation process drawing it back out.

Whether the chemisorbed oxygen observed in XPS is the same as the clusters observed in BEEM is a question which has yet to be answered conclusively. BEEM scans on samples which have been annealed or electron bombarded do not show any significant decrease in the surface cluster coverage [1], even for samples where XPS scans show a decrease in the chemisorbed oxygen peak intensity.

The behaviour of the Al/AlO\textsubscript{x} system at high oxygen exposures (10\textsuperscript{7} torr-s and above) requires further study, particularly at the stage where the chemisorbed oxygen peak intensity increases sharply. As this occurs when the oxide growth rate slows down, there may be a correlation between the two events. It is also an open question whether the oxide growth is truly self limiting [2, 3] or continues at a very reduced rate.
The oxidation process has also not been thoroughly investigated for ultrathin oxide layers (less than 10 Å), such as those used in magnetic tunnel junctions. The difficulty in doing this lies mainly in the fact that it is difficult to obtain accurate values for the oxide thickness, which is required for a quantitative analysis of the oxide. Other problems include weaker signals from the thin oxide, and the possibility of overlapping spectral regions from the layers below the oxide.

6.2 Overlayers

Depositing a niobium or cobalt overlayer onto a thick, oxidised layer of aluminium resulted in an unexpected increase in the thickness of the oxide, whereas depositing an yttrium layer produced no increase. For the first two metals, the increase in the thickness seems to be proportional to their work function values. Hence, a hypothesis is that the higher work function values of niobium and cobalt lead to an increase in the electrochemical potential across the oxide, resulting in an enhanced oxide growth process where the surface chemisorbed oxygen is driven into the oxide, making it thicker. Naturally, data from a wider variety of metal overlayers, with work functions both above and below that of aluminium, would be needed to test this.

Another aspect which has not been investigated is the formation of oxides of the electrode materials at the interfaces. Some of our recent XPS experiments appear to indicate that the extent of interfacial electrode oxidation depends also on the work function of the electrode, relative to the aluminium. For high work function metals like cobalt, no interfacial cobalt oxide was seen, whereas some oxidation was observed with niobium overlayers. One difficulty in these experiments was distinguishing between interfacial oxidation and surface oxidation of the electrodes.
The latter can be minimised by adding another capping layer; however this
would also reduce the signal intensity significantly, making the data collection
process harder.

One further question is whether this work function difference also has the same
effect on ultrathin AlO$_x$ layers. For magnetic tunnel junctions, the deposited
aluminium layer is extremely thin and often fully oxidised before the top electrode
is deposited. If the same metal is used for the top and bottom electrodes, an
electrochemical potential difference might not be present. Even if so, the lack of
metallic aluminium might cause the chemisorbed oxygen to react with the electrode
materials instead.

6.3 Modification methods

Both the annealing and electron bombardment processes studied here produced
significant changes in the Al/AlO$_x$ system.

Annealing an oxide at high temperatures (around 500°C) resulted in an increase
in the oxide thickness, but not the oxide O/Al ratio. There is some evidence of
a decrease in the chemisorbed peak intensity, but more experiments would be
required to confirm this.

Although annealing can potentially improve the oxide quality [4], possibly by
removing some of the chemisorbed oxygen which may result in oxidation at the top
electrode interface, this must be carefully carried out to avoid problems of contam-
ination and interfacial diffusion. Appropriate anneal temperatures and durations
must be chosen to minimise these problems.

The changes to the AlO$_x$ layer due to the floodgun electron bombardment
process were more noticeable. After a one hour electron bombardment at a bias
voltage of 10 eV, the oxide O/Al ratio increased to ~1.2 from its initial value of ~1.0. This was often accompanied by a slight thickness increase, as well as a decrease in the chemisorbed peak intensity. The oxide reverted back to its oxygen-deficient form, although not completely, upon a subsequent re-exposure to oxygen. The chemisorbed peak intensity also increased after the oxygen re-exposure, to a value lower than what it was originally, after the formation of the AlOₓ layer.

Again, the effects of annealing and electron bombardment on ultrathin AlOₓ layers, as well as on subsequent overlayer depositions, have not been thoroughly investigated. Multilayer stacks containing such ultrathin layers would be more representative of actual tunnel junctions. Doing an XPS analysis on such systems would be more difficult however.

As the XPS floodgun only allowed a limited degree of control over its output, many aspects of the electron bombardment process could not be examined; for instance, the effect of different emission current densities. An electron source where both the emitted current and voltage can be independently controlled would be required for this purpose. As a result, only a tentative explanation for the observed changes can be proposed: the electron bombardment produces a surface charge on the AlOₓ surface and causes the chemisorbed O₂⁻ clusters to dissociate into O⁻ ions. The enhanced electrical potential from the surface charge then drives the O⁻ ions into the oxygen vacancies within the oxide. These ions are however only weakly bound, and further oxidation draws them back onto the surface.

A chemisorbed oxygen peak was also observed on cobalt thin films oxidised at room temperature. Electron bombardment on these cobalt/cobalt oxide systems also affect the oxygen peaks in a similar fashion — a reduction in the chemisorbed peak intensity was observed, accompanied by an increase in the cobalt oxide peak
intensity.

Such behaviour may not be specific only to aluminium oxide and cobalt oxide systems; it is possible that a wider variety of metal oxides also behave in a similar fashion.

6.4 Tunnel Junctions with AlO$_x$ barrier

Although aluminium-based magnetic tunnel junctions may soon drop out of fashion as a result of some recent work [5], aluminium oxide continues to be the insulating barrier of choice for niobium-based Josephson junctions.

At 4.2 K, the noise figures for Al/AlO$_x$/Al tunnel junctions incorporating electron bombarded oxide barriers are about a factor of 10 lower than that observed in junctions whose oxide barriers were not electron bombarded. Given that the starting trilayer was grown in a fairly crude way (repeated exposure to air, no seed layers to minimise roughness), the observed improvement in noise is very encouraging.

More work would be required to determine the full extent of the benefits brought about by the electron bombardment. These include the fabrication of Al/AlO$_x$/Al and Nb/AlO$_x$/Nb junctions with thinner electron bombarded barriers, and electrical testing of such junctions at low (4.2 K) temperatures.
References for Chapter 6


