MOLECULAR BEAM EPITAXY
IN THE LITHIUM-NIOBIUM-OXYGEN SYSTEM

by Mario Petrucci

Department of Electrical and
Electronic Engineering,
University College London.

A thesis submitted to University College, University of London
for the degree of Doctor of Philosophy.

October, 1989
To the memory of my father, Vincenzo Petrucci.

"We work not only to produce
But to give value to time."

Eugène Delacroix

"Oh, Mr. Scientist: you take what you see
And fashion a wondrous soliloquy;
But greater magic is forged in what you write:
Where night becomes day and day becomes night!"
ABSTRACT

The Nb-Li-O materials system offers an extensive combination of properties useful to integrated optics. Nb$_2$O$_5$ and LiNbO$_3$ already have applications in waveguiding devices, such as electro-optic modulators, Fresnel lenses, and SAW transducers. In several cases, however, it would be desirable to grow these oxides on lattice-matched substrates as epitaxial thin films of controlled composition, crystallinity, and thickness: this thesis describes work aimed at achieving this goal.

For the first time, Molecular Beam Epitaxy (MBE) was employed in depositing polycrystalline and single-crystal niobium oxide layers on z-cut LiNbO$_3$ and z-cut sapphire. Two new phases were grown epitaxially: a variant of niobium monoxide (termed "NbO-6C fcc"), and a hexagonal phase (composition NbO$_{1.25}$, termed "hex-\(\pi\)"). Thin-film niobium metal was also deposited on z-cut LiNbO$_3$. The post-deposition oxidation of oxygen-deficient, MBE-grown niobium oxide was studied, and optical waveguiding achieved in the resulting pentoxide films. The problem of oxygen deficiency in the as-grown material was addressed, leading to the design, construction and investigation of a novel oxygen radical source. Structural, compositional, and optical data are presented for all layers.

Process control was greatly enhanced, giving reproducible growth in this system for the first time. A 50keV RHEED unit was constructed, capable of probing insulating substrate and oxide-layer surfaces. Using this, original data was obtained for LiNbO$_3$ substrates and their pre-deposition surface behaviour, the crystal inner potential ($V_0$) was deduced for LiNbO$_3$, and improved electron diffraction data was obtained for grown layers.

An understanding was achieved of the limitations and promise of the MBE technique as applied to the Nb-Li-O system. The kinetics of the growth process were examined: this included the first detailed study of oxygen sticking coefficients for growth with and without Li flux. The prospects of MBE were assessed for the deposition of Nb$_2$O$_5$/LiNbO$_3$ layers that can form the basis of device structures.

298 words.
ACKNOWLEDGEMENTS

Financial support for the project was supplied by the DTI/SERC JOERS programme *Integrated Optical Devices*, and by EEC ESPRIT programme #866. SERC also provided funding under the aegis of a JOERS award *Improved Lithium Niobate*. GEC Hirst Research Centre supplied CASE support under the supervision of Dr. C. Dineen.

My family, friends and UCL colleagues have supported me throughout this project. Henry Robinson was a first-rate sounding board (and provider of accurate home truths). With humour and argument, both he and Steve Reynolds made long hours memorable. Maria Jones, Fred Stride, David Darbyshire, Mark Abbott, Tony Overbury, Fay Morris, Kevin Lee, Andy Lynch and Adrian Bailey have all provided help, and have stood in as drinking partners at one time or another. Ralph Betts (now at the University of New South Wales, Australia) gave help with initial operation of the equipment and ideas for future work. Clive Hall helped with orientation and X-ray studies. Maurice Gillett, Alan Gorrod and co-workers at UCL workshop were assiduous allies during system alterations, and I. Rangue of the Physics Department at UCL provided assistance with vacuum hardware.

Dr. H.J. Milledge, Dr. M. Mendelssohn and P.A. Woods (*UCL, Crystallography Unit, Department of Geological Sciences*) took Weissenberg and inclined-beam X-ray photographs of grown films. Dr. Milledge’s expertise was vital to their interpretation; in fact, the assistance of this team has been central to the success of my project. The continued interest they have shown me, and their readiness to assist at the most difficult of times, can only be described as philanthropic. Much the same can be said of Dr. C. Dineen, W.G. Freeman, A.J. Vale and B.R. Brown of *GEC Hirst Research Centre*, who answered innumerable questions on XRF/XRD analysis and SOS, and also gave invaluable assistance with the X-ray analysis of niobium oxide films and powders.

Thanks are also due to Dr. P.J. Dobson of *Phillips (Redhill)*, for guiding me safely through the labyrinthine corridors of RHEED analysis, and for putting right my unusual (but embarrassingly wrong) pronunciation of “Ewald”. N. Hill, J. Eaves, R. Attwood and others of *V.G. Hastings* were involved in the evaporator modifications, and Dr. G. Lovis was more than helpful in his advice on the problems thus encountered. F. Tothill and co-workers of *V.G. Scientific* assisted with the RHEED hardware described in Chapter 3. Dr. C. Whitehouse, G. Williams, Dr. R. Hardiman and Dr. D. Gasson (*RSRE, Malvern*) were generous with RHEED equipment and consultation time. Dr. A.M. Glazer of *The Clarendon Laboratory* (Oxford) provided the crystal structure projections and access to the Inorganic Crystal Structure Data File at the *SERC Chemical Data Bank System, Daresbury*. Dr. R. King (*National Physical Laboratory*) kindly performed the ellipsometry measurements reported in Chapter 5. D. Hall and I. Sutherland of *Loughborough Consultants Ltd.* conducted the ex situ SIMS, AES and XPS studies. Professor E.H.C. Parker and R.F. Houghton (Warwick University) performed trial silicon MBE depositions; CVD silicon was donated by C.M. Shaw, D.B. Meakin and R.S. Kean of *GEC Hirst Research Centre*.

No acknowledgement would be complete, however, without a mention of Professor C.W. Pitt, my supervisor. His encouragement, foresight and insight have been instrumental in converting this project from a feasibility to an actuality. Thank you, Chris.

Finally, my (too often unexpressed) thanks go to Mary and Michelle, for listening.
# TABLE OF CONTENTS

| (1)   | TITLE PAGE ................................................. | 1 |
| (2)   | ABSTRACT .................................................... | 3 |
| (3)   | ACKNOWLEDGEMENTS .......................................... | 4 |
| (4)   | TABLE OF CONTENTS .......................................... | 5 |
| (5)   | LIST OF TABLES ................................................ | 10 |
| (6)   | LIST OF FIGURES ............................................... | 11 |
| (7)   | LIST OF AUTHOR'S PUBLICATIONS ............................ | 14 |

| (8)   | CHAPTER 1: THE GROWTH OF NIOBIUM OXIDES AND LITHIUM-NIOBIUM OXIDES BY MOLECULAR BEAM EPITAXY: Project Concept & Background | 15 |

1.1 ABSTRACT ................................................. 15

1.2 INTEGRATED OPTICS: BACKGROUND ...................... 15

1.3 USEFUL MATERIALS IN THE Nb-Li-O SYSTEM ............... 16

1.3.1 Lithium Niobate, LiNbO₃ ..................................... 16

1.3.2 Niobium Pentoxide, Nb₂O₅ ..................................... 17

1.4 NIOBIUM OXIDE DEPOSITION TECHNIQUES .................. 20

1.4.1 Introduction ..................................................... 20

1.4.2 Growth Methods for Thin-Film Niobium Oxide: A Review ................................................. 20

1.4.3 A Note on Lithium Niobate Deposition .................. 21

1.5 MOLECULAR BEAM EPITAXY ..................................... 21

1.5.1 The MBE Process ..................................................... 21

1.5.2 MBE: Areas of Application .................................... 22

1.5.3 MBE of Niobium Oxides: Potential Benefits .................. 22

1.6 REASONS FOR NIOBIUM OXIDE DEPOSITION BY MBE; PROJECT AIMS ................................................. 24

1.6.1 Understanding of Li-Nb-O Growth by MBE; Improved Material ............................................. 24

1.6.2 Niobium Oxide: Materials Research and Device Applications ............................................. 24

1.7 THE SCOPE OF THIS WORK ...................................... 25

1.8 SUMMARY ......................................................... 25

REFERENCES .................................................... 26
CHAPTER 4: PROVISION OF OXYGEN IN Li-Nb OXIDE MBE:
Aims, Developmental Work, Summary of Results ............... 94

4.1 INTRODUCTION ................................................. 94

4.2 MOLECULAR EFFUSION SOURCES .............................. 94
4.2.1 Original Oxygen Sources ...................................... 94
4.2.2 Effusion Source and Pumping: Assessment and Modifications ........................................... 94
4.2.3 Results with Modified Effusion Source ...................... 96

4.3 ATOMIC OXYGEN:
A SOLUTION TO OXYGEN DEFICIENCY IN OXIDE MBE? ........ 98
4.3.1 Introduction; Reasons for choosing an Atomic Source .......... 98
4.3.2 Aims of Work with Atomic Source ............................ 99
4.3.3 Construction and Operation of the Atomic Source .......... 101

4.4 RESULTS OF MBE GROWTH RUNS WITH ATOMIC SOURCE .... 102

4.5 MEASUREMENT OF OXYGEN FREE RADICAL FLUX ............ 103
4.5.1 Introduction .................................................. 103
4.5.2 Calibration of the Thickness Monitor System .................. 103
4.5.3 Measurements: Vacuum Background and Surface-Saturation Effects ......................... 104
4.5.4 Graphs of Mass Gain versus Time: Atomic Flux Rates ......... 105

4.6 DISCUSSION OF FLUX RATE RESULTS; THRESHOLD EFFECT .... 110
4.6.1 Threshold Effect at Small Discharge Currents ................ 110
4.6.2 Re-evaluation of RUN 15 ..................................... 111

4.7 CONCLUSIONS REGARDING THRESHOLD MECHANISM .......... 112

4.8 FURTHER INVESTIGATIONS
IN VOLVING THE ATOMIC SOURCE .................................. 112
4.8.1 Introduction .................................................. 112
4.8.2 Experimental Details; Results .................................. 113
4.8.3 Cold Oxidation by Atoms: Discussion of Results ............... 113
4.8.4 Kinetics of Oxygen Incorporation for Niobium Oxides .......... 113
4.8.5 Atomic Oxidation: Summary ................................... 116

4.9 FURTHER WORK; SOLUTIONS TO EXISTING PROBLEMS ........ 117

4.10 SUMMARY ................................................... 118

REFERENCES ...................................................... 119
6.4 PROSPECTS FOR MBE AS A VIABLE DEPOSITION TECHNIQUE IN THE Nb-Li-O SYSTEM ........................................... 157

6.5 CONCLUDING REMARKS ...................................................... 158

REFERENCES: ............................................................................. 160

(14) APPENDICES:

APPENDIX 2.1: Limitations of SIMS for Quantitative Analysis of Composition ... 162

APPENDIX 3.1: Details on Ewald Sphere Construction ................................. 164

APPENDIX 3.2: Aluminium-backed Phosphor Screen for RHEED ................ 166

APPENDIX 3.3: Calculation of Electron Penetration Depth, D ....................... 167

APPENDIX 3.4: Structure Factor Considerations in Lithium Niobate ............. 170

APPENDIX 3.5: Mean Inner Potential (V₀) Calculation for LiNbO₃ ................. 171

APPENDIX 3.6: Coherence Length Calculations ......................................... 172

APPENDIX 4.1: Molecular Effusion Source for Oxygen ............................... 174

APPENDIX 4.2: Discharges in Oxygen .................................................. 180

APPENDIX 4.3: Data Checks; Validity of Chapter 4 Oxidation Data ............... 188

APPENDIX 5.1: Tables of Typical X-ray Data for Chapter 5 ......................... 190

LIST OF TABLES

(1) TABLE OF CONTENTS

(2) TABLE 2.1: Typical Run Procedure

(3) TABLE 3.1: Analysis Algorithm for RHEED Patterns

(4) TABLE 3.2: Ar⁺ Etch Rates for LiNbO₃, Sapphire, Si & Other Substrates

(5) TABLE 4.1: Atomic Oxidation Data for Silver at Room Temperature

(6) TABLE 5.1: X-ray Investigation of an NbO-6C fcc Layer on z-cut LiNbO₃

(7) TABLE 5.2: Oxidation Process: Relevant Crystal Data

IN THE APPENDICES:

(8) TABLE A3.1: RHEED Data for LiNbO₃ (Σ and Penetration Depth)

(9) TABLE A5.1: X-ray Powder Diffraction and RHEED Data for a Mixed-Phase Niobium Oxide Layer

(10) TABLE A5.2: X-ray Powder Diffraction Data for an Oxidised Niobium Oxide Layer
11
(17) FIG. 3.11: Z-cut LiNbO$_3$ Substrates: RHEED Patterns at Various Stages of Thermal Processing, Ion Bombardment Cleaning, and Thermal Reconstitution

(18) FIG. 3.12: Amorphous Niobium on z-cut LiNbO$_3$: RHEED Sampling Depth; Thermal Behaviour of Layer

(19) FIG. 3.13: Auger Composition Depth Profiles for LiNbO$_3$ Substrate at Various Process Stages

(20) FIG. 4.1: (a) Comparison of Molecular Flux Distributions from Various Geometrical Sources
(b) Schematic Diagrams of Original and Modified Micro-Capillary Array Arrangements

(21) FIG. 4.2: (a) Typical Mass Spectrum taken on Axis of Capillary-Array Oxygen Source
(b) Mass Spectrum taken on Axis of Atomic Radical Source

(22) FIG. 4.3: (a) Schematic of Discharge Source
(b) Photograph of Source

(23) FIG. 4.4: Oxidation and Reduction of Metal/Metal-Oxide Films Deposited on a Thickness Monitor Crystal: Predicted Graph Shapes of Oscillation Frequency vs. Time

(24) FIG. 4.5: Oxidation of 810Å Silver Film by Atomic Beam

(25) FIG. 4.6: Oxidation of 570Å Silver Film by Atomic Beam (Discharge Current Varied)

(26) FIG. 4.7: Atomic-Oxygen Flux Rate versus Discharge Current for New Oxygen Source

(27) FIG. 4.8: Dynamic Auger Depth Profiles for an NbO$_{1.2}$ Layer before & after Exposure to the Oxygen Atomic Beam

(28) FIG. 5.1: Typical 38.3 keV RHEED Data for an Epitaxial, NbO-6C fcc Layer Grown on z-cut LiNbO$_3$ by MBE

(29) FIG. 5.2: A Selection of X-ray and RHEED Data for Polycrystalline Niobium Oxide Layers Grown on z-cut LiNbO$_3$ and Sapphire by MBE: (a) X-ray Texture Photograph for a 4100Å Layer of NbO$_{0.9}$ Grown on z-cut LiNbO$_3$
(b) Inclined-beam X-ray Photographs
(c) 38.3 keV RHEED for a Mixed-Oxide Layer

(30) FIG. 5.3: 38.4 keV RHEED Data for a 1200Å Epitaxial Layer of NbO-6C fcc Grown on z-cut Sapphire by MBE
(31) FIG. 5.4: Inclined-beam X-ray Oscillation Photograph for a 1200Å NbO-6C fcc Film Grown on z-cut Sapphire

(32) FIG. 5.5: X-ray Data for a 910Å Layer of NbO₁₂₅ (Hex-π Phase) Grown on z-cut Sapphire by MBE
(a) Inclined-beam X-ray Oscillation Photograph
(b) Example of a Weissenberg Photograph for the above Sample

(33) FIG. 5.6: Composition Profile through a Niobium Oxide Layer as Determined by Dynamic Auger

(34) FIG. 5.7: (a) Surface Lattice Nets: LiNbO₃(001) and NbO-6C fcc (111)
(b) Ordered Vacancy Arrangement for the NbO-6C (111) Surface

(35) FIG. 5.8: 38.3 keV RHEED Patterns for an 800Å Layer of Niobium Metal Grown on z-cut LiNbO₃

(36) FIG. 5.9: Plot of Initial Layer Composition against Measured Expansion when Converted to the Gamma-Pentoxide

(37) FIG. 5.10: Oxidation of Niobium Oxide Layers - A Selection of X-ray Data

(38) FIG. 5.11: Sticking Coefficient Data for Niobium Oxide and Lithium-Niobium Oxide Growth by MBE

(39) FIG. 5.12: Dynamic Auger Composition Profiles for Lithium-Niobium Oxide Layers Deposited on Thermally-Oxidised Si by MBE

FIGURES IN APPENDICES:

(40) FIG. A4.1.1: Characterisation Data for the Microcapillary (Bellows) Array
(a) Growth Chamber Pressure and Off-Axis Beam Pressure as a function of p₀ (Oxygen Gas used throughout)
(b) Typical Plots of Chamber Pressure versus Time for various Growth Pressures

(41) FIG. A4.2.1: Oxygen-Atom Flux Rate versus I⁺²

(42) FIG. A4.2.2: Characterisation Data for the Atomic Source
LIST OF AUTHOR'S PUBLICATIONS


Throughout this thesis, journal references are generally laid out as follows:

AUTHOR(S)
TITLE of PAPER (if included; usually in italics)
TITLE of JOURNAL (standard abbreviation)
VOLUME NUMBER (underlined)
PART NUMBER (if included)
DATE (year, in brackets)
PAGE NUMBERS (sometimes preceded by p. or pp.)

Other types of reference, such as texts, follow a similar format.
CHAPTER 1

THE GROWTH OF NIOBIUM OXIDES AND LITHIUM-NIOBIUM OXIDES BY MOLECULAR BEAM EPITAXY:
PROJECT CONCEPT AND BACKGROUND

1.1 ABSTRACT

The aim of this chapter is to explain the project philosophy and to provide a context for the research reported in this thesis. To begin with, a brief description will be given of Integrated Optics (IO) and of how it has spurred interest in the thin-film deposition of certain crystalline materials. The most important oxides in the Nb-Li-O system will then be reviewed: emphasis is given to their current applications and status in IO and other fields. A brief account is also given of the various thin-film deposition methods applied to these materials to date. The thin-film growth technique of Molecular Beam Epitaxy (MBE) is then discussed, along with an analysis of its merits. These preliminary reviews provide the backdrop for the subsequent discussion of the project itself: the basic aims of the research are outlined, and the reasons for investigating niobium oxide growth by MBE are dealt with in depth. The principal aims were to improve the understanding of Li-Nb-O growth by MBE, and to deposit epitaxial niobium oxide for device applications. The chapter is rounded off with a summary of the scope of the work undertaken.

1.2 INTEGRATED OPTICS: BACKGROUND

Integrated Optics\(^1\) can be described as the optical analogue of integrated electronics. The impetus for the technology is the increasing need in telecommunications, sensing, and signal processing to operate at high frequencies and to exploit the enormous bandwidth of light\(^2\) -\(^4\). Most IO structures consist of a thin film of crystalline material on a suitable substrate of lower refractive index\(^1\) : this forms a compact planar waveguide\(^1\) which provides essentially a two-dimensional, low-volume transport of light. High values of applied electric field are achievable, and tight confinement of the light can be obtained: this gives waveguide devices significant advantages over their bulk counterparts in terms of speed, drive power, size, ruggedness, and efficiency (including coupling efficiency to optical fibres and lasers\(^1,1,5\)). These advantages can be brought to bear in waveguiding surface acoustic wave (SAW) and electro-optic devices, which use the acousto-optic\(^1,6\) and electro-optic\(^1,6\) interactions respectively for the manipulation of guided light.

Research is needed to explore the viability of new heterostructure combinations involving oxides, and to assess the suitability of thin-film growth methods for their deposition.
An understanding of the structures, growth regimes, and growth kinetics of these oxides is important in correlating the growth conditions to layer quality, aspects of which may be linked to device performance.

1.3 USEFUL MATERIALS IN THE Nb-Li-O SYSTEM

1.3.1 LITHIUM NIOBATE, \( \text{LiNbO}_3 \)

\( \text{LiNbO}_3 \) is one of the materials most used for IO and SAW devices\[^{1-2,17-14,26} \]. The rhombohedral phase exhibits strong non-linear optical behaviour\[^{1,27,28} \], and its figures of merit for the electro-optic and acousto-optic interaction are among the best for materials in which optical waveguides are, at present, easily formed\[^{1,6,9} \]. Important acoustic applications include acoustic microscopy\[^{1,9} \], radar signal processors\[^{1,29} \] and spectrum analysers\[^{1,30,31} \]. Here, the high electromechanical coupling coefficient\[^{1,22} \] and the low acoustic attenuation of \( \text{LiNbO}_3 \) (0.05 dB/cm at 500 MHz\[^{1,6} \]) are a bonus. The electro-optic behaviour is mostly utilised in optical fibre communications and control\[^{1,33} \]. For SAW applications, the surface acoustic wave is launched along the piezoelectric axis (the \( c_{14} \)-axis for \( \text{LiNbO}_3 \)), and the light is guided perpendicularly to this. Hence x- or y-cut \( \text{LiNbO}_3 \) is used, with the \( c_{14} \)-axis in the plane of the surface and across the waveguide\[^{1,23} \]. The y-cut section offers a particularly high acousto-optic efficiency\[^{1,25,34} \]. Z-cut material is mostly used for electro-optic applications.

There is also a vast potential for \( \text{LiNbO}_3 \) in high frequency (20→30 GHz) modulation and in IO chips that form the external cavity of a semiconductor laser, effecting spectral control of the laser output and/or modulation. The non-linear optical properties are attractive for parametric oscillation, optical bistability, optical rectification\[^{1,35} \], and second harmonic generation\[^{1,36-1,38} \]. The photorefractive effect in \( \text{LiNbO}_3 \) gives rise to the problem of optical damage\[^{1,9,39} \], but can be utilised for holographic storage\[^{1,39,1,40} \].

\( \text{LiNbO}_3 \) waveguide technology is well established\[^{1,25} \], and modulator devices have been realised with bandwidths beyond 10GHz\[^{1,25,41} \], reasonable drive power (typically <100mW\[^{1,25} \]) and with a number of advantages over direct modulation of semiconductor lasers\[^{1,41,42} \]. Other materials\[^{1,35,43,41,44} \], such as GaAs\[^{1,42,45-1,47} \], are likely to offer long-term competition to \( \text{LiNbO}_3 \) for IO applications; however, \( \text{LiNbO}_3 \) has superior electro-optic, SAW, and non-linear optical characteristics to GaAs\[^{1,47-1,50} \], and is less lossy\[^{1,25,1,49} \]. \( \text{LiNbO}_3 \) also has the advantage of being predominant in current waveguide fabrication technology\[^{1,49} \]. Present techniques for fabricating waveguides in \( \text{LiNbO}_3 \) are relatively simple, and mostly involve indiffusion\[^{1,9} \]. However, there is tremendous scope to improve devices (notably in terms of size, efficiency and bandwidth) by making use of thin-film, epitaxial \( \text{LiNbO}_3 \). Possibly one of the next stages for IO research, then, includes the controlled deposition of thin-film, single-crystal \( \text{LiNbO}_3 \) of high quality: this may require the application of new epitaxial growth techniques for \( \text{LiNbO}_3 \). The controlled
deposition of high refractive index epilayers on LiNbO$_3$ substrates is also worthy of research (see next section). The investigation of new heteroepitaxial combinations involving LiNbO$_3$ may also be of interest, particularly for hybrid opto-electronic and IO circuits$^{[1,45]}$ (e.g. modulators and switching networks operating in the IR$^{[1,41,1,51-1,53]}$).

1.3.2 NIOBIUM PENTOXIDE, Nb$_2$O$_5$

(a) Structure and Properties

The properties and structures of the various niobium oxides$^{[1,54]}$ have not been studied in any great depth, except within very narrow areas of interest: much remains to be done to understand this complex system$^{[1,54,1,55]}$. In crystallographic work, the pentoxides have received most interest: a number of papers report complex structures and behaviour (see Ch. 5). The basic structural unit of most of the pentoxides is an oxygen octahedron with a Nb at the centre, NbO$_6$; this is similar to the structural description of LiNbO$_3$.$^{[1,10]}$ The different phases correspond to different ways in which the octahedra are distorted and conjoined. The dielectric constants of a number of phases have been measured, both at d.c.$^{[1,59]}$ and in the frequency range 20–100 MHz$^{[1,56]}$: they were comparable to, sometimes greater than, those of LiNbO$_3$, and often displayed marked anisotropy. The latter suggests a likelihood of pyroelectric and piezoelectric properties, and, possibly, optical birefringence. Some IR absorption work was also performed$^{[1,56]}$, and the phase diagrams for NbO-NbO$_2$-Nb$_2$O$_5$ were mapped out$^{[1,54]}$. A review of the electronic properties and oxidation behaviour of the niobium oxides can be found in Halbritter$^{[1,57]}$; further data is given by the author in Ch. 5.

The quadratic electro-optic and electro-strictive coefficients of amorphous Nb$_2$O$_5$ are high$^{[1,60]}$. However, no studies have been reported on the possible linear electro-optic, pyroelectric, and piezoelectric properties of single-crystal niobium oxides, and no structural investigations have sought the non-centrosymmetricity needed for such effects. Available data is sparse, and tends to concentrate on factors relevant to superconductivity.

(b) Device Applications

Niobium pentoxide is rapidly emerging as a material of significant interest$^{[1,60]}$. The figure of merit most commonly quoted for acousto-optic materials, $M_5^{[1,61]}$, depends on the refractive index (n) raised to the sixth power. The high n and favourable acoustic properties of niobium pentoxide$^{[1,62]}$ make it a prime candidate for efficient acousto-optic devices. Test devices have now been demonstrated in amorphous Nb$_2$O$_5$.$^{[1,63]}$ (see also below). However, it is not known which phases, if any, might be suitable for single-crystal waveguide applications.
In most cases, amorphous pentoxide layers have been deposited; few workers have attempted single-crystal growth, bulk or otherwise\textsuperscript{[1,56]}.

The outstanding acousto-optic and electro-optic properties of LiNbO$_3$ have already been described: the use of niobium pentoxide as an overlaying waveguiding material on LiNbO$_3$ substrates is attractive for a number of reasons, as follows.

(i) The refractive indices of deposited Nb$_2$O$_5$ thin-films (at He-Ne wavelength) are generally high, mostly between 2.10 and 2.35\textsuperscript{[1,60,1,63-1,67]}, but sometimes as high as 2.40\textsuperscript{[1,59,1,67]}. This makes Nb$_2$O$_5$ eminently suitable for fabricating electro-optic and acousto-optic devices on LiNbO$_3$. Also, efficient waveguide lenses (such as Fresnel lenses) can be made using Nb$_2$O$_5$ on LiNbO$_3$\textsuperscript{[1,31,1,63]}, and chirped grating lenses fabricated in Nb$_2$O$_5$ waveguides on $y$-cut LiNbO$_3$ have exhibited efficient focusing action compared with those fabricated on titanium in-diffused LiNbO$_3$ waveguides\textsuperscript{[1,65]}. Nb$_2$O$_3$ can also be used on titanium-indiffused LiNbO$_3$ waveguides as a phase-shifting cladding material.

(ii) Nb$_2$O$_5$ overlayers improve the acousto-optic interaction on LiNbO$_3$ substrates\textsuperscript{[1,63,1,68]} (particularly the coupling efficiency of SAW transducers): this may be utilised in waveguiding Bragg Cells, giving greater acoustic bandwidth.

(iii) The stability of amorphous niobium pentoxide waveguides is excellent near room temperature\textsuperscript{[1,64]}, and good optical losses\textsuperscript{[1,64,1,67,1,69,1,70]} have been achieved.

Epitaxial deposition of niobium oxide waveguides, for example on LiNbO$_3$, is an interesting proposition:

(iv) Good epitaxy is to be expected by virtue of the strong chemical bonding between the oxides.

(v) Grain-boundary optical scattering has been observed in sputtered Nb$_2$O$_5$ material\textsuperscript{[1,67]}, and the films give high acoustic losses at high frequencies ( $> 32 \rightarrow 34 \text{ dB/cm at 1.1 GHz}$\textsuperscript{[1,68]}). These problems have limited their potential for optical and high-frequency devices. Present thin-film deposition methods concentrate on the growth of amorphous layers in order to achieve low loss, and rely on the electro-optic and acousto-optic properties of the substrate for the device application. The growth of single-crystal Nb$_2$O$_3$ overlayers could lead to improved acoustic loss, especially at high frequency, and may provide better optical quality pentoxide films. Such layers would also offer the possibility of investigating and exploiting any anisotropy or useful properties in the crystal phase grown.

(vi) The minimum waveguide thickness for optical guiding in oxygen-deficient, homoepitaxial LiNbO$_3$ was much larger than ever achieved in Betts' apparatus\textsuperscript{[1,9]}, and only
extraordinary rays would be guided. Homoepitaxial, oxygen-deficient waveguides were never demonstrated\(^1\) and the required control over oxygen composition was not achieved (Ch. 2). Growth on sapphire (\(n = 1.76\)) eased the thickness limitation\(^{11,74}\), but always gave cubic, non-birefringent, and lossy Li-Nb oxide films. (These shortcomings prompted the equipment modifications described in Ch. 2, aimed at achieving higher growth rates and better flux rate control). \(\text{Nb}_2\text{O}_3\) waveguides, on the other hand, should support both polarisations, and in much thinner layers than for oxygen-deficient LiNbO\(_3\). Depending on the properties of the grown layer and the application, the epitaxial growth of a high-\(n\) phase of \(\text{Nb}_2\text{O}_3\) on LiNbO\(_3\) \((\Delta n > 0.06)\) could be superior to oxygen-deficient LiNbO\(_3\) homoepitaxy; the combination might also provide an alternative SAW device fabrication technology to that of titanium in-diffused LiNbO\(_3\), with lower optical damage and improved device performance. Of course, \(\text{Nb}_2\text{O}_3\) waveguides could only effectively replace LiNbO\(_3\) in modulator or SAW devices if the \(\text{Nb}_2\text{O}_3\) proved to be suitably electro-optic or piezoelectric.

(vii) Amorphous \(\text{Nb}_2\text{O}_3\) is usually intolerant to processing above \(400^\circ\text{C}\)\(^{11,65}\), due to crystallisation. Single-crystal layers would not suffer from this effect.

(c) Some further applications for thin-film Nb oxide and Nb

The requirements of some solid-state devices and components cannot be fulfilled by silicon dioxide films\(^{11,72}\). What is known about the resistivity, permittivity and thermal stability of \(\text{Nb}_2\text{O}_3\) films makes them attractive for use in high-resolution vidicons\(^{11,72}\), IO decouplers\(^{11,72}\), thin-film capacitors\(^{11,73}\), and other dielectric and micro-electronic devices\(^{11,59}\). For these, the higher dielectric constants observed for the crystalline phases make single-crystal growth a desirable goal. Novel components, such as switchable resistors\(^{11,74}\), may also be fabricated in \(\text{Nb}_2\text{O}_3\).

\(\text{Nb}\) is used in most superconducting r.f. cavities, and has the characteristics of a potentially outstanding Josephson junction material\(^{11,57,1,75}\). \(\text{NbO}\) is also a superconductor\(^{11,76}\). So far, r.f. sputtered and plasma-oxidised Josephson junctions have experienced difficulties with oxygen deficiency and interface reactions and roughness. MBE may, for example, be able to overcome the interfacial problems.

A final point: it is proving difficult at present to deposit high-\(T_c\) multicomponent oxide superconductors\(^{11,76}\) as epitaxial thin films with high quality interfaces and no oxygen deficiency\(^{11,77}\). The study of niobium oxide (and lithium niobate) growth by MBE may suggest solutions to these problems and those encountered in the vacuum deposition of other oxide materials.
1.4 NIOBIUM OXIDE DEPOSITION TECHNIQUES

1.4.1 INTRODUCTION

Owing to the recent interest in LiNbO$_3$ and LiTaO$_3$, current work in the field tends to concentrate on Nb-Li and Ta-Li oxides$^{[1-9]}$, and rather less work has been performed on niobium oxides. Broadly speaking, there are two approaches to the fabrication of optical waveguides in these materials:

(i) the modification of a thin layer at the surface of a bulk-grown crystal;
(ii) the deposition of thin films on appropriate substrates.

In the case of niobium oxide, (i) is largely irrelevant, since single-crystal boules are not available. In any case, the deposition approach makes possible novel device configurations and heterostructures, and offers the potential for greater control over layer properties, geometry, and refractive index profiles. The following paragraphs review the studies on the growth of thin-film niobium oxide reported so far.

1.4.2 GROWTH METHODS FOR THIN-FILM NIOBIUM OXIDE: A REVIEW

The growth of niobium oxide by anodic oxidation or pyrolytic vapour deposition$^{[1,59,78]}$ tends to produce amorphous layers$^{[1,72]}$. The vapour-deposited material is remarkably stable thermally, and does not crystallise until beyond 850°C: however, it has very low values of $n$ (= 2.2) and dielectric constant (= 11). Niobium oxide deposited by the halogen transport method$^{[1,59,72,73]}$ has high $n$ and dielectric constant (= 100), but requires high growth temperatures (1000°C); the grown layers tend to be polycrystalline. R.f. plasma oxidation has also been used to grow amorphous films, but the material is oxygen-deficient$^{[75]}$. None of these methods seem particularly promising for advanced IO applications.

R.f. sputtering$^{[79]}$ involves the bombardment of suitable target material by ions produced in a low pressure, gaseous, r.f.-induced glow discharge. Species from the bombarded target arrive at the earthed or biassed substrate, along with the target gas, giving rise to a deposited film. R.f. sputtering commonly suffers from a number of difficulties: back-sputtering, impurity and sputter gas incorporation, gas occlusions, rough surfaces, oxygen deficiency, and target and layer compositional drift. The method does not lend itself easily to in situ analytical techniques, and very low growth rates must be used for Nb$_2$O$_5$ (and LiNbO$_3$). The main difficulty is in maintaining a chosen layer stoichiometry$^{[80]}$. However, it remains a versatile and simple approach. In the case of niobium oxide, a reasonable body of work has accumulated dealing with thin-film deposition by r.f. sputtering for waveguide devices: the
limitations of the material grown in these studies, particularly for high frequency devices, have already been discussed in Section 13.3.2. All r.f. sputtered and reactive d.c. sputtered niobium oxide layers reported to date have been either amorphous or polycrystalline; the latter films displayed ionic instability. Refractive index and optical loss of the layers were difficult to reproduce: most films had moderate losses (typically 2 dB/cm), but the very low losses (< 0.5 dB/cm) occasionally observed (e.g. after laser annealing) indicate that Nb2O5 has potential as a low-loss waveguide material.

The conclusion, then, is that the techniques so far used for fabricating waveguides in Nb2O5 mostly suffer from limitations, particularly in terms of controlling waveguide composition, structure and purity. No single-crystal layers have been deposited. Many techniques have employed crude (or no) in situ substrate preparation and growth monitoring. For some applications (e.g. high-frequency Bragg cells) the material grown has been of inadequate quality for device manufacture. There remains a need for a versatile, low-temperature deposition technique that is able to exercise strict control over layer properties, and that offers thin-film, single-crystal growth in the niobium oxide system. MBE presents itself as a possible candidate. R.f. sputtering onto heated substrates may be another approach. The availability of in situ analyses in MBE, however, makes it more attractive as a research tool.

1.4.3 A NOTE ON LITHIUM NIOBATE DEPOSITION

R.f. sputtering is now the predominant technique for depositing thin film Nb-Li and Nb-Ta oxides (mostly LiNbO3 and LiTaO3) for IO applications. The growth of Nb-Li oxide layers by various techniques, including sputtering, has not yet supplied high-quality epitaxial material suitable for IO device applications. During the course of this project, however, a few papers by other authors indicated that some progress was being made in the deposition of single-crystal LiNbO3 waveguides on sapphire by r.f. sputtering: the ramifications of this work for the prospects of MBE growth in the Nb-Li-O system cannot be discussed at this early stage; further comment is postponed until Ch. 6.

1.5 MOLECULAR BEAM EPITAXY

1.5.1 THE MBE PROCESS

The MBE technique is discussed, along with its underlying principles, in the cited references. In brief, crystalline thin films are grown by the evaporation of elements or simple compounds in an ultra-high vacuum (UHV) environment. Furnaces or electron-beam evaporators are usually used to produce the molecular beams, which impinge on a heated substrate of suitable crystal structure and properties, where they react chemically to form the
overlayer. Judicious use of ion etching and thermal annealing can yield atomically-clean and single-crystal substrate surfaces suitable for epitaxy ("epitaxy" is achieved when the structure of the overlayer conforms to, and aligns with, that of the substrate).  

1.5.2 MBE: AREAS OF APPLICATION  

MBE is making a contribution to the epitaxial deposition of many important semiconductor materials. These include silicon, and the II-VI, III-V and IV-VI compound semiconductors (GaAs, GaAlAs, GaAlSb, GaAsSb, CdTe, PbTe, and so on). Epitaxial metal films have also been deposited, but very few reports have appeared on the growth of oxides using this technique. This is presumably because of the refractory nature of many of the oxides, the frequent problem of non-congruent evaporation, and the difficulties associated with the use of oxygen in an MBE kit. In the case of Nb₂O₅, no thin-film epitaxial deposition studies have been reported by any technique; as for LiNbO₃, most devices are currently fabricated in single-crystal bulk material.  

1.5.3 MBE OF NIOBIUM OXIDES: POTENTIAL BENEFITS  

MBE offers the potential for excellent control over layer stoichiometry, morphology and uniformity, as well as reproducible monolayer thickness control and abrupt (< 1 second) initiation/cessation of growth. These capabilities are attractive for IO applications, since they allow for "tailoring" of device characteristics. MBE could give better control over the film refractive index than other thin-film deposition techniques for niobium oxide; refractive index inhomogeneity scattering, observed in sputtered niobium oxide films, might also be reduced. The further advantages of using an epitaxial growth technique for niobium oxide have already been discussed. Other thin-film deposition methods for Li-Nb oxides have generally encountered severe problems in one or more of the above respects, for example in terms of structural quality of the layers and waveguide uniformity.  

Doping of MBE-grown material is relatively straightforward, and the control over dopant profiles can be used to optimise coupling efficiency with fibres and chip-based components. The relatively low growth temperatures involved in MBE (usually < 700°C) typically reduces interdiffusion to within a few monolayers, so that sharp dopant profiles and abrupt interfaces are feasible. However, system down-time can be a problem, and MBE rigs are expensive to build and run.  

Even for purely optical applications, MBE allows the use of different substrate materials (and cuts) which can be selected to give a large difference in n between film and
substrate: single- and multi-mode waveguides may then be achieved in thinner layers than for the in-diffusion technique, giving tighter optical control and confinement, and improving many aspects of device efficiency (though small mode sizes can sometimes exacerbate bend losses and interfacing difficulties with optical fibres).

Scattering reduces the efficiency of optical waveguides, and degrades dynamic range in IO signal processing devices\(^{11,69,70}\). It can arise from defects, multiple domains, grain boundaries, stress, surface or interface roughness, impurities, or layer inhomogeneities\(^{1,98}\). MBE is, in principle, a very clean growth technique, and the moderate growth rates allow surface-diffusion processes to dominate, so that single-crystal growth is possible. With a suitable substrate, a growth regime can be found for many materials which yields epitaxial, uniform layers of good single-crystal quality, high purity, and low defect density\(^{1,91}\). With proper substrate preparation and a low lattice mismatch (typically < a few %), good interfaces are possible. Smoothing of the growing surface on an atomic scale (a frequent occurrence in MBE) reduces surface scatter. Also, in the case of LiNbO\(_3\) deposition, optical damage may be alleviated by eliminating those impurities and inhomogeneities believed to be largely responsible for the phenomenon. However, heteroepitaxy sometimes gives rise to strained overlayers, misfit dislocations, or thermal mismatch problems, all of which can have serious consequences for waveguide scattering losses or film stability.

The low pressures (< 10\(^{-9}\) Torr) employed in MBE originally arose from the need to reduce unwanted doping during growth\(^{1,91}\) (i.e. film impurity). However, the UHV ambient is also conducive to the use of a range of vacuum analytical techniques: using these in situ avoids atmospheric contamination of the surface to be studied, and can also give information vital to effective substrate preparation and process control (see Ch. 2).

In summary: MBE provides a controllable process for the deposition of Nb-Li oxides at moderate temperatures, and could rival the present technology for making epitaxial, thin-film waveguides in these materials. MBE would also be compatible with established semiconductor technology and CMOS processing requirements. MBE had not been applied to any great extent in the deposition of dielectric oxides (the only MBE work with Nb-Li oxides had been performed at UCL\(^{1,8}\)). The apparatus now employed for the deposition of these oxides differs in several important respects from typical (usually semiconductor) MBE systems: a complete description, and a review of previous work, is given in Ch. 2.
1.6 REASONS FOR NIOBIUM OXIDE DEPOSITION BY MBE;
PROJECT AIMS

1.6.1 UNDERSTANDING OF Li-Nb-O GROWTH BY MBE;
IMPROVED MATERIAL

Very little is known regarding the growth kinetics for the deposition of niobium-lithium oxides by MBE\cite{1,9}. The epitaxial growth of various phases of LiNbO$_3$ by MBE has been reported by Betts\cite{1,9,1,00}, but substrate and growth monitoring were poor. An estimate was made by Betts\cite{1,9} of the sticking coefficients of Li and O$_2$ during MBE: however, this data was very approximate and was only applicable to a narrow range of growth conditions and for amorphous substrates. Thus the considerations of greatest importance to the kinetics of a vapour deposition process such as MBE (for example, surface energy, surface mobility, sticking coefficients, surface residence times, chemical bonding, lattice matching, beam flux rates, symmetry relationships, etc.) have remained virtually unexplored in the Nb-Li-O system. Also, a number of unresolved problems were thrown up by Betts' work, and reproducible growth of the rhombohedral phase of LiNbO$_3$ was not achieved (see Ch. 2).

To improve the situation, it was proposed to characterise the MBE-growth of niobium oxides on LiNbO$_3$ and other substrates, and to measure oxygen sticking coefficients with and without Li flux. It was hoped that work of this kind would shed light on the problems encountered in lithium niobate MBE, and perhaps clarify the roles of Li and Nb in the growth process; in particular, the results of the sticking coefficient and epitaxy experiments might indicate appropriate action for growth optimisation in LiNbO$_3$ MBE. One of the key points was to ascertain the importance of the niobium sub-lattice in determining the crystal structure of grown Li-Nb-O material. The ultimate aim was to determine whether or not MBE was a viable technique for the growth of these oxides, and to establish the oxide growth regimes. Also, some important surface studies were performed in-house using the new RHEED equipment described in Ch. 3. Further discussion, and the results of this work, are to be found in Chs. 3, 4 and 5.

1.6.2 NIOBIUM OXIDE:
MATERIALS RESEARCH AND DEVICE APPLICATIONS

As we have seen, several workers have deposited thin-film amorphous or polycrystalline niobium oxide, but no single-crystal layers have been reported. An investigation of the epitaxial growth of niobium oxides, in this case by MBE, was therefore of intrinsic research interest. In fact, this study is the first exploration of MBE growth behaviour for niobium oxides. Any characterisation of grown layers (structure, composition, optical/acoustic properties, etc.) would make a valuable contribution to the sparsely studied materials aspects of the niobium oxides.
The deposition work might also establish what devices are feasible with MBE-grown material. Certainly, a primary aim was to characterise the material optically, and to grow epitaxial waveguides that would form the basis of devices such as those mentioned in Section 1.3. The epitaxial deposition of Nb was also of interest.

1.7 THE SCOPE OF THIS WORK

The first task was to assess, and then to modify, the inherited apparatus. The need was to ensure accurate process monitoring, good beam control, and reproducible growth runs for a wide range of beam flux rates. This work is described in Ch. 2. The subsequent two chapters each discuss an important modification in greater depth. Ch. 3 describes the implementation of 50keV RHEED for the surface analysis of insulators, particularly LiNbO₃ and sapphire. The chapter contains a substantial body of new RHEED data for LiNbO₃, including an analysis of the effects of 3keV Ar⁺-etching and thermal annealing. Ch. 4 traces the evolution of the oxygen sources used in the MBE system: this culminated in the design, manufacture and assessment of a free atomic radical source whose purpose was to alleviate oxygen deficiency in the grown layers. Ch. 5 describes the bulk of the deposition and analytical work for MBE-grown niobium oxide. Some Li-Nb oxide and Nb metal layers were also grown. Sticking coefficients for molecular oxygen were obtained (with and without Li flux present); layer quality and structure were correlated to growth and processing parameters; and the effects of post-deposition processing were assessed. Ch. 6 discusses the extent to which the project aims were met. A specification is proposed for an MBE system that could aim for the reliable deposition of these oxides for commercial applications. Suggestions are put forward for effective future work in the field.

1.8 SUMMARY

The Nb-Li-O system offers a number of materials covering a wide range of acousto-optic and electro-optic applications. MBE may be able to meet the need for thin, pure, defect-free, single-crystal films in this oxide system having controlled properties. Such layers would offer considerable scope for improving on existing device material, and might open up exciting novel applications.

This thesis reports the first attempt to grow niobium oxides by MBE. The main benefits envisaged were two-fold. Firstly, it was hoped that the research would lead to the deposition of epitaxial Nb₂O₅ for device fabrication. Secondly, an earlier study of the MBE growth of lithium niobate had laid open a number of unanswered questions: a thorough study of the niobium oxide lattice (as grown by MBE) was needed to resolve these problems and to improve the understanding of Nb-Li-O MBE growth generally (e.g. to establish the factors
that make the reproducible growth of rhombohedral LiNbO₃ difficult). Some further studies on Nb-Li oxide deposition were also conducted. The principal aims of the growth studies were to deposit niobium oxide by MBE over a wide range of growth conditions, to characterise the layers, to deconvolve the roles of Li and Nb in the growth process, and to establish the growth regimes and equipment limitations, especially those concerning the provision of oxygen.

The ultimate aim was to deposit Nb₂O₅ and LiNbO₃ epitaxially on insulating substrates as high-quality crystal layers. The use of MBE to grow these materials was not expected to be a straightforward task; the growth of niobium oxide layers by MBE, and their characterisation, was entirely new. The potential reward, however, was the realisation of a growth capability that could significantly advance the IO and SAW technologies.

REFERENCES

1.26  Crystal Technology, Circle No. 23, 1035 East Meadow Circle, Palo Alto, California 94303.

27


For further references to single-crystal bulk growth, see Ch. 5.


1.93 Y. Ota, Thin Solid Films 106 (1983) 3-136 (See also review by J.C. Bean, ref. 1.43).
2.1 ABSTRACT

In this chapter, the evolution of the MBE system is described. The substrate processing procedure is explained, and typical run conditions are summarised. Previous work in the field is reviewed, and the main shortcomings of the inherited equipment are identified. The most important equipment modifications are categorised and discussed; these can also be traced in recent publications.[2.1→2.3]

2.2 GENERAL DESCRIPTION OF MBE PROCESS: UCL MBE SYSTEM

The technique of MBE was discussed briefly in Ch. 1, and has been covered by Betts[2.1]. However, a brief description of MBE, and of the system as it now stands, will be given, to put the rest of this chapter into context.

The major requirements in an MBE system are:

(1) Ultra-high vacuum (UHV) environment;
(2) In situ processing of substrate surfaces to produce an atomically-clean surface with well-ordered structure (to promote epitaxy);
(3) Elemental or molecular sources;
(4) Capability to control and reproduce growth conditions such as substrate temperature and beam flux rates.

The UHV environment minimises both the impurity levels in the grown material and the degree of recontamination of prepared substrate surfaces by background vacuum species. Furthermore, the operation of electron beam evaporators requires low background pressures (< 10^-7 Torr). UHV also facilitates the implementation of in situ diagnostic techniques such asSIMS and RHEED.

The present system, as developed for the MBE-deposition of oxide layers composed of Li, Nb and oxygen, is illustrated schematically in Fig. 2.1, with photographs in Fig. 2.2. It comprises two main chambers, separated by a gate valve: this dual-chamber arrangement minimises contamination of the growth region by the pre-deposition processing, and allows uninterrupted base vacuum (< 10^-9 Torr) to be maintained in the growth area while substrates are loaded, prepared and analysed prior to growth. After growth, the probe is returned to the diagnostic region to evaluate the grown layer.
SCHEMATIC REPRESENTATION OF
MACHINE EMPLOYED FOR THIN-FILM DEPOSITION
OF LITHIUM-NIOBIUM OXIDES.

A. substrate holder, heater and manipulator; B,C. RHEED gun
and screen; D,E. SIMS analysis; F. diffusion pumps;
G. gate valve; H. beam-monitoring and residual gas analysis;
I. oxygen source (into plane of paper); J. beam-defining
aperture of low vacuum conductance; K. charged-particle
filters and thickness monitors; L. liquid nitrogen cryoshield;
M. electron-beam evaporator guns; N. cryopump and ion-pump.
FIGURE 2.2: PHOTOGRAPHS OF THE MBE EQUIPMENT

(a) DIAGNOSTIC AND DEPOSITION CHAMBERS

A: PROBE: substrate holder, heater and manipulator;
B, C, D: 50keV RHEED gun, screen and flood gun respectively;
E, F: SIMS ion gun and detector; G: Gate valve;
H: Mass spectrometer (beam monitor); I: Atomic oxygen source;
J: Beam-defining aperture and charged-particle filter;
K: Thickness monitor; L: Liquid N\textsubscript{2} cryoshield;
M: Electron-beam evaporators; N: Cryopump and ion-pump;
O: Argon-ion etching unit; P: Differential pumping.
FIGURE 2.2: (b) DEPOSITION CHAMBER: VIEWED FROM ABOVE

Probe inserted, showing mounted sample (rotate anticlockwise by 135° for growth position).

Probe retracted into diagnostic chamber, shutter open:

View of Nb electron-beam evaporator, approximately as seen by the mass spectrometer used for metallic-beam monitoring.
The diagnostic chamber houses Secondary Ion Mass Spectrometry (SIMS)\textsuperscript{24,25}: this provides data on surface composition with good sensitivity to surface impurities (type and coverage). Depending on the probed species, the UCL SIMS system can typically detect impurity coverages to less than a few per cent of a monolayer. In addition, a novel 50keV Reflection High Energy Electron Diffraction (RHEED) system has been developed, replacing the 5keV MEED (Medium Energy Electron Diffraction)\textsuperscript{12} equipment implemented by Betts\textsuperscript{11}, and giving improved data on surface structure and order. It is also a useful probe for surface contamination and topography. The principles of RHEED in general, and the construction and use of the 50keV RHEED system in particular, are described more fully in the references\textsuperscript{12}, and in Ch. 3. SIMS and RHEED have provided extensive pre- and post-deposition data on surface composition, structure and contamination. Unfortunately, the SIMS facility was not always available during the latter part of this project: in situ substrate preparation for these runs was achieved primarily by adhering to a recipe known to give good results, and by using the improved RHEED as a surface monitor. Ex situ RBS (Rutherford Back-Scattering), XPS (X-ray Photoelectron Spectroscopy) and dynamic SIMS and AES (Auger Electron Spectroscopy) were then used to give detailed information on layer composition and interface cleanliness.

A cold-cathode ion discharge source, employing argon as source gas, provides an ion-milling and ion-cleaning facility. A number of features are incorporated into the sample holder (referred to as the sample "probe"): these include d.c. biasing, sample manipulation and transfer, precision RHEED goniometry, a thermocouple arrangement, and an electron-bombardment heater capable of heating the sample table to 900°C.

The deposition chamber is furnished with two electron beam evaporator guns (Vacuum Generators, EG5 units). These supply the beams of lithium and niobium through a low vacuum-conductance, beam-defining plate which supports a charged-particle filter. For the metallic sources, flux rates are monitored by a dedicated, cross-axis quadrupole mass spectrometer and (for the niobium) a quartz crystal thickness monitor. The mass spectrometer also gives information on beam purity and stability, and provides data on vacuum background species (residual gas analysis, RGA). Extensive cryoshielding is employed for improved vacuum and heat-sinking in the deposition chamber; a differential pumping line, sited near the substrate growth position, reduces the oxygen overpressure in the rest of the chamber.

Until recently, the oxygen was introduced via a molecular effusion source, viz. a glass micro-capillary array mounted close to the substrate. This gave a collimated beam of molecular oxygen whose flux rate could be varied over a wide range. A free atomic radical source now replaces this unit. Also, oxygen flux monitoring has been greatly improved. Full details regarding provision of oxygen are contained in Ch. 4.

The elemental beams impinge on the heated substrate and, under suitable conditions,
epitaxial growth occurs\textsuperscript{[2.1--2.3]}. The composition of the grown layer is determined by the relative flux rates of the constituent beams, and their sticking coefficients (the latter will vary with substrate temperature and material). The crystallinity and structure of the layer are dependent on many factors: the relative impingement rates of the constituent species; the overall growth rate; and the temperature, structure, and state of cleanliness of the substrate surface. Process monitoring, optimisation and reproducibility are of critical importance to the successful growth of an epitaxial layer of desired composition and phase, since the required layer may only be achievable under a narrow range of growth conditions.

As far as MBE is concerned, the top few monolayers or so of the substrate are vital in determining the nature of subsequent growth. Two of the basic requirements for good epitaxy are:

(i) good substrate crystal quality and order;
(ii) a clean, well-defined interface.

The implications of this for RHEED and SIMS will be discussed in Sections 2.3 and 2.4. The original substrate preparation procedure was developed by Betts\textsuperscript{[2.1]}, but it has been modified and optimised in this project. The current procedure is given below in Section 2.3.1. The evolution of the modified MBE system and substrate preparation procedure are discussed in detail in Section 2.4, which highlights the development of more accurate monitoring of growth conditions and of the pre-deposition substrate surface.

2.3 TYPICAL RUN PROCEDURE;
PROBLEMS WITH INHERITED RUN PROCEDURE

2.3.1 DESCRIPTION OF RUN PROCEDURE ADOPTED

Typical substrate preparations, assessment procedures, and the run "philosophy", are outlined in Table 2.1. For surface preparation studies, +z- or y-cut LiNbO$_3$ substrates were used, though some experiments were also performed on z-cut sapphire (\(\alpha\)-alumina) and Si(111). Substrate specifications and as-received quality are given in Ch. 3, along with the surface studies; a full account of the choice of substrate and growth conditions used are presented with the deposition results in Ch. 5.

RHEED/MEED and SIMS have played a dominant role in arriving at a routine surface evaluation and preparation procedure (see also Betts\textsuperscript{[2.1]}). Betts' substrate preparation process was by no means optimum (see next section). Also, process control for substrate preparation and layer deposition was rather poor in the inherited system. The understanding of the effects on the surface of various in situ processing and treatment techniques was also incomplete. The next stage of the project therefore had to include the following:
<table>
<thead>
<tr>
<th>PROCEDURE</th>
<th>DETAILS</th>
<th>PURPOSE/HISTORY</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) Chemical Etch</td>
<td>I.P.A.; Decon; Degrease; Etch in 2:1 (by vol.) of conc. HNO₃:HF (20 min. at room T); H₂O rinse; I.P.A. (For sapphire, omit HNO₃ in etch.)</td>
<td>Production of clean, smooth LiNbO₃ surface. Arrived at using MEED, RHEED and SIMS as monitoring techniques. Etch based on a surface preparation by Nassau[1,2,3].</td>
</tr>
<tr>
<td>(3) Light Bake</td>
<td>200°C for approx. 30 minutes[4].</td>
<td>Removes volatile adsorbants. Use higher temp. if needed.</td>
</tr>
<tr>
<td>(4) SIMS &amp; RHEED</td>
<td>SIMS: Ar⁺ ion beam (see text for details); 70° incidence angle. Glancing incidence; Up to 40 keV.</td>
<td>SIMS: If Li, Nb peaks show ab initio this implies less than 100% impurity coverage. RHEED: Data on surface contamination and crystal quality.</td>
</tr>
<tr>
<td>(5) Ion Clean.</td>
<td>Using Ar⁺, 3 keV, &gt; 2×10¹⁵ ions/cm². Required ion dose depends on (4).</td>
<td>Sputters surface contaminants. Use with care (ion damage). This step not always used - depends on quality of (4).</td>
</tr>
<tr>
<td>(6) SIMS and RHEED</td>
<td>As (4).</td>
<td>SIMS: Reassess surface impurity coverage (&lt; 5% acceptable; this is an arbitrary standard). RHEED: Assess surface damage.</td>
</tr>
<tr>
<td>(7) Heat Cycle.</td>
<td>Typically &gt; 600°C, 1 hr. (or as needed).</td>
<td>Regain acceptable surface order by thermal annealing.</td>
</tr>
<tr>
<td>(8) SIMS &amp; RHEED</td>
<td>As (4).</td>
<td>SIMS: Any changes due to (7)? RHEED: Good enough surface for epitaxy? Structural changes?</td>
</tr>
<tr>
<td>(9) If needed, repeat (5)→(8)</td>
<td>If surface deemed unsuitable for MBE, reject sample!</td>
<td>Aim: To ensure growth occurs on a clean, well-ordered surface.</td>
</tr>
<tr>
<td>(10) Layer Growth</td>
<td>Flux rates and growth temperatures arrived at empirically[5,6,7].</td>
<td>Aim: growth of optically &amp; acoustically active waveguiding layers of high quality and controlled properties.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>EX SITU PROCESSING AND ANALYSES:</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Talstep</td>
</tr>
<tr>
<td>(b) Film analyses</td>
</tr>
<tr>
<td>(c) X-ray Photography</td>
</tr>
<tr>
<td>(d) Oxygenate (oxidise)</td>
</tr>
<tr>
<td>(f) Repeat above analyses.</td>
</tr>
</tbody>
</table>
A re-evaluation of the substrate preparation process to improve our understanding of its effects on the crystal surface, and to indicate appropriate action for obtaining cleaner and structurally more perfect pre-deposition surfaces (see Ch. 3);

Better correlation of in situ and ex situ analyses (see Chs. 3 & 5);

Improvement in the means by which a given set of growth conditions can be established and maintained.

In order to meet these aims, instrumental improvements to monitoring capability and accuracy were required. These are discussed, along with the reasons for their implementation, in Section 2.4. First, a brief review of the aims and results of previous work conducted in this laboratory is needed, to put Section 2.4 into proper context.

2.3.2 REVIEW OF WORK BY BETTS; INHERITED SYSTEM LIMITATIONS

The aim of Betts' thesis was to prove the feasibility of growing thin-film, single-crystal, epitaxial LiNbO$_3$ on a variety of suitable substrates using MBE. MBE offered a number of advantages over other thin-film deposition techniques, but the epitaxial growth of this ternary dielectric oxide was expected to be difficult. Attempts to evaporate LiNbO$_3$ or its constituent oxides directly proved unsatisfactory, owing to their non-congruent evaporation. An MBE system was then built specifically for the deposition of lithium niobate using elemental beams. A number of runs were performed under various conditions of substrate preparation, relative beam flux ratios, and substrate temperature, and on a variety of substrates (Si(111), z-cut sapphire, z- and y-cut LiNbO$_3$): significant progress was made in determining the required growth regime for single-crystal LiNbO$_3$ of the desired (electro-optic) phase (Fig. 2.3).

However, process control was poor. Also, the 5keV electron diffraction data lacked resolution (see Ch. 3), and the SIMS was not optimised (Section 2.4.2). Most of the films grown were either amorphous or polycrystalline; all of them grew oxygen-deficient. Improved oxygen stoichiometry and practicable operation of the system were in direct conflict. The approach was to perform as many growth runs as possible over a range of deposition conditions, and to analyse the resulting films. X-ray texture and inclined-beam oscillation photography were used to determine the crystal structure of the film and its epitaxial relationship to the substrate. Ex situ dynamic AES and SIMS, and in situ "static" (low damage) SIMS, provided data on film composition and purity, while in situ MEED gave some further data on film surface structure.

Fig. 2.3 demonstrates that the growth regimes were not well-delineated; the data points are rather sparse. There are broad regions in which certain (unwanted) modes of growth appear
Fig. 2.3

GENERAL GROWTH TRENDS IN LiNbO₃ BY MBE

Li/Nb RATIO (by Auger)

SUBSTRATE TEMPERATURE (°C)

(Courtesy of R.A. Betts[2,9])
to be favoured: the desired material was single-crystal, epitaxial, rhombohedral (optically
active) LiNbO$_3$ of correct stoichiometry. This target appears to be a rather narrow one. In fact,
rhombohedral LiNbO$_3$ was only achieved homoepitaxially (and only on z-cut LiNbO$_3$
substrates): here, the lattice matching and chemical bonding requirements are perfectly met
("parallel epitaxy" occurs). However, there are only two data points in this region. Note also
that a cubic form of LiNbO$_3$ dominates the MBE-growth scenario. It is very similar in structure
to the bulk Li$_3$NbO$_4$ phase, possessing a body-centred cubic lattice$^{[1,2]}$ (see Chs. 5 and 6), but
the measured composition of the cubic films was very different to the expected stoichiometry
of the Li$_3$NbO$_4$ phase; also, careful analysis of X-ray data (inclined-beam and texture) for these
films demonstrates that the structure was by no means proven in Betts’ study, an uncertainty
that remains unresolved. There was, therefore, a need to clarify the roles of Li and Nb in
determining the structure of the grown material.

Both Betts’ and the author’s own studies confirm that certain considerations are
relevant to the prevalence of the cubic phase. These include the pre-growth processing,
particularly the extent of surface damage produced by ion cleaning. The cubic Li$_3$NbO$_4$ phase
appears to be encouraged by a failure to achieve a very clean surface after the wet etch
preparation, or by excessive ion-cleaning in situ. A surface giving a clean initial SIMS
spectrum usually requires only a very low ion-dose in situ clean ($< 2 \times 10^{13}$ Ar$^+$ ions/cm$^2$ $^{[2,3]}$)
to produce an atomically clean surface. We shall see (Section 2.4.3 and Ch. 3) that the
inherited system could not monitor many of these substrate processing parameters reliably.

Betts proposed that the layer growth was rate-limited by niobium, whose sticking
coefficient appeared to be always unity; lithium and oxygen were then taken up as required,
and according to the growth conditions. Excess Li, for example, appeared to be rejected by
the growing surface. However, owing to the poor process control inherent in the early system,
no firm conclusions about sticking coefficients or growth mechanisms could be drawn from
the growth runs performed. Also, growth rates and layer thicknesses in Betts’ work were low
(frequently $< 1000$Å/hr, and $< 500$Å respectively), and the homoepitaxial layers of LiNbO$_3$
grown by Betts were far too thin to support an optical guided mode. The films which were
claimed to have the rhombohedral structure were not tested for birefringence or electro-opticity:
they were too thin and conducting for such tests to be easily performed. Monomode Li-Nb
oxide waveguides were grown on sapphire, but these tended to be rather lossy ($\approx 20$ dB/cm).

Summarising, then, the main limitations of the inherited system were as follows:

(i) poor process monitoring and control;
(ii) inability to produce thick (> a few thousand Å) layers;
(iii) inability to grow oxygen-stoichiometric material.

Betts achieved the goal of devising a skeletal process within which the feasibility of LiNbO$_3$
growth by MBE could be explored, and significant evidence for the homoepitaxial growth of
oxygen-deficient LiNbO$_3$ by MBE was obtained. However, a definitive understanding of the
growth kinetics of LiNbO$_3$ was lacking, and the proposed use of controlled oxygen deficiency to give optical waveguiding in MBE-grown, homoepitaxial LiNbO$_3$ was not demonstrated. The considerations outlined in this section justify the assertion (of Section 23.1) that improvements in process control were needed before further progress could be made: the aims were to increase growth rates (to obtain thicker layers) and to improve the yield with which a desired material (such as Nb$_2$O$_5$ or electro-optic LiNbO$_3$) could be grown.

2.4 SYSTEM IMPROVEMENTS I:
IN SITU ANALYSES, PROCESS CONTROL

2.4.1 FLUX MONITORING AND BEAM ANALYSIS

It was evident from Betts' work$^{[2,1]}$ that the reproducibility in layer growth rate and thickness was extremely poor. Variations by factors of up to 10 or more could occur under ostensibly identical deposition conditions. The identified causes were poor (or no) beam-flux monitoring and inadequate control over growth conditions (especially evaporator operation). For example, a badly-aligned filament could give an order of magnitude loss in flux with the gun operated under otherwise identical conditions. The need to establish direct beam flux measurement during a run was therefore deemed paramount.

A Vacuum Science Workshop "Mass Analyst" quadrupole mass spectrometer was installed (Model VSW 300, V1.OX). This was of a "cross-axis" design, in which the exposed components of the head were arranged perpendicularly to the incoming beams and shielded to prevent direct line-of-sight with the evaporators. This design gave a slightly lower sensitivity to the beams, but was much less prone to contamination effects or head failure due to oxide-coating. The unit was used to monitor the metallic beam purity, stability, and (when calibrated) flux rate, and was linked to an IBM PC to enable a number of useful functions, e.g. the simultaneous monitoring of several beam and background species during a run.

An Intellemetrics (Model IL004) quartz-crystal oscillator thickness (and rate) monitor head was installed close to, and above, the beam defining plate and ion filter, giving data on deposited Nb mass. The deposited mass is converted to a Nb thickness (and flux rate) at the substrate via the IL004 software: the program uses a standard algorithm which processes the frequency information from the crystal, and uses various system and materials parameters determined from a series of calibration depositions. Ex situ Nb thickness determinations were performed with a Talystep machine. The assumption that the flux rate arriving at the substrate when the probe is at 0 degrees (horizontal) is $2^{1/2}$ times the flux rate when at 45 degrees (growth position) is not correct, since the Nb source-sample line is offset from the axis of rotation of the probe: this gives a systematic error of 20% in Betts' flux estimates. The thickness monitor was therefore directly calibrated for the substrate growth position.
Using the IL004, complementary flux rate data to that obtained from the dedicated quadrupole mass spectrometer was readily achieved, and any serious drift in the mass spectrometer gain could now be detected by cross-checking the two instruments. The IL004 software was adapted to increase rate sensitivity (to about ± 0.1 Å/s); also, the position of the head was chosen to optimise flux sensitivity and facilitate calibration experiments (the normal to the monitor crystal was made to point directly at the Nb source). The quartz crystal cut employed had a low temperature sensitivity; nevertheless, a series of test experiments showed that the thickness monitor readings were significantly influenced by the temperature changes associated with switching the Nb gun on and off: the use of adequate "soak" times for temperature stabilisation was therefore adopted. The "tooling factor" is the ratio of the measured Nb thickness deposited at the substrate to that deposited at the thickness monitor. This was measured, and compared with the value calculated using the "Cosine Distribution" law for a point evaporation source (positions of monitor and substrate relative to the Nb source were accurately known). There was a 40% discrepancy between the two, showing that the Nb evaporator did not quite behave as an ideal point-source.

Manual control of the modified system gives greatly-improved reproducibility over the inherited system (see Section 2.7). Tying the IL004 (or the mass spectrometer) into a feedback loop to the EG5 evaporators might provide automatic flux control and improved stability. Steps have been taken in this direction, but are not yet to fruition: loop instabilities appear to be a major difficulty.

2.4.2 SURFACE ANALYSIS: SIMS and RHEED

The construction of the 50 keV RHEED system used for analysing insulating substrates is dealt with in Ch. 3.

The technique of SIMS is based upon the phenomenon of secondary ion emission excited by primary ion impact on solid surfaces: it is extremely sensitive to surface composition (since the sputtered ions largely originate from the top monolayer of the surface), but can be difficult to quantify reliably. The UCL SIMS facility consists of a Vacuum Generators quadrupole mass spectrometer, with an argon ion sputtering unit providing 3keV ions and beam currents of up to 5x10⁸ A/cm². Sensitivity is enhanced by use of a pulse-counting technique, enabling the system to detect (typically) a few % of a monolayer surface impurity coverage, and to give qualitative compositional data. When used in conjunction with the high current argon ion discharge source (up to 1mA/cm²), it may also be used for dynamic (depth-profiling) SIMS, though in this mode the data is less reliable owing to charging of the probed surface. Further details are given by Betts.
Fig. 2.4 VARIATION OF SIMS SPUTTER YIELD WITH PRIMARY BEAM ANGLE OF INCIDENCE

Detector count rate (arbitrary units)

- : Nb\(^+\) (EHT = 3.0 kV)
- : Li\(^+\) (lower EHT, 2.5 kV)

NbO\(^+\) follows same curve shape

Max. instrumental fluctuations

Detector

Ion gun

Sample

\[ \Theta \]
Normally, the ion source is inclined, and the detector is normal, to the surface studied. The probe goniometer, originally constructed for the new RHEED system, was used to investigate the dependence of SIMS ion yield with angle (for fixed angle between sputtering beam and detector). Results are shown in Fig. 2.4. Note the strong angular dependence of the sputter yield for Li⁺ and Nb⁺. This had not been previously recognised, and the technique had probably been used in a low sensitivity regime. This angular dependence may be purely geometrical in origin\textsuperscript{[2,14]}. This discovery adds weight to the claim that, in this system, SIMS can only be effective as a sensitive, \textit{qualitative} detector of impurities; at best, the system may provide semi-quantitative data on impurity coverage and comparative surface composition. A full discussion of these limitations is given in Appx. 2.1.

2.4.3 ION CLEANING

Modifications were made to the argon ion etching and cleaning unit which have considerable bearing on the ion-cleaning stage of the run procedure. The sensitivity of the unit was increased by a factor of 40 and the procedure adapted to improve reliability. This meant that much lower ion doses could now be administered (so as to avoid the cubic phase of LiNbO₃ and to enhance epitaxy). An analysis of the effects of various ion doses on LiNbO₃ substrates, and a discussion of the present understanding of how ion cleaning influences LiNbO₃ and niobium oxide MBE, are given in Ch. 3 so as to collate the surface studies.

2.5 SYSTEM IMPROVEMENTS II: THICKER LAYERS

2.5.1 INTRODUCTION

The Li-Nb-O films previously grown by MBE\textsuperscript{[21]} had been relatively thin, typically only a few hundred Å thick. The advantages of growing thicker films are as follows:

(i) thicker films can support optical guided modes;

(ii) thicker films facilitate some \textit{ex situ} analyses: for example, improved X-ray data can be obtained, and multimode waveguides can yield detailed optical and physical characterisation of grown material;

(iii) if higher growth rates are used, a smaller percentage of impurities might appear in the films;

(iv) larger flux rates make for easier flux monitoring and control.

The need for thicker single-crystal layers could only be met by increasing run times or growth rates. Modifications towards these ends will now be discussed.
2.5.2 NIOBIUM AND LITHIUM EVAPORATORS: REQUIRED MODIFICATIONS

Increased flux (growth) rates were needed to provide thicker layers and to avoid having to run the system at the edge of its performance limit. The desired increase in growth rate over Betts' system was a factor of about 10. However, the niobium gun was already operating at the limits of its capability.

Magnetic field strength was mapped throughout the entire chamber: local $B$-fields of between 2 and 10 Gauss (d.c.) were recorded in the vicinity of the guns, sufficient to influence electron trajectories in the electron-beam evaporator gun by as much as a mm or so. Magnetic shielding of the chamber from the surrounding ion pumps, etc. reduced the stray magnetic fields inside the chamber by more than half, improving electron-focus spot size and hence flux rate. Also, the gun efficiency was improved by using better alignment procedures for evaporator filaments, and more rigorous gun degassing procedures. However, these steps only led to an increase in flux rate of about $x3$. A comparison of Nb evaporator performance before and after these improvements is given in Fig. 2.5: this shows a mass spectrum taken above the Nb source for an optimised evaporator (Fig. 2.5(a)) and Betts' published spectrum (Fig. 2.5(b)). Note the reduction in background species. To increase Nb flux rates further, the following additional modifications to the EG5 unit were performed.

(i) **A facility allowing continuous variation of filament drive voltage** gave higher filament powers than previously used. This made possible the following: higher temperature operation of the filament; the capability to use higher emissivity (e.g. thoria-coated Iridium) filaments; "boosting" of flux rate during a run if gun emission could not be maintained. The latter was often essential in maintaining high flux rates of Nb.

(ii) **A new design of the EG5 hearth** increased the thermal isolation of the Nb target without using a crucible. The modified hearth\textsuperscript{12,15} is conical, with a cone angle designed to facilitate maximum water-cooling; it contacts a specially-shaped Nb slug around a ring, thereby minimising the thermal contact between slug and hearth. The slug also remains solid whilst evaporation takes place, which avoids the alloying problems associated with the use of a crucible\textsuperscript{12,11} (Fig. 2.6).

The conical hearth in (ii) was extensively tested. Nb flux rates were easily increased by a factor of 3, even with a poorly-aligned filament. An added bonus was that tripping could be substantially reduced (thereby increasing run times) by operating the gun at a lower voltage: e.g. the Nb flux previously achieved at 8kV and 240mA with the optimised hemispherical hearth was now obtainable at 6.6kV and 230mA with the unoptimised conical hearth. The conical hearth gun was still prone to instabilities at very high Nb flux rates in the presence of high pressures of $O_2$, but these were usually not as severe as with the hemispherical hearth.
Fig. 2.5 a) MASS SPECTRUM OVER CLEANED OPTIMISED NIOBium EVAPORATOR

Counts/sec.

93 Nb⁺

Equivalent beam pressure: 93 Nb⁺ peak corresponds to \(4.5 \times 10^{-7}\) torr and \(=10\) x total background

Fig. 2.5 b) A MASS SPECTRUM OF THE BEAM ABOVE A NIOBium EVAPORATOR (BETTS)

Counts/sec. \((x 10^4)\)

5

4

3

2

1

0

M/q (AMU/e)

(100)

Background peaks 46.5 Nb⁺⁺

\(46.5\) Nb

\(69\)

\(93\) Nb⁺

(equivalent max. beam pressure \(=2.5 \times 10^{-7}\) torr)
(a) ELECTRON-BEAM EVAPORATOR HEARTH ARRANGEMENTS

(i) Hemispherical hearth + crucible  (ii) Conical hearth

(b) NIQUEM ELECTRON-BEAM EVAPORATOR CHARACTERISTICS

Nb flux rate
(A/s at substrate position)

For both curves:
Gun voltage = 8kV;
No O₂ in chamber.

Usual growth regime

Filament emission (mA)
Slug melt-down could occur if the conical hearth was over-driven, giving a sudden and irreversible drop in gun efficiency for that slug; however, flux rates were still up to x2 greater than those obtained with the optimised hemispherical hearth driven at the same power. Also, at moderate and low Nb flux rates (similar to those used by Betts), and in conjunction with the thickness monitor, the growth rate for the conical hearth could be controlled remarkably well under conditions of high oxygen pressure: e.g. at 0.1Å/s, Nb flux rate was held to within 5% or so (as measured over 5 minute intervals) over a total period of 3 hrs. These improvements in stability and run time were essential for growth at high O₂:Nb beam-flux ratios. The hemispherical and conical hearths are compared in Fig. 2.6.

Some of these gun modifications led to higher operating temperatures and thence to chamber over-heating and outgassing (though improved degassing procedures and the new bakeout jacket mitigated the problem). A series of liquid nitrogen-cooled panels were installed around the outside of the chamber walls: these reduced tripping by quelling pressure bursts.

The lithium evaporator was used by Betts at minimum power, which was erratic and difficult to control. An alternative source would be more appropriate. A suitable candidate was identified in the form of a modified Knudsen Cell with a multi-source array, but the cost was inhibitive. As an interim solution, the lithium evaporator circuitry was modified to deliver lower powers in a controlled fashion. Also, a screen was incorporated into the grid assembly of the Nb evaporator: this prevented its ceramics from being coated by Li (a problem which caused flashover), and also acted as a heat shield for the Li metal source (thus alleviating a dependence of the Li flux rate on the Nb gun power dissipation!)

2.5.3 PROVISION OF OXYGEN

The need to provide controlled, higher flux rates of oxygen was the second, and more severe, problem. All layers grown in the MBE system had been deficient of oxygen compared with the highest bulk oxides. The use of larger oxygen pressures led to electron-beam evaporator instabilities, a reduction in Nb flux, pumping problems, and inhibitably short filament lifetimes. A new, bellowed effusion system was designed and constructed, but this did not yield oxygen-saturated films. Later, in an attempt to increase oxygen incorporation in the grown layers, the molecular effusion source was replaced by an oxygen radical source which employed a magnetically-confined d.c. discharge. A detailed account of the evolution of the various oxygen sources, including the rationale behind the changes, is given in Ch. 4.
48

2.6 MISCELLANEOUS IMPROVEMENTS

To report all the remaining system modifications would be prolix: the most important are outlined below.

(1) **Reliability and accuracy of substrate temperature measurement.** Optical pyrometry proved difficult due to the transparency of LiNbO₃ from 0.35 μm to 5 μm, so the thermocouple was reshaped for more reliable contact with the substrate table, giving estimated temperature reproducibility to within a few K.

(2) **The "electron extraction filter"** implemented by Betts had a 500 Gauss magnetic field, with a parallel electric field (50V applied to two plates about 6cm apart). Ions and electrons associated with the metallic beams were largely removed (charged particles in such beams have been shown to cause adverse effects for growing films). A higher voltage (400V) was implemented to improve the efficiency of electron/ion removal.

(3) **The shutter arrangement was redesigned** to improve process control and flexibility; for example, the beam-monitoring mass spectrometer can now view each metallic beam separately without the substrate being exposed.

(4) **General improvements to system reliability, cleanliness, and base vacuum.** High-voltage tripping of the EG5 guns during a run caused lengthy equipment down-time: many leads, and some chip-based units, were not adequately shielded; the chamber and equipment racks were poorly earthed. These problems were isolated and, as far as possible, rectified. Also, a large number of control parameters required recording and stabilisation during a run. A degree of automation or computer-aided control and data-storage was desired: the cross-axis mass spectrometer was linked to a computer, making beam monitoring and control easier; also, an automatic liquid nitrogen distribution system was installed. Pumps and evaporators were regularly serviced, and new cryopump regeneration procedures were implemented to reduce chamber re-contamination during regeneration. Equipment supports were re-designed to reduce vibrations, and new alignment procedures were devised for the sample probe and instrumentation in order to optimise efficiency and reproducibility. Ionisation gauge shields were fitted in order to rectify the under-reading of pressure incurred by stray electrons from the evaporators. A bakeout jacket arrangement was installed.

2.7 COMPARISON OF OLD AND NEW SYSTEMS

The result of the various changes was a growth system with greatly superior process monitoring. Substrate analysis and processing were enhanced, and a greater range and reproducibility in flux rates was achieved.
The inherited system had no reliable flux monitoring for the metallic beams: identical evaporator conditions were set, but this led to flux and growth rate fluctuations from run to run of typically 100% for the Nb and usually more for the Li. In some cases, the variation was as much as x10. The present detection thresholds for flux rate changes are: < 0.1Å/s for the Nb (< 15% of the flux rate for a typical run), and < 25% for the Li. The measurement of the oxygen pressure behind the source gives an estimated oxygen molecular beam flux reproducibility of a few per cent. For the new oxygen radical source, the flux rate is directly related to a measured discharge current in the source, and a backing-pressure monitor is included: this should reduce errors to less than about 2%; other sources of error may exist, such as drift in the atomic production efficiency due to ageing of the unit or fluctuations in ambient oxygen pressures, but these are not likely to be serious.

2.8 THE IMPACT OF THE IMPROVED MBE SYSTEM: A PREVIEW

The aim of the system modifications described above was to provide a smooth-running, closely-monitored MBE process which was able to deliver a wide range of growth rates and much longer run times. The desire was to grow single-crystal, epitaxial, oxygen-saturated waveguides of good structural quality in a reproducible fashion.

Ch. 5 reports how the modified system was used to investigate the MBE-growth of niobium oxides. The improved system reliability and stability made longer growth runs possible: for the first time, films exceeding 1 μm thickness were grown in the system. In addition, the improvements in run time, flux control and available flux-rate range yielded reproducible layers (of adequate thickness for X-ray analysis and optical waveguiding) at low Nb flux rates - an important step forward. Analysis of these films extended the understanding of the influence of growth rate and layer thickness on film quality. However, there were problems associated with the as-grown quality of the thicker films: higher growth rates led to strained layers, poorer crystal quality, smaller crystallites, or more defects. Also, since higher Nb flux rates were often used in growing the thicker layers, it was even more difficult to supply sufficient oxygen flux: the oxygen deficiency became worse for these layers, and subsequent oxidation was particularly disruptive to the crystal structure and film adherence. These problems spurred attempts to increase oxygen flux rates and improve oxygen beam collimation: this ultimately led to the search for an alternative form of oxygen with improved sticking coefficient. This work is contained in Ch. 4. Later, interest was shifted towards the growth of electro-optic device structures employing sub-micron oxide films (Ch. 6): the thinner layers envisaged for these devices are less prone to many of the problems described above.

In summary: without the improvements described in this chapter, the prospects for controlled MBE-growth in the Li-Nb-O system were poor, and the quantitative analysis of the growth trends in this materials system, as expounded in Ch. 5, would not have been possible.
REFERENCES


2.8 M. Petrucci and C.W. Pitt, "RHEED studies on z-cut LiNbO₃", El. Letts. 22 (1986) 954-956.

2.9 Ref. [2.1]; p. 192, Fig. 5.18b.


2.12 JCPDS Powder Diffraction File 1985, Card no. 16-459; see also Ref. [2.1] and Ch. 5.

2.13 Ref. [2.1], p.193 and erratum pages; see also Ch. 3.


2.15 Designed and built in association with Gordon Lovis and Bob Attwood, Vacuum Generators (Components) Ltd., Menzies Road, Hastings.


CHAPTER 3

CONSTRUCTION AND USE OF HIGHER ENERGY RED SYSTEM; RELATED SURFACE STUDIES.

3.1 ABSTRACT

This chapter explains why improved electron diffraction was needed in the inherited MBE system, and describes the design, construction and implementation of a 50keV RHEED unit modified for use with insulating substrates. The facility was used to make the first detailed RHEED study of crystalline lithium niobate. The patterns are compared with previous work, and with theoretical predictions for the lithium niobate reciprocal lattice. An algorithm was devised for the analysis of RHEED patterns. This was used to calculate the surface lattice parameters of probed substrates: the results are compared with bulk values obtained by X-ray and neutron diffraction. The algorithm also yielded a value for the mean inner crystal potential in lithium niobate, useful when accounting for RHEED refraction effects. RHEED patterns were obtained for other materials, including sapphire and silicon, and for a variety of MBE-grown oxide layers (see also Ch. 5). A synopsis is given of the effects, as assessed by RHEED, of various in situ processing steps on the lithium niobate surface: these included surface mobility studies, and the effects of argon-ion cleaning and thermal annealing.

3.2 RHEED: INITIAL CONSIDERATIONS; INTRODUCTION

3.2.1 THE NEED FOR A NEW RHEED SYSTEM

The discussions of Ch. 2 explained how, at the start of the project, the growth of thin-film niobium oxides (and lithium-niobium oxides) by MBE was subject to poor process control and layer reproducibility. Inadequate monitoring of substrates prior to growth was an important shortcoming. Improved in situ surface structural analysis was necessary to ensure the quality and reproducibility of the layers. Reflection Electron Diffraction, RED\[^{[3.1]}\], is an outstanding technique for substrate characterisation and assessment in MBE systems: for this reason, a superior RED system was constructed, superceding the 5keV system implemented by Betts (see Section 3.3).

3.2.2 RHEED: DEFINITION AND BACKGROUND INFORMATION

The subject of electron diffraction is vast. Several excellent accounts of the theory, geometry and practice of the technique are to be found in the cited references\[^{[3.1\text{-}3.10]}\] (in particular, Bauer’s text). These deal predominantly with the use of Reflection Electron
Diffraction (RED). Some of the theory relevant to this project is discussed below.

RED was originally developed by Nishikawa and Kikuchi\textsuperscript{[2]} for the study of the structure of calcite cleavage surfaces. The technique involves impinging a collimated beam of electrons on a flat, electrically neutral surface at shallow incidence angles in a UHV environment. The electrons are scattered by the periodic charge-distributions in the surface, and strike a fluorescent screen or other suitable detector. The resulting diffraction pattern is analysed to obtain information on the surface structure of the sample.

At low electron energies (typically up to 1\,keV) the technique is referred to as LEED (low-energy electron diffraction) and at high energies (10 to 100\,keV) as HEED (high energy electron diffraction\textsuperscript{[3,4]}). HEED is more often termed RHEED (reflection high-energy electron diffraction), in order to distinguish it from pure transmission electron diffraction (TED). There is also an intermediate regime (roughly 1 to 10\,keV) which may be labelled MEED (medium energy electron diffraction\textsuperscript{[3,4]}). Note that, in RED studies, there may be a contribution from TED due to the passage of the electron beam through surface asperities - true RED is only approximated to in the case of an atomically smooth, flat surface at grazing incidence.

With the advent of UHV crystal growth techniques during the last decade or so, there has been a revival in interest regarding the use of RHEED for the analysis of crystalline substrates and overlayers. This is especially so in the semiconductor field, where RHEED has yielded information on the structure, reconstruction, cleanliness, and topography of substrate, growing and grown crystal surfaces\textsuperscript{[3,4,8,9]}. Also, growth rates can be determined using the RHEED oscillation technique\textsuperscript{[3,4,8,9]}. Furthermore, a degree of depth data may be obtained by varying the angle of incidence of the primary beam\textsuperscript{[3,9]}.

The energy range 10 to 100\,keV corresponds to de Broglie wavelengths, $\lambda$, from 0.12 to 0.04\,\AA\textsuperscript{[3,4]}. This is to be compared with the wavelength range from 0.5 to 400\,\AA in LEED, and from 0.2 to 2\,\AA in X-ray diffraction. The total elastic scattering cross-sections, $Q(V)$, of atoms for RHEED electrons are many orders of magnitude greater than those for X-rays\textsuperscript{[3,4]}, so that RHEED is generally far more sensitive to the surface. Although the $Q(V)$ for LEED electrons is about two orders of magnitude greater than for RHEED electrons, both RHEED and LEED are comparably surface-sensitive. This is due to the different geometrical set-ups: LEED generally has the incident beam at near-normal incidence to the substrate, and the back-scattered electrons are analysed; on the other hand, RHEED uses grazing incidence, since angles of only a few degrees or less are required to fulfill typical Bragg conditions (see Section 3.6). Hence, in spite of the smaller $Q(V)$ for RHEED, only a very thin surface layer is penetrated, as for LEED. Also, the differential elastic scattering cross section curve for RHEED shows a strong forward-scattering tendency at grazing incidence (as opposed to the more isotropic scattering of LEED electrons and X-rays\textsuperscript{[3,4]}). These factors make RHEED one of the most surface-sensitive probes available to modern analytical technology.
LEED continues to be widely used, but in some contexts suffers from experimental and theoretical drawbacks\textsuperscript{[3,31,39]}. For example, RED patterns can be conveniently recorded on a photographic plate or fluorescent screen normal to the electron beam, making RED eminently suitable in MBE configurations; LEED and X-ray diffraction require a large angular region to be sampled. In RED, there has been some confusion as to the origin and interpretation of spot-streaking\textsuperscript{[3,14]} and in the unambiguous interpretation of certain diffraction features from reconstructed surfaces. Fortunately, recent work has suggested that many of the recognised limitations of RHEED may at last be resolvable\textsuperscript{[3,3,31,41]}: state-of-the-art RHEED may now be regarded, at least in principle, as equal or superior to LEED in most respects\textsuperscript{[39]}. In our case, the presence of stray magnetic fields, the surface charging problem (Section 3.2.4), and the availability of only a single viewport, made RHEED the natural choice over LEED.

3.2.3 CHOICE OF ANALYTICAL PROCEDURE FOR RHEED PATTERNS

The "geometrical" model of RED\textsuperscript{[3,1]} , which neglects the scattering characteristics of individual centres, predicts that, at typical RHEED electron energies, the diffraction pattern on the screen will be approximately equivalent to taking a plane section (in fact, a sphere of large radius) through the reciprocal lattice perpendicular to the incident electron beam. This leads to the Ewald sphere construction. For quantitative work, a scale factor (or camera constant) is then required to relate screen measurements to reciprocal lattice dimensions (see Section 3.6).

According to the Ewald sphere construction, a reciprocal lattice feature must be intersected by the sphere if it is to appear as a "spot" on the screen. It might seem, on first inspection, that this would only yield a very few, if any, reflections at a given angle of incidence. In practice, the Ewald condition is relaxed owing to the energy spread and divergence of the electron beam (which makes the sphere "fuzzy") and because the reciprocal lattice "spots" are of finite size\textsuperscript{[3,1,15,3,16]}. Usually, then, a semicircular annulus of reciprocal space near the origin is observed\textsuperscript{[3,1,3,15,3,16]}, termed the Laue Circle. There is also reason to believe that thermal diffuse scattering leads to observable streaking for true RED features, even for a perfect primary electron beam possessing no energy or angular spread\textsuperscript{[3,5,3,17]}. Further discussion of the Ewald sphere is to be found in the references and in Appx. 3.1.

Advanced theories take into account the atomic scattering factors for electrons, and thereby seek to relate the intensity distribution of the observed features to the distribution of atoms, etc. within the unit cell (kinematic and dynamic theories\textsuperscript{[3,1]}). However, these models require advanced measurement techniques and analyses beyond the scope of this work: dynamical interpretations of RHEED often require a quantitative measurement of the intensity and phase distribution of RHEED features to be made. Fortunately, the "reciprocal lattice/Ewald sphere" construction has, in most cases, proved adequate in interpreting the RHEED patterns.
obtained here. Qualitative observations of intensity (e.g. of background haze, spot-streaking, etc.) have often yielded additional information. In this chapter, we will be primarily concerned with the positions of intensity maxima (which are assumed to correspond to the ideal reciprocal lattice points/features), rather than with intensity distributions about the reciprocal lattice points. However, some dynamical effects, such as double diffraction, need to be understood; others, such as Kikuchi lines, can be used to advantage. These effects shall be considered as required, but theoretical discussions of their origins, etc. may not always be given.

3.2.4 PROBLEMS IN APPLYING RHEED TO LiNbO₃ AND OTHER INSULATORS

RHEED analysis usually requires a well-grounded, conducting substrate, to avoid charging the surface with the incident electron beam. Surface charge accumulation can lead to significant changes in the crystal electron wavelength and distortion of the observed pattern, accompanied by spot-spreading and large increases in background haze (due to randomly scattered electrons). In severe cases, the incident beam can be totally deflected from the crystal surface. In the case of a piezoelectric material, such as LiNbO₃, the internal voltages developed by charge accumulation cause distortion of the crystal lattice¹³¹⁸¹, and artefactual features may then appear in the patterns. For these reasons, electron diffraction as a surface-study technique under UHV conditions has been largely restricted to conducting and semi-conducting substrates¹³⁶¹.

Previously, 5keV MEED had been used on the UCL system to analyse various substrates (including LiNbO₃) and MBE-grown Li-Nb oxide epilayers¹³¹⁹³²⁰¹. The patterns gave a crude assessment of surface cleanliness and ordering, but were lacking in detail and resolution. Some 42keV work was also performed, but with poor results. In both cases, surface charging and distortion of the patterns were severe (LiNbO₃ is an insulator: reliable values are unavailable for surface conductivity¹³¹⁸¹, but bulk resistivity ≈ 5x10⁸ Ω cm at 400°C for z-cut material¹³²¹¹, dependent on impurities and surface condition¹³²²¹). Other workers attempting to use RHEED on similar insulators have found charging effects to be inhibitive¹³⁴³²³¹, resulting in very little reported RED work on LiNbO₃ and related oxides such as LiTaO₃.

3.3 DEVELOPMENT OF RHEED SYSTEM

3.3.1 RHEED GUN

In order to overcome the problems described in Section 3.2, a RHEED unit was constructed capable of achieving up to 50keV in electron energy (Figs. 3.1 → 3.3). This was installed in the Diagnostic chamber. The electron gun was a Vacuum Generators RHEG1 unit.
Fig. 3.1

PRINCIPLE OF RHEED FOR INSULATING CRYSTALS
Fig. 3.2  Schematic diagram of 50kV RHEED gun

Fig. 3.3  Photograph of 50kV RHEED gun assembly

Caption: 1. Re-entrant lead glass envelope with 8-pin base.  
5. Anode, and collimating apertures. 6. Gold vacuum seal.  
10. Precision micrometer and stepper motor. 11. Rotatable  
coil arrangement or permanent magnet. 12. X-ray and EHT shield.  
Electrostatic and magnetic deflection and focussing can give rise to beam distortion: to avoid this, a long, cylindrical collimation aperture (diameter 0.1mm), and a mechanical steering arrangement were employed. This also obviated the need for the expensive stable high voltage supplies required for magnetic focussing arrangements.

The gun was a conventional triode arrangement, consisting of a filament, grid (which controls brightness and definition) and anode, the latter being at earth potential and shaped to give a good beam profile. The filament was driven by a stable direct current supply, variable from 1A to 4.5A, and giving up to about 0.1mA emission. An R.F. oscillator-driven supply provided 0 to 50kV, with 0.01% stability (mains ripple; 50Hz); this was capable of delivering a total current of up to 0.1 mA. Beam currents of approx. 100nA were obtained for electron energies between 6 and 40 keV. In normal operation, the filament was at -EHT, and the grid bias was applied between the filament and grid. The grid could be made negative relative to the filament by up to 200V, but < 50V was usually used.

The electron-beam gun was mounted on bellows combined with a perpendicular gimbal assembly allowing x and y steering of the beam. A micrometer and stepper-motor arrangement enabled beam positioning at the sample to better than 0.1mm. The lateral position of the sample and holder was adjustable to ±0.5mm; a remotely-operated precision goniometer enabled the angle of incidence to be chosen to within 5° of arc, and the azimuth to within 3° of arc. Spot positions and pattern clarity were very sensitive to these angles, and slight misorientation of the sample (azimuthally) could lead to misleading patterns. Much time and effort were therefore devoted to designing and implementing the required quality of goniometry. Residual magnetism in the gun was counteracted by a coil arrangement which provided highly localised magnetic fields. An ambient vacuum better than 3x10^-8 Torr was achieved by means of a cryo-trapped diffusion pumped system. All RHEED controls were located near the phosphor screen, so that adjustments could be made whilst viewing the pattern.

A P20-type phosphor screen was employed to image the diffraction patterns; this was mounted 96cm from the gun (53cm from the substrate holder). The resulting beam width at the screen was less than about 1.5 mm, in agreement with the value predicted from the geometry and electron optics of the gun and collimator assembly. Beam width was reduced by the application of the grid bias voltage, but with a corresponding loss in brightness. In the worst case, the beam was roughly 1 mm in diameter at the substrate position, fixing a lower limit on the spatial resolution of diffraction information obtainable from the sample by this system. At 35keV, beam divergence was less than 2 mrad (no grid bias). This is close to the value, calculated by Ichikawa, below which the diffraction condition for incident electrons on a Si surface could be regarded as effectively "fixed". Naturally, a further reduction in beam divergence would be desirable, but the sharpness of the specular spot on the 000 rod showed that the resolution of the system was adequate for our purposes and comparable to other RHEED systems; further refinements were therefore deemed unnecessary.
Towards the end of the project, the RHEED screen was redesigned to incorporate a thin backing layer of evaporated aluminium: this reduced haze and acted as a trap for low energy electrons. RHEED could then be used during electron bombardment heating of the sample for the first time in this system. Further details are given in Appx. 3.2.

3.3.2 RHEED FLOOD GUN

In early accounts of RED performed on insulators, surface discharge was sometimes effected by stray, positively-charged ions present in the poorly-pumped vacuum systems employed. The concept of using a low energy, electron flood gun to discharge an insulating surface in UHV is not new\[31\], but has not, to the authors' knowledge, been applied to lithium niobate. A 5keV, 10 μA/cm² electron flood gun was directed at normal incidence to the sample, bathing the substrate region uniformly with electrons of low energy and discharging the surface by secondary electron emission. Adequate surface discharge requires that the incident energy and current density of flood electrons be set to give a secondary electron emission coefficient of greater than unity.

The optimum flood gun voltage for minimum residual surface charge was about 600V, in accordance with experimental results for other materials, and theoretical predictions\[326\]. The flood gun electron beam, when focussed, had a spot diameter of 3 to 4 mm and gave a highly non-uniform electron flux spatially: with this, it proved difficult to "tune" the surface discharge. The electronics of the supply were altered to give a uniform flood beam of approximately 2.5 cm diameter: this improved the discharge performance. (Flood gun beam characteristics were investigated using suitable phosphor-coated "samples").

The probe beam was made to impinge at the edge of the substrate. This enabled the zero order (beam) spot to be viewed directly, and was found to improve pattern clarity; it also fixed the camera length, L (see Fig. 3.9). Furthermore, the surface charging problem was reduced, and fine tuning of the surface discharge was obtained by varying the fraction of the probe beam incident on the sample. The main worry was that the edge of the sample may not have been representative of the substrate/film as a whole; but patterns obtained away from the edge, although of slightly poorer visual quality, did not show any quantitative differences. The details of the surface discharge mechanism are not yet fully understood, but some progress has been made in formulating models to explain the effects arising from incomplete discharging of the surface. For example, the streak-splitting observed under certain conditions (Fig. 3.4) may be attributable to the formation of oppositely-charged regions on the substrate surface, generated by the flood gun and primary beams.
It is important to estimate a typical depth to which the RHEED electrons penetrate the probed surface - this will be needed later. Empirical equations exist that relate the attenuation length (or total inelastic mean free path), $\Sigma$, of electrons in most inorganic crystals to the electron energy. $\Sigma$ was calculated for LiNbO$_3$, and the value used in a simple scattering model to estimate the average sampling depth, $D$, of electrons in the crystal. Details of the calculation can be found in Appx. 3.3, along with estimates of $\Sigma$ for LiNbO$_3$ obtained by other means. The important conclusion from Appx. 3.3 is that 40keV and 5keV RHEED electrons probe comparable distances normal to the surface when used at their respective angles of incidence. However, the greater lateral distance traversed through the crystal by the probing electrons in the 40keV case improves the quality of the diffraction information obtained.

For LiNbO$_3$, $D$ for 40keV electrons was about 4Å (calculated using a typical grazing angle of incidence, $\theta$, of about 3°). An approximate, experimental value for the sampling depth of the RHEED electrons was also obtained: very thin films of Nb of various thicknesses were deposited on clean, z-cut LiNbO$_3$ substrates at room temperature. The resulting amorphous layers were probed with RHEED to determine the thickness of Nb which obscured the underlying LiNbO$_3$ RHEED features: this occurred when about 13Å of Nb had been deposited, which was therefore taken as an order of magnitude upper limit for the penetration depth of 38.3keV RHEED electrons in Nb for the angle of incidence used (2°). The RHEED data from this experiment is discussed further in Section 3.8.

One last point: the "mean free path", $\Sigma$, is not to be confused with the "extinction distance", $\Gamma$, which is the distance within the crystal over which the incident beam is diffracted away. $\Gamma$ will give a truer measure of the "sampling depth" for a given reflection than does $\Sigma$. $\Gamma$ is, however, far more difficult to calculate, and is different for each reflection. It is a parameter of importance in the dynamical theory of contrast in electron diffraction (see Section 3.2). Fortunately, precise values of $D$ were not needed for this project. Also, $\Gamma$ is typically of the order of a few hundred Å for observable reflections, comparable in size to $\Sigma$, and is expected to behave in a similar manner as $\theta$ is changed: the estimates and arguments above, therefore, retain general significance.

3.5 PRESENT LiNbO$_3$, RHEED DATA: COMPARISON WITH PREVIOUS WORK

Figs. 3.5 and 3.6 give a direct comparison of the earlier 5keV MEED and 42keV RHEED work with the present 38keV RHEED patterns. Fig. 3.5 shows the detrimental effects of surface charging and of using MEED-energy electrons. Fig. 3.6 is a significant improvement on the LiNbO$_3$ RHEED patterns obtained by Bocharova and Nunomura.
FIGURE 3.4: 38.3 keV RHEED OF AN INSULATING SUBSTRATE POSSESSING RESIDUAL SURFACE CHARGE

z-cut sapphire, [010] azimuth.

Streak-splitting is evident.

Note: Rod spacing confirms -8% lattice mismatch with z-cut LiNbO₃.

FIGURE 3.5: PREVIOUS MEED/RHEED WORK ON Z-CUT LiNbO₃

(a) 5keV MEED (Petrucci\textsuperscript{[3,15]}), [120] azimuth, after standard chemical clean and light bake in situ.
(Also shown, for comparison, is the first (unoptimised) 38.3keV RHEED pattern obtained with the new RHEED system, again for z-cut LiNbO₃ [120], and under similar conditions).

(b) 42keV RHEED (Betts\textsuperscript{[3,20]})

Azimuth, etc. not given.

The effects of surface charge are evident.
FIGURE 3.6: 38.3 keV RHEED PATTERNS FOR LiNbO$_3$

"S" denotes a specular spot; $i$ = angle of incidence; square brackets give azimuth along which RHEED beam is aligned.

(a) $z$-cut, [120]: $i = 1° \ 30'$; $i = 3° \ 20'$

(b) $z$-cut, [010]: $i = 2° \ 5'$

(c) $z$-cut, [110]: $i = 1° \ 55'$; $i = 1° \ 35'$

(d) $y$-cut, [100]: $i = 2° \ 0'$

Early work, Kikuchi features highlighted
Bocharova's RHEED study was aimed at determining the point at which a chemical etch removed the surface amorphous layer on z-cut LiNbO₃ substrates (introduced by mechanical polishing). However, the published pattern was of very poor definition, especially in the zeroth order Laue zone, where no details of any kind could be seen. There was also severe surface charging. Nunomura's RHEED data, obtained for r.f.-sputtered LiNbO₃ films, was of fair quality (compared with Fig. 3.6). However, the films were grown on a substrate with a high secondary electron yield (MgO), and were significantly off-stoichiometry with a high impurity content (which may have led to electrical conductivity); the r.f. growth environment was low vacuum and therefore conducive to the presence of stray ions. If the RHEED work had been performed in situ, these factors could explain the absence of surface charging. More recently, some RED patterns have been published for r.f.-sputtered LiNbO₃ films grown by Nozawa[3,32]; these were of poor definition, similar in quality to the 5keV work of Fig. 3.5(a); no compositional data was supplied for the films.

None of the above studies supplied details of the RHEED set-up, and no quantitative measurements were given. Together with the work conducted by Betts[3,19,3,20], no other published RHEED data for LiNbO₃ is known to the author. The work presented in this chapter represents a marked improvement on all previous literature in this area: the 38keV RHEED analyses of LiNbO₃ substrates performed by the author are summarised in a recent series of publications[3,15,3,16].

3.6 ANALYSIS OF RHEED PATTERNS FOR LiNbO₃ AND SAPPHIRE

3.6.1 CRYSTAL STRUCTURE; CONCEPT OF RECIPROCAL SPACE

The structure and properties of lithium niobate are well known[3,18,3,35–3,37]. At room temperature, LiNbO₃ belongs to the rhombohedral (trigonal) space group R3c, point group 3m[3,18]. In the hexagonal indexing system, which has six formula units per unit cell, the lattice parameters are:

\[ a_n = 5.149 \pm 0.002 \text{ Å}, \quad \text{and} \quad c_n = 13.867 \pm 0.005 \text{ Å}. \]

These have been obtained from X-ray diffraction work, and confirmed by neutron diffraction studies[3,13,3,38,3,39]. The error limits include the variation in lattice parameter due to deviations from the ideal stoichiometry[3,38]. Sapphire is hexagonal, and belongs to the space group R3c owing to the fact that all the metallic ions are equivalent. Its lattice parameters are: \( a_n = 4.763 \text{ Å} \) and \( c_n = 13.003 \text{ Å} \).

The most convenient way of interpreting RED patterns is to employ the concept of the reciprocal lattice, defined by a set of vector equations[3,39] which give the three axes of
reciprocal space in terms of the unit vectors of the crystal unit cell. The equations also define the orientation of the reciprocal lattice relative to the real crystal. Having determined the geometry and orientation of the reciprocal lattice, it is then necessary to consider which reciprocal lattice points are forbidden by the structure factor[3,3.40] (see also Appx. 3.4): such points will not be observed in the diffraction pattern, except by means of dynamic effects such as double diffraction[3.1]. Once the forbidden reflections have been removed from the reciprocal lattice, the Ewald sphere construction can be applied directly (Appx. 3.1).

3.6.2 SUBSTRATE PREPARATION;
DESCRIPTION OF RHEED PATTERNS

The LiNbO₃ source wafers for all RHEED studies and the growth work of Ch. 5 were supplied by Barr and Stroud Ltd. (now Pilkington Electro-Optic Materials): these were cut from characterised boules and Syton polished to an optical finish. For z-cut material, the positive face was used, as in previous MBE work[3.20]. Orientation of axes was accurate to better than half a degree. Wafers were typically 1.0 mm thick, of single domain, and with no refractive index inhomogeneities > 10⁻⁶; these were diced up into 1 cm squares for the surface studies and growth work. The sapphire substrates were of similar specification (suppliers: Roditi International Ltd.). Substrates were subjected to a chemical etch[3.16,3.20] (also see Table 2.1). This was followed by a light bake in vacuo (= 250°C for 30 min.) to remove volatile surface contaminants. Often, no further processing was required for RHEED patterns to be obtained.

Fig. 3.6 shows 38.3 keV RHEED patterns obtained for +z-cut and y-cut LiNbO₃ at various angles of grazing incidence (here denoted "i") and with the RHEED beam aligned along several in-plane azimuths. In each case, a different section in reciprocal space was sampled. Fig. 3.7 clarifies the relationship between the real and reciprocal lattices of LiNbO₃: Fig. 3.7 (a) gives their relative orientation on the z-cut [(00.1), or "basal"] plane; the dotted lines in Fig. 3.7 (b) indicate the relevant intersections of the Ewald sphere with the basal plane. The hexagonal system[3.18] was used throughout to index azimuths and planes: hexagonal crystal axes are indicated as xₜ, yₜ and zₜ; the corresponding reciprocal lattice axes are marked with an asterisk. The "orthohexagonal" axes[3.8] (denoted by x, y and z) are also shown, since these are frequently referenced in the manufacturers’ literature accompanying supplied material.

Fig. 3.8 gives the predicted reciprocal lattice sections for LiNbO₃, arrived at using the Ewald sphere construction, and taking into consideration the X-ray selection rules and the full structure factor for LiNbO₃ (see Appx. 3.4 and the references[3.20,3.23,3.33,3.41]). (a) to (c) are for z-cut LiNbO₃; (d) and (e) are for y-cut LiNbO₃. The primary electron beam is at glancing incidence to the following azimuths (out of the paper):
z-cut: (a) y axis, equivalent to [120];
(b) yH axis, [010] (rotation of sample 30° clockwise);
(c) [110] azimuth (rotation of sample 30° anticlockwise).

y-cut: (d) -xH axis, [T00];
(e) +zH axis, [001].

The magnitudes of the reciprocal lattice vectors are defined by $|G_{\text{real}}| = 1/d_{\text{obs}}$ (e.g. $|G_{\text{obs}}| = |y_{\text{s}}| = 1/d_{\text{obs}}$). Square brackets indicate real lattice directions. The reciprocal lattice indices of a reflection are equivalent to the Miller-Bravais indices of the planes that give rise to it.

In Fig. 3.6 (a), the RHEED beam was aligned to the [120] azimuth (orthohexagonal y axis). The sampled section in reciprocal space was thus the plane containing the vectors $z_{\text{H}}$ and $x_{\text{H}}$, as in Fig. 3.7 (b) (i) and Fig. 3.8 (a). ($x_{\text{s}}$ is equivalent to the direction: $2x_{\text{s}} - y_{\text{s}}$). Rotation of the sample through 30° clockwise ($\pm 6'$ of arc) gave glancing incidence to the $y_{\text{H}}$ axis ([010] direction); the resulting RHEED pattern is shown in Fig. 3.6 (b). The relevant reciprocal lattice section is now a plane containing $x_{\text{H}}$ and $z_{\text{H}}$, shown in Fig. 3.7 (b) (ii) and Fig. 3.8 (b). Finally, rotation of the sample through 30° in an anti-clockwise sense gave the pattern in Fig. 3.6 (c) with the beam parallel to the [110] azimuth: the expected pattern is given by Fig. 3.8 (c), corresponding to Fig. 3.7 (b) (iii). Typical RHEED work on y-cut LiNbO$_3$ is shown in Fig. 3.6 (d); predicted sections for y-cut RHEED are given in Figs. 3.8 (d) and (e). Comparing Fig. 3.6 with Fig. 3.8 shows good agreement throughout.

Figs. 3.6 (b) and (c) are laterally-inverted versions of each other (see also Fig. 3.8). The difference arises from the fact that the true symmetry of the crystal is trigonal as opposed to hexagonal. Betts' indexing of the patterns$^{[3,20]}$ has been revised here in order to clear up any ambiguities. The non-equivalence of the $\pm 30^\circ$ rotation patterns above, though a subtle source of error in interpretation and indexing, does not greatly affect quantitative work. However, for detailed studies, one must be aware that "lateral inversion" of this type can occur for some of the hexagonally-equivalent azimuths (such as [100] and [T00]) in LiNbO$_3$ RHEED. In fact, the effect can be used to distinguish such axes.

RHEED patterns were also obtained for z-cut sapphire substrates: typical examples can be seen in Fig. 3.4 and in Ch. 5. The reciprocal lattice for sapphire is very similar to that for LiNbO$_3$, except that it has the full hexagonal symmetry$^{[3,42]}$, and slightly different lattice parameters. The surface preparation is described elsewhere$^{[3,20]}$: it is essentially the same as for LiNbO$_3$ except that no nitric acid is used in the chemical etch.

Kikuchi lines (and sometimes bands)$^{[3,23,43,3,44]}$ were clearly visible in many of the patterns (both for LiNbO$_3$ and sapphire), indicating good long-range order in the crystal
interior; they also provided an accurate means of sample alignment, which was vital in the reliable interpretation of the patterns. For many of the substrates, the intersection of the Ewald sphere with the First Order Laue Zone\(^{3,20}\) produced a ring of diffracted features at the far edges of the screen, particularly when the RHEED pattern was of high quality.

A note is needed here on the validity of using X-ray structure factors to predict electron diffraction patterns. It was expected that, to a first approximation, the X-ray and electron diffraction selection rules should concur: the good agreement between the observed RHEED patterns and the indexed sections of reciprocal space as predicted in Fig. 3.8 (obtained from X-ray selection rules, etc.) suggest that this assumption was justified. There is also fair agreement with the reciprocal lattice sections obtained from a TEM study of LiNbO\(_3\)^{241}, though this included reflections due to double diffraction.

### 3.6.3 QUANTITATIVE ANALYSIS OF RHEED PATTERNS: SIMPLE APPROACH

Diffraction features on the RHEED screen can originate either from elastic or inelastic scattering events in the crystal surface. The latter includes thermal diffuse scattering\(^{3,16}\) and other inelastic mechanisms\(^{31,33}\). Refraction of the electrons must also be taken into account, and there is sometimes difficulty in establishing an accurate vertical origin. Certain reflections may be treated quantitatively using the Bragg Law; for small angles of grazing incidence such as those used in this work, this yields\(^{3,1,12,3,29}\):

\[
\frac{r}{d_{(hkl)}} = \frac{\lambda L}{d_{(hkl)}}, \quad \text{for}\ \text{small}\ \text{angles} \quad \text{of}\ \text{grazing}\ \text{incidence}.
\]

(Eqn. 3.1)

where:

- \(\lambda\) = electron wavelength (Å);
- \(L\) = camera length (mm);
- \(d_{(hkl)}\) = interplanar spacing for (hkl) planes (Å);
- \(r\) = distance between straight-through spot and the reflection from (hkl) planes, as measured on the screen (in mm). See text and Figs. 3.1 & 3.9.

Eqn. 3.1 can be used when "r" represents the separation of features for which refraction effects do not apply (e.g. for ring patterns from polycrystalline films, or for features spaced parallel to the shadow edge or at large distances from the shadow edge and straight-through spot). Measurements made in the vicinity of the shadow edge which have a "vertical" component (i.e. a component perpendicular to the shadow edge) are affected by refraction: to analyse features such as these, an alternative approach must be adopted, based on the electron wavevector changes within the crystal (Section 3.6.5). However, "horizontal" measurements (i.e. those made parallel to the shadow edge) yield \(d_{(hkl)}\) directly using Eqn. 3.1.
The horizontal spacing of the streaks observed in the above RHEED patterns can be associated with particular lattice planes. For example, the separations of the streaks in Figs. 3.6 (a) and (b) are related to planes of the type (210) and (100) respectively (see Fig. 3.7 (c)). For these particular patterns, the vertical spacings of features are related to interplanar spacings of the type (00z). The streak spacings were measured and compared with values predicted using Eqn. 3.1. Rauber's values for the lattice constants were used; \( L \) was measured directly; \( \lambda \) was calculated from the electron energy. The calculated separations agreed with the measured values to better than 6%.

To achieve greater accuracy, calibrations were performed using X-ray-orientated Si(100) and Si(111) wafers: these yielded a more precise value of \( \frac{\lambda L}{x} \), the "camera constant", in Eqn. 3.1. Improved photographic equipment was also installed, giving precise 1:1 magnification and reducing measurement errors in \( r \). As a result of this work, the discrepancy between the measured and quoted \( a_\parallel \) lattice parameters was reduced to less than 2%, which is within the estimated limits of error (ruler errors, alignment and positional errors, etc.)

If true reflection diffraction takes place (as opposed to diffraction through surface asperities), then the vertical reciprocal lattice features merge into rods: these intersect the Ewald sphere to produce short, vertical streaks. The streaks obtained in Fig. 3.6 are more or less as expected for a surface which is smooth and clean, and for which the diffraction is predominantly reflection.

At low angles of grazing incidence, the quantitative interpretation of features perpendicular (and close) to the shadow edge required that a correction for refraction be made. For this, the value of the mean inner crystal potential, \( V_0 \), for LiNbO\(_3\) was needed.

### 3.6.4 THE MEAN INNER CRYSTAL POTENTIAL, \( V_0 \)

A full description of the significance of \( V_0 \) is to be found in Vainshtein's text. Essentially, \( V_0 \) is the first term in the Fourier Transform of the Crystal Potential Function. Put crudely, it is the term that gives rise to the crystal's electron refractive index, and it represents the difference between the vacuum level and the average crystal potential found between the ions in the lattice. \( V_0 \) is needed when accounting for refraction effects in RHEED patterns, but it is also of use in other branches of physics (e.g. in the interpretation of transmission electron diffraction/microscopy data; in angularly-resolved ultra-violet photoelectron spectroscopy (ARPES); and in the correct description of the surface states of a crystal, where it is a fundamental parameter).

The angles of grazing incidence of the electron beam inside and outside the crystal are termed \( \theta_i \) and \( \theta_o \) respectively (Fig. 3.9 (c)). These angles can be related to each other by
assuming that the electron momentum parallel to the crystal surface is conserved as the electron is "refracted" at the vacuum-crystal interface. This gives the following equation:

\[ \cos \theta_0 = \cos \theta_i (1 + V_0/E)^{1/2} \]  

(Eqn. 3.2)

where: \( V_0 = \) mean inner potential of crystal (electron volts);
and: \( E = \) incident electron energy (in electron volts).

When the Bragg condition is used to determine the angles at which diffraction maxima occur, it is the \( \theta_i \) that should be used. For the small angles of grazing incidence employed in RHEED work, the difference between \( \theta_0 \) and \( \theta_i \) is usually significant: for example, if \( \theta_0 = 2^\circ \), \( V_0 = 10\text{eV} \) (fairly typical), and \( E = 30\text{keV} \), then \( \theta_i = 2.3^\circ \). Hence, measured values of \( \theta_0 \) must be converted into \( \theta_i \) using Eqn. 3.2 before indexing the "spots".

Vainshtein formulated an approximate method for calculating \( V_0 \) from the atomic scattering factors of the individual components of the crystal lattice. The method and theory are fully discussed elsewhere. Using Thomas-Fermi-Dirac (TFD) Factors yields a value of about 16eV for LiNbO\(_3\) (see Appx. 3.5). This seems a credible result: the reported values of \( V_0 \) for a variety of semiconductor crystals lie in the range 11 to 15 eV.

The procedure for determining \( V_0 \) empirically was as follows:

(a) a systematic set of diffraction patterns was recorded as a function of \( \theta_\infty \);
(b) an estimated value of \( V_0 \) was used in the algorithm of Table 3.1 to calculate the reciprocal lattice vectors associated with the RHEED features observed in these patterns;
(c) the predicted Bragg reciprocal lattice vectors (\( G(hk0) \)) were calculated from the known lattice parameters and compared with the observed values in (b). \( V_0 \) was then iteratively adjusted to optimise the agreement between them.

Using the above procedure, the best fit was obtained for \( V_0 = 15 \pm 3 \text{ eV} \). It is encouraging that the value of \( V_0 \) calculated in Appx. 3.5 lies within this range. Using \( V_0 = 15 \text{ eV} \), it was possible to index all the diffraction features observed on the [120], [010] and [110] azimuths for z-cut LiNbO\(_3\), and the indexed patterns were in close agreement with the predicted reciprocal lattice sections of Fig. 3.8 (e.g. 003, 009, etc. were generally absent, as predicted from the structure factor).

The above procedure was repeated for y-cut LiNbO\(_3\): the value for \( V_0 \) was confirmed, to the same degree of accuracy. Furthermore, the spacing between the streaks for the y-cut patterns yielded independent data on the value of \( c_0 \), which agreed (to within ± 2%) with the published bulk values. The y-cut sections of reciprocal space are also shown in Fig. 3.8.
Fig. 3.7  REAL AND RECIPROCAL LATTICE
SECTIONS
FOR HEXAGONALLY INDEXED LITHIUM NIOBATE

a) Angular relationship between reciprocal and real (direct) axes
b) (00.1) SECTION IN RECIPROCAL SPACE FOR LITHIUM NIOBATE

RHEED beam parallel to:

i) [120], c.f. fig.3.8a)
ii) [010], c.f. fig.3.8b)
iii) [110], c.f. fig.3.8c)
c) z-cut Lithium Niobate:

diagram illustrating the types of planes
giving rise to the major reflections in fig.3.6 (a)→(c),
and their interplanar spacings.
Fig. 3.8
PREDICTED SECTIONS IN RECIPROCAL SPACE

a), b) & c) are for z-cut LiNbO$_3$ substrates; 
d) & e) are for y-cut LiNbO$_3$ substrates.

All figures are drawn to scale, giving their observed size on the RHEED screen (at 38.3 kV). Refraction effects are not included.
The quoted indices are for reciprocal space, i.e. $(x^*,y^*,z^*)$; square brackets give directions relative to the real lattice, i.e. $[x_H^*,y_H^*,z_H^*]$.

<table>
<thead>
<tr>
<th>a) RHEED beam parallel to [120]</th>
<th>(c.f. Fig. 3.7(b)(i))</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(x_H^<em>,y_H^</em>,z_H^*)$</td>
<td>$z_H^*$</td>
</tr>
<tr>
<td></td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>3</td>
</tr>
<tr>
<td>$63z_H^*$</td>
<td>42z$_H^*$</td>
</tr>
<tr>
<td>$21z_H^*$</td>
<td>$00z_H^*$</td>
</tr>
<tr>
<td>$21z_H^*$</td>
<td>42z$_H^*$</td>
</tr>
<tr>
<td>$63z_H^*$</td>
<td>0</td>
</tr>
</tbody>
</table>

| b) Beam parallel to [010]      | (c.f. Fig. 3.7(b)(ii)) |
| c) Beam parallel to [110]      | (c.f. Fig. 3.7(b)(iii)) |

71
Fig. 3.8  d) & e) are for y—cut LiNbO₃ substrates.

d) RHEED beam parallel to [100]

\[ \begin{array}{ccccccc}
1.0 \text{ Å}^{-1} & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 2 \\
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot & 1 \\
0_{y}^{*}12 & 0_{y}^{*}6 & 0_{y}^{*}0 & 0_{y}^{*}6 & 0_{y}^{*}12 & 0_{y}^{*}
\end{array} 
\]

\[ \text{Z}_H \text{ axis} \]

e) RHEED beam parallel to +zₜ_axis, [001]

(spots individually indexed)

\[ \begin{array}{cccccc}
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\
\cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\
1.0 \text{ Å}^{-1} & \cdot & \cdot & \cdot & \cdot & \cdot \\
\cdot & 40 & 020 & 220 & \cdot & \cdot \\
\cdot & 120 & 110 & \cdot & \cdot & \cdot \\
\cdot & 420 & 210 & 000 & 210 & 420 \\
\end{array} 
\]

\[ \text{2x}_{H}^{*} - y_{H}^{*} \quad (= [100]) \]
3.6.5 FULL RHEED ANALYSIS ALGORITHM

When an electron is diffracted, its k-vector (wavevector) undergoes a change. The various $\Delta k$'s in Table 3.1 represent the change in the k-vector resolved horizontally and vertically, i.e. parallel to, and perpendicular to, the shadow edge on the screen. The $\Sigma \Delta k$'s are related to the TOTAL electron momentum changes: Step (7) of the algorithm is to ensure that these are their values INSIDE the crystal. For an observed Bragg reflection on the screen, the measured $\Sigma \Delta k$ for that reflection is assumed equal to the reciprocal lattice vector, $G_{(hkl)}$, of the set of planes giving rise to the diffraction event. By measuring the various $\Sigma \Delta k$'s, and repeating the analysis for different azimuths, we can arrive at the reciprocal (and hence real) lattices for the crystal surface.

This approach has wide application, and is approximately valid even when inelastic scattering mechanisms prevail. Certainly, in the case of thermal diffuse scattering, the measured $\Sigma \Delta k$'s for spots excited via a thermal phonon should correspond closely to the $G_{(hkl)}$, since energy and wavevector conservation must apply\(^{[3,16]}\).

Note that, to analyse vertical features, distances on the screen should be measured relative to the shadow edge, as shown in Fig. 3.9 (b). The shadow edge position can be estimated by sight, but it is more accurate to make sure that a specular reflection is obtained: this is then bisected (with respect to the straight-through spot). The algorithm in Table 3.1 is then applied to $r_1$ and $r_3$, separately; $r_2'$ should NOT be used in accurate work (even for specular reflections). However, measurements such as $r_1'$, are valid because, horizontally, there is no refraction. In some cases (and especially for grown films) the streaks have little or no intensity modulation along their length: the calibration factor $C_2$ is then used to convert $r_1$ values directly into the $|G_{(hkl)}|$. $d_{(hkl)}$ values can then be obtained using:

$$d_{(hkl)} = \frac{1}{|G_{(hkl)}|} \quad \text{(Eqn. 3.3)}$$

Again, several azimuths can be used, and the results collated to yield the surface lattice net spacings.
TABLE 3.1: ANALYSIS ALGORITHM FOR RHEED PATTERNS

1. Check, or inform computer, as to: (a) Crystal: parameters, type, cut, orientation; (b) RHEED beam direc., accelerating voltage, etc.

2. Calculate screen calibration factors, C1, C2 (obtained using a Si calibration crystal); these convert distances on the screen, r, to angles and reciprocal lattice vectors respectively. At 38.3keV, 24mm on the screen corresponded to 2.74° or 0.775Å⁻¹.

3. Determine the centre of the straight-through (or (000)) spot, and the centres of intensity for arcs/spots/streaks under consideration. If required, determine the shadow edge position (bisect (000) spot and a specular feature directly above it). See Fig. 3.9 (b).

4. Measure r1, r2, r3 accurately (see Fig. 3.9 (b)).

5. Use C1 to convert: 
   (a) r1 to \( \theta_{\text{latt}} \);  
   (b) r2 to \( \theta_{\text{net}} \);  
   (c) r3 to \( \theta_{\text{inc}} \)  
   \( \theta_{\text{inc}} \) = beam angle of incidence

6. Calculate: 
   (a) Relativistic wavelength, \( \lambda' \), of electrons\(^{13,31} \);  
   (b) Electron wavevector, \( k_{\text{net}} \) (\( k_{\text{net}} = 1/\lambda' \)).

7. If refraction effects apply, convert: 
   (a) \( \theta_{\text{inc}} \) to \( \theta_{\text{inc}}' \);  
   (b) \( \theta_{\text{net}} \) to \( \theta_{\text{net}}' \).  
   (Use Eqn. 3.2. This gives the angles inside the crystal (Fig. 3.9 (d)). If \( V_s \) is not known, find it using the iterative method of Section 3.6.4.)

8. Use: \( \Delta k/k_{\text{net}} = \sin \theta' \) to convert: 
   (a) \( \theta_{\text{latt}} \) to \( \Delta k_{\text{latt}} \);  
   (b) \( \theta_{\text{net}}' \) to \( \Delta k_{\text{net}}' \);  
   (c) \( \theta_{\text{inc}}' \) to \( \Delta k_{\text{inc}}' \).

9. Deduce total "momentum" changes: 
   (a) \( \Sigma \Delta k_{\text{latt}} = \Delta k_{\text{latt}} \);  
   (b) \( \Sigma \Delta k_{\text{net}} = \Delta k_{\text{net}} + \Delta k_{\text{inc}} \).

10. Compare \( \Sigma \Delta k \) values to known \( G_{\text{hkl}} \) and/or convert them to real lattice spacings.  
    Repeat above procedure for different RHEED azimuths and crystal cuts. Hence deduce surface net/crystal structure?
Fig. 3.9 PARAMETERS RELEVANT TO RHEED ANALYSIS ALGORITHM

a) SIDE VIEW

b) SCREEN VIEW
c) INSIDE CRYSTAL
Simple Diagram illustrating $\Theta_o$ and $\Theta_i$

![Diagram of inside crystal showing angles and planes]

---

d) GENERAL CASE (angles exaggerated)

![Diagram of general case showing angles and planes]

$\Theta_{000}$

$\Theta_{000}^i$

$\Theta_{Bragg}$

Bragg scattering event

$\Theta_{000}^i + \Theta_i^i_{vert}$

($\alpha \sum \Delta k$ in crystal)
Quantitative analysis of RHEED patterns is sometimes difficult, and usually laborious. Some workers have used a video camera to observe and monitor RHEED patterns, and a computer to model and analyse them\cite{3,12,34,35}, but the UCL RHEED computer system was designed from first principles. The RHEED pattern or photograph was recorded by a video camera, digitised, and displayed as an intensity pattern. Software was written to enable manipulation of the digitised image, for example to highlight a desired feature or type of reflection, adjust contrast, magnify a selected region, find the centre of intensity of a spot or streak (imperative in quantitative analysis), make spatial measurements, and so on. Typical screen resolution was 0.1 mm. The software included an algorithm based on Table 3.1: this allowed reciprocal lattice vectors to be measured directly, once a calibration pattern with a test crystal (silicon) had been obtained. This facility was used to map out the section of reciprocal space under observation.

A greater degree of user-interaction is now being included, so that the operator may override or adjust decisions made by the computer, or feed in new values of crystal or electron gun parameters. The system has already yielded surface periodicity values for LiNbO$_3$ two orders of magnitude faster than by hand. A data bank is now being set up, so that the observed pattern can be compared with data stored from previous runs or with theoretically-predicted reciprocal lattice sections for the crystal. A full account of the hardware may be found in the cited reference\cite{3,46}. Fig. 3.10 shows typical, processed images.

### 3.6.7 COHERENCE LENGTH

The electron wavevector can be considered in phase only within a characteristic distance known as the *Coherence Length*. This dimension defines a limit of resolution for the diffraction experiment: electron scattering from periodic surface features will only give rise to diffraction information on the RHEED screen if the path difference is less than the coherence length. The calculation of a meaningful coherence length for any given set-up is fraught with problems, though in most cases it depends mainly on the angular divergence of the primary electron beam. An order of magnitude calculation gives 80\(\text{Å}\) and 900\(\text{Å}\) as the coherence width and length for the 38keV RHEED beam used in this system. Further details are given in Appx. 3.6.
FIGURE 3.10: COMPUTER-PROCESSED RHEED IMAGES

(a) Accurate streak-separation measurement using contrast control (38.3keV, z-cut LiNbO$_3$, [120] azimuth)

(b) Measurement of weak features in the 38.3keV RHEED pattern of an NbO$_{1.4}$ film grown on z-cut LiNbO$_3$ (RHEED beam parallel to LiNbO$_3$[100] azimuth)
3.7 SURFACE STUDIES, PART I: 
Ar⁺ ETCH RATES, ETCH UNIFORMITY & ION DAMAGE DEPTH

3.7.1 ETCH RATE RESULTS FOR SUBSTRATES USED IN 
THE UCL SYSTEM

Ion etch rate and damage depth data are relevant to the RHEED surface studies of 
Section 3.8 (Part II); they are also important considerations in the development of an MBE 
process suitable for device manufacture (e.g. it is useful to know how ion-etch cleaning will 
affect the ribbed precursor structures of the vertical modulator device mentioned in Ch. 6).

Table 3.2 gives the argon-ion etch rates for LiNbO₃ and other substrates of relevance 
to this thesis. The entries marked "EXPT 33" are values obtained in the UCL rig, using the 
modified ion discharge gun described in Ch. 2 and below. An aluminium grid was deposited 
on the substrate to act as a mask; this was irradiated in situ with Ar⁺ ions. The mask was then 
removed with a selective wet etch, and a Talystep machine used to determine step heights 
across the substrate, giving etch rate and uniformity data. The experiment was repeated for 
various fluences, energies, times, and substrate position. Agreement with the published etch rate 
values was good.

3.7.2 DETAILS FOR EXPT 33: ION SOURCE MODIFICATIONS, 
ETCH UNIFORMITY, DAMAGE DEPTH, ETC.

The ion-etching unit as used by Betts could not reliably deliver or detect ion doses 
below about 5 x 10¹⁴ Ar⁺/cm², and 1.5 x 10¹⁶ Ar⁺/cm² was a typical dose used²⁰. If LiNbO₃ 
substrates are ion-cleaned prior to deposition, small ion doses (< approx. 3 x 10¹³ Ar⁺/cm², at 
3keV) must be used to ensure good epitaxy²⁰ and to avoid the unwanted cubic phase of 
LiNbO₃ (see next section): previously, this could only be obtained using the SIMS ion gun in 
defocussed mode, with poor repeatability. For the work reported here, the discharge gun was 
modified to improve its sensitivity by a factor of 40, so that these low doses could be achieved 
reliably. The ion doses were quantified by means of calibration experiments involving a 
Faraday Cup collector. Improvements were also made to the ion cleaning procedure: the 
substrate was shielded from the etching beam whilst establishing the required ion flux, and the 
substrate irradiation position was made more reproducible.

The LiNbO₃ substrates suffered varying degrees of greying on the surface, depending 
on the ion dose and the angle of incidence used: this may have been due to the generation of 
oxygen vacancies²⁰. The greying cleared up after exposure to air for a few weeks at room 
temperature. The optimised etching position corresponded to a 35° angle of incidence and a 
lateral setting for the substrate different from that used by Betts. This position (denoted in
**TABLE 3.2: \( \text{Ar}\text{\textsuperscript{+}} \) ETCH RATES FOR LiNbO\textsubscript{3}, SAPPHIRE, SILICON & OTHER SUBSTRATES OF INTEREST**

<table>
<thead>
<tr>
<th>Material and cut</th>
<th>Ion energy; Beam Angle of incidence.</th>
<th>Fluence (( \mu A/cm^2 ))</th>
<th>Etch rate (( \text{Å per }10^4/cm^2 ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ref. 3.47</td>
<td>z-cut LiNbO\textsubscript{3}</td>
<td>1keV, 0( ^{\circ} )</td>
<td>1000</td>
</tr>
<tr>
<td></td>
<td>z-cut sapphire</td>
<td>1keV, 0( ^{\circ} )</td>
<td>1000</td>
</tr>
<tr>
<td>Ref. 3.48</td>
<td>y-cut LiNbO\textsubscript{3}</td>
<td>3keV, 0( ^{\circ} )</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>sapphire\textsuperscript{\dagger}</td>
<td>4keV, 0( ^{\circ} )</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>Si (100), (111)</td>
<td>3keV, 0( ^{\circ} )</td>
<td>100</td>
</tr>
<tr>
<td>Ref. 3.30</td>
<td>LiNbO\textsubscript{3}\textsuperscript{\dagger}</td>
<td>0.5keV( ^{\dagger} )</td>
<td>3.0</td>
</tr>
<tr>
<td>Ref. 3.49</td>
<td>z-cut LiNbO\textsubscript{3}</td>
<td>1keV, Near-normal (= 0( ^{\circ} ))</td>
<td>50</td>
</tr>
<tr>
<td>Ref. 3.50</td>
<td>y-cut LiNbO\textsubscript{3}</td>
<td>0.5keV, 0( ^{\circ} )</td>
<td>1000</td>
</tr>
<tr>
<td></td>
<td>Nb\textsuperscript{\dagger}; SiO\textsubscript{2}\textsuperscript{\dagger}; Si\textsuperscript{\dagger}</td>
<td>0.5keV, 0( ^{\circ} )</td>
<td>1000</td>
</tr>
<tr>
<td></td>
<td>sapphire\textsuperscript{\dagger}</td>
<td>0.5keV, 0( ^{\circ} )</td>
<td>1000</td>
</tr>
<tr>
<td>EXPT 33 (UCL)</td>
<td>z-cut LiNbO\textsubscript{3}</td>
<td>1keV, 0( ^{\circ} ) (50 min.)</td>
<td>1000</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1keV, 0( ^{\circ} ) (2.5 min.)</td>
<td>1000</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3keV, 70( ^{\circ} )</td>
<td>12.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3keV, 35( ^{\circ} )</td>
<td>12.5</td>
</tr>
<tr>
<td></td>
<td>y-cut LiNbO\textsubscript{3}</td>
<td>1keV, 0( ^{\circ} ) (50 min.)</td>
<td>1000</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1keV, 0( ^{\circ} ) (2.5 min.)</td>
<td>1000</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3keV, 0( ^{\circ} )</td>
<td>12.5</td>
</tr>
<tr>
<td></td>
<td>z-cut sapphire</td>
<td>1keV, 0( ^{\circ} ) (50 min.)</td>
<td>1000</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1keV, 0( ^{\circ} ) (2.5 min.)</td>
<td>1000</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3keV, 35( ^{\circ} ) (60 min.)</td>
<td>1000</td>
</tr>
</tbody>
</table>

**Calibration:** \( 1\mu A/cm^2 \) for 1 hr. = \( 2.25 \times 10^8 \) \( \text{Ar}^{\text{+}} \) ions/cm\(^2\). The quoted ion doses include the cos\( \theta \) factor.

**Footnotes:**  
'Cut and incident angle unspecified; \( \dagger \) Cut unspecified; " Betts' etch position; ** Optimised etch position.
Table 3.2 by **) gave the most uniform etching and virtually no greying effect: for a fluence of 100 μA/cm², the region of uniform etching was centralised on the substrate, and the etch rate was uniform to ± 20%. The etching was a little less uniform at 12.5 μA/cm². The non-uniformities in etch rate for Betts’ etch position (marked *) were several hundred per cent, and etch rates were lower; there were also areas in which no observable etching took place.

No difference in etch rate was observed between virgin and pre-etched samples (data not shown). For the optimised position, the measured ratio of etch rates for LiNbO₃ and sapphire (= 3.5) was in agreement with the average ratio in published data (= 3.0), and there was no observable surface roughening. For 70° incidence, though, Talystep showed very low etch rates and considerable surface roughening.

Ion damage can extend deeply into the substrate: damage minimisation and surface cleaning criteria can, therefore, be in conflict, and an optimum surface preparation must be established for each type of substrate. The average damage depth due to 3keV Ar⁺ ions is about 40Å in Nb[3.51], and about 150Å in Si[3.53]. The value for LiNbO₃ is within this range[3.53].
3.8 SURFACE STUDIES, PART II: 38.3 keV RHEED ON ION-CLEANED AND THERMALLY CYCLED SUBSTRATES: SURFACE KINETICS.

3.8.1 PREVIOUS WORK

Betts' results\textsuperscript{[13-20]} suggest that the epitaxial quality of grown layers was sensitive to the amount of surface damage induced by ion cleaning. Excessive ion doses (> 10\textsuperscript{17} Ar\textsuperscript{+}/cm\textsuperscript{2} at 3\textrightarrow{}4 keV) made it difficult to reconstitute the surface, and thence to grow epitaxial layers. According to the limited data available\textsuperscript{[13-20]}, single-crystal, rhombohedral LiNbO\textsubscript{3} films could only be grown on z-cut LiNbO\textsubscript{3} substrates that had required little or no ion cleaning prior to growth: i.e. substrates needed to show reasonable MEED patterns and relatively clean SIMS upon initial inspection in the system. In fact, these "clean" SIMS spectra corresponded to significant impurity coverages (estimated at > 5\%), since the impurity peak heights diminished accordingly upon subsequent ion cleaning. Results of early growth runs in this project showed that even much smaller ion doses (down to roughly 3 \times 10\textsuperscript{13} ions/cm\textsuperscript{2}) could be detrimental to epitaxy, and cause damage which favoured the growth of the cubic phase of LiNbO\textsubscript{3} (see Ch. 2).

Townsend\textsuperscript{[3,54]} showed that an ion dose of 5 \times 10\textsuperscript{15} to 5 \times 10\textsuperscript{16} ions/cm\textsuperscript{2} achieved surface amorphisation of LiNbO\textsubscript{3} and similar materials (the bombarding species used were similar to Ar\textsuperscript{+}). Also, work conducted by Gotz and Karge\textsuperscript{[3,55]} showed that, for LiNbO\textsubscript{3}, bombardment with N\textsuperscript{+} ions can be broadly characterised into three stages:

(a) \ < 10\textsuperscript{15} N\textsuperscript{+}/cm\textsuperscript{2} ("predamage stage") in which point defects are generated;

(b) \ 10\textsuperscript{15} to 5 \times 10\textsuperscript{15} N\textsuperscript{+}/cm\textsuperscript{2}, in which heavy damage is produced, but the preferential direction of the c-axis is partially preserved;

(c) \ > 5 \times 10\textsuperscript{15} N\textsuperscript{+}/cm\textsuperscript{2} ("saturation stage") for which the damage saturates, but a little preferential order is retained.

With these results in mind, experiments were performed to assess the damage caused to z-cut LiNbO\textsubscript{3} by 3keV Ar\textsuperscript{+} ions from the new ion cleaning unit.

3.8.2 RESULTS OF 38.3 keV RHEED STUDY ON Ar\textsuperscript{+}-ETCHED LiNbO\textsubscript{3}

Fig. 3.11 shows a series of RHEED photographs taken for z-cut LiNbO\textsubscript{3} substrates (standard ex situ clean, as in Ch. 2) at various stages of heat treatment and ion bombardment cleaning, and then after thermal reconstitution.
FIGURE 3.11

Z-CUT LiNbO₃ SUBSTRATES:
RHEED PATTERNS AT VARIOUS STAGES OF THERMAL PROCESSING,
ION BOMBARDMENT CLEANING,
AND THERMAL RECONSTITUTION.

(a) Standard ex situ etch: as-loaded, and after 500°C, 60 min.

(b) 600°C, 30 min.

(c) 650°C, 90 min. (underexposed)

(d) 650°C, 60 min., 2 x 10⁻⁶ torr O₂

(e) 3keV Ar⁺, 9.6 x 10¹⁵ ions/cm² (max. dose)

(f) 3keV Ar⁺, 9.8 x 10¹⁵ ions/cm² (max. dose)

(g) 530°C, 60 min.

(h) 590°C, 60 min.

(120) azimuth.

(i) 670°C, 60 min.
AMORPHOUS NI OB IUM ON
Z-CUT LiNbO$_3$: RHEED
SAMPLING DEPTH; THERMAL
BEHAVIOUR OF LAYER.

(a) LiNbO$_3$ substrate:
z-cut; [120] azimuth.
Standard preparation;
Probe heater "on"
(temperature = 120°C).

(b) Approximately 13Å
(≈ 4 monolayers)
of Nb metal deposited
on (a) at 40°C.

The RHEED conditions
were adjusted to
optimise the residual
periodic features.
Pattern recorded at
room temperature.

(c) Heat treatment of (b):

60 minutes at 580°C.
Pattern recorded
at 200°C.
Considering the ion damage first: the small ion doses, up to a few $10^{14}$ Ar$^+$ cm$^{-2}$ at 3keV, had only a minor effect on the RHEED patterns. Less than 0.5–1.0Å of the surface was removed for an ion dose of $4 \times 10^{14}$ Ar$^+$ cm$^{-2}$ at 3keV (see Table 3.2), though the ion damage extends deeper than this. However, as Fig. 3.11 shows, surface damage was certainly evident at an ion dose of $10^{15}$ Ar$^+$ cm$^{-2}$. An ion dose of circa $10^{16}$ Ar$^+$ cm$^{-2}$ obliterated the pattern completely, giving a haze of randomly scattered electrons typical of an amorphised surface (between 25 and 50 Å of material was removed). These results seem to be consistent with those of Townsend and Gotz (quoted in the previous section), despite the differences in experimental set-up.

In early ion-etching experiments, scanning the RHEED beam along the edge of etched samples showed that the distribution of surface damage across the substrate was not uniform (in the inherited system, the substrate cleaning position was not centralised in the ion beam). The optimised position (Table 3.2) gave uniform damage along the sample edge, as observed by RHEED.

3.8.3 38.3 keV RHEED STUDY: THERMAL TREATMENT OF VIRGIN & ION-DAMAGED LiNbO$_3$ SUBSTRATES; SURFACE KINETICS (Clues)

Ritz's work suggested that low fluence ion cleaning (of the order of $2 \times 10^{16}$ Ar$^+$ ions/cm$^2$ at 500eV) followed by a short (< 2 hr.) anneal at 650°C produced well-ordered surfaces with reduced carbon impurity and possessing ELS (electron-energy-loss) spectra closely similar to those obtained for UHV-cleaved LiNbO$_3$ surfaces. Unfortunately, long thermal annealing of LiNbO$_3$ in vacuo above 650°C produced drastic changes in the spectra: a lowering of the threshold of optical damage usually resulted, as well as a degradation of stoichiometry and structure (Li out-diffusion, surface reduction, defect generation, and surface stoichiometry changes). Thermal annealing studies were also performed on LiNbO$_3$ by the author: these are reported below.

The LiNbO$_3$ substrates were cleaned in the standard way (no ion etch) and heated in vacuo and in $2 \times 10^6$ Torr of O$_2$. In both cases, the first signs of change in the RHEED patterns occurred at just under 600°C (Fig. 3.11): the sharp RHEED features became slightly fuzzy; background intensity rose; and the "rods" lost some intensity modulation and became more streaky. The effect was more pronounced at 640°C. These results are consistent with the generation of surface disorder, which was probably caused by lithium out-diffusion. Fig. 3.11 also shows the effects of in situ thermal reconstitution on substrate surfaces amorphised by Ar$^+$ bombardment. Periodic features, characteristic of LiNbO$_3$ RHEED patterns, began to reappear between 530°C and 550°C. Surface reconstitution was well under way after 1 hr. at 590°C, and was achieved rapidly at 670°C.
The threshold temperature for the growth of epitaxial LiNbO$_3$ by MBE was reported as 550°C by Betts$^{3,20}$. We have seen that there is some surface reordering of amorphised LiNbO$_3$ just below 550°C. The concurrence of these temperatures suggests that the threshold temperature for epitaxial growth is linked to the threshold temperature for surface mobility of atomic/ionic species. This idea is consistent with a diffusion-assisted layer by layer growth$^{3,56}$. Supportive evidence for the above hypothesis was obtained from the niobium layers used in the penetration depth experiments of Section 3.4: these were heated in situ whilst being monitored by RHEED. A typical RHEED sequence is shown in Fig. 3.12: reordering processes were initiated at about 550°C, and were well advanced at 580°C (after 1 hr. at this temperature, epitaxial, streaky patterns were observed that were very similar in appearance to those of the thermally treated or reconstituted LiNbO$_3$ surfaces). Furthermore, the MBE-grown, epitaxial NbO$_x$ layers of Ch. 5 were smooth and uniform, which is consistent with a layer by layer growth mechanism.

Strictly speaking, the latter experiment only tells us the temperature at which Nb atoms near, or in, the surface become mobile; arriving adatoms from the Nb molecular beam may have enhanced mobility on the growing surface due to their incoming kinetic energy. However, the results of this section make a strong case for claiming that surface mobility is a key factor in the epitaxial growth of lithium-niobium oxides by MBE (as would be expected).

Heavy heat-treatment of the substrates (Fig. 3.11 (d)) or ion amorphisation followed by thermal reconstitution (Fig. 3.11 (i)) tended to give streaky RHEED patterns exhibiting pseudo-cubic symmetry: this supplies a plausible reason for the observed propensity for cubic growth on LiNbO$_3$ substrates "disrupted" in this way.

### 3.8.4 OTHER SURFACE STUDIES

The etch rate of the HF:HNO$_3$ wet-etch described in Ch. 2 was measured for the degreased, z-cut faces of LiNbO$_3$ at room temperature. Various etch times were used: for long etches (> 20 mins.), substrates were simply halfway-dipped in the etch solution; a thick layer of resist was used for short etches (a few minutes). In both cases, a reasonably sharp step could be obtained at the boundary between the etched and unetched regions; the step height was measured using Talystep. The etch rate was between 0.6 and 0.8 μm/hr for the -ve face and rather less for the +ve face (< 40 Å/hr.). SEM and Talystep showed that the +ve face remained smooth, but the -ve face experienced severe surface roughening.

Auger depth profiles are shown in Fig. 3.13 for a +z-cut LiNbO$_3$ substrate at various processing stages: the spectra were compared with a LiNbO$_3$ standard in each case. The main observations are summarised overleaf.
FIGURE 3.13:
AUGER COMPOSITION DEPTH PROFILES FOR LiNbO$_3$
SUBSTRATE AT VARIOUS PROCESS STAGES

- (a) LiNbO$_3$ substrate, as supplied (degassed)
- (b) After standard pre-loading chemical etch (HF:HNO$_3$)
- (c) Just prior to deposition (full vacuum preparation, including ion clean and thermal reconstitution as for Fig. 3.11)

Li/Nb ratio in substrate

Data obtained at Loughborough Consultants Ltd.
Degreased LiNbO$_3$ substrates were 5→8 atomic % Li-deficient down to a depth of about 750Å, probably owing to the chemical polish used in their preparation by manufacturers.

After the pre-loading wet etch (see Table 2.1), Auger showed a Li/Nb ratio closer to that of the standard; at depths exceeding about 1000Å, the results agree with (a) within the error bars. There was some evidence for a surface Li enrichment of about 6 atomic %.

After ion-cleaning (dose = $10^{16}$ Ar$^+$/cm$^2$) and thermal reconstitution (670°C, 1 hr.), the composition profile in the bulk of the substrate closely resembled that of the wet-etched LiNbO$_3$. However, there were indications of a loss of Li from the top 150Å or so (perhaps due to Li out-diffusion), and a large carbon signal (circa 10 atomic %) was registered in the top 10Å or so.

Owing to limited space, only a representative selection of the Auger data, the Li/Nb ratios, is given in the profiles of Fig. 3.13: other plots, such as Nb/O ratio versus depth, add little further information. The conclusion, then, is that rigorous substrate preparation results in a satisfactory near-surface stoichiometry for the LiNbO$_3$ (except for carbon contamination) and, perhaps, a slight Li deficiency.

### 3.8.5 PRE-DEPOSITION CLEANING OF LiNbO$_3$: POLICY DECISIONS

Ion cleaning, followed by a suitable thermal anneal, may reduce most contaminant species on LiNbO$_3$ substrate surfaces: but if 3keV Ar$^+$ ions are used, residual stoichiometry changes (oxygen deficiency) and ion damage may be induced, and these are detrimental to subsequent epitaxy. Low ion doses should therefore be administered: an ion dose of $<1.0 \times 10^{15}$ Ar$^+$/cm$^2$ (100 μA/cm$^2$ for 2s in the optimised ion etching position) does not produce serious lattice damage, but only removes about 1.4 Å of surface material. The quality of the wet etch therefore becomes even more important: i.e. the epitaxial growth of single-crystal niobium oxide and the rhombohedral phase of LiNbO$_3$ will be more likely on substrates that show good SIMS and RHEED on first inspection, since these will not require heavy ion cleaning$^{[20]}$. The deposition work reported in Ch. 5 confirmed that the best quality niobium oxide layers were grown on substrates that had had little, or no, ion treatment.

The optimised ion etching position (35° angle of incidence) was used: it gave better results than normal incidence etching (better etch uniformity and greater sputter yield; also, the incorporation probability for Ar$^+$ was probably lower, and ion damage would be confined nearer to the surface). Also, a close check was kept on carbon contamination, especially after long thermal treatments. Finally, the RHEED results showed that processing LiNbO$_3$ surfaces in vacuo to temperatures in excess of about 650°C produces surface disorder, and should be avoided if at all possible.
3.9 FUTURE WORK; CONCLUDING REMARKS

The majority of published work on the vacuum behaviour of LiNbO$_3$ has been concerned with the bulk properties, rather than with the surface, or thin films. The quality of the RHEED data obtained for LiNbO$_3$ in this project, and the good agreement of derived lattice constants with the published values, suggest that a viable technique has been developed for the analysis of crystal structure and cleanliness for insulating substrates and overlayers. A list of suggestions for future work is now given:

(i) Use of RHEED to determine surface lattice parameters and the degree of lattice mismatch for new substrate materials, and also for the exploration of successful surface preparation techniques for new substrates;

(ii) RHEED studies during ion etching of hot substrates (> 400°C), to compare the ion damage with that of room temperature etching (it may be that the ion-impact-generated defects will tend to move into the bulk of the crystal, or to the surface, or they may anneal out altogether);

(iii) Further RHEED studies during thermal treatments, and the use of resistance heating of the probe to avoid electron noise;

(iv) RHEED studies during layer growth by MBE.

The present ion-cleaning facility should be replaced by one which induces less lattice damage. The best situation is where the ion damage is largely restricted to the top monolayer of the substrate (from which the bulk of the sputtered species originate anyway). This should occur at ion energies < about 1 keV$^{3,51}$, but if too low an ion energy is used the sputter yield may drop below unity. The optimum voltage for most materials is in the vicinity of 300eV$^{3,51}$. Less argon incorporation might be expected at lower voltages, but, owing to reduced sputter yields, a much higher beam current is needed (between 0.1 and 1 mA/cm$^2$): an ion source is therefore required that can provide beam energies down to a few hundred eV whilst giving a high beam current. The improvement in ion-etching uniformity and yield obtained upon optimising the 3keV system shows that similar care should be taken with any new etch unit (to characterise the etch dependence on incidence angle, beam energy, etc.).

(iv), however, is probably the most appealing area of further investigation. The use of RHEED during the MBE growth of GaAs and Si$^{3,12,13}$ has led to improved process control and considerable advances in the understanding of the MBE growth dynamics for these materials. The technique could give information on the nucleation mechanisms and kinetics of thin-film growth in the lithium-niobium-oxygen system, and may provide a means of growth rate calibration. It would also give an indication of when epitaxy was not going to plan, thereby saving time, and could help to pinpoint growth conditions or layer thicknesses for which the growth mode changes. However, there are practical obstacles to this in the present
UCL system: for example, an unsuitable system geometry and the proximity of other electron sources.

MBE has been used to grow epitaxial niobium oxide (Ch. 5) and lithium-niobium oxide\textsuperscript{[1-3,20]} layers. The provision of high resolution RHEED analysis at every stage of the process was essential to this work: routine evaluation of surface cleanliness and order is of paramount importance in ensuring good epitaxy. It was also hoped that RHEED would provide information regarding surface kinetics, changes of phase, reconstructions, twinning, and surface morphology: this data would then be linked to the various processing stages, or to the epitaxial growth itself. The 50 keV RHEED system described in this chapter has already fulfilled several of these expectations, and has yielded original data in the niobium oxide growth studies (see Ch. 5).

In conclusion, then: the work described in this chapter constitutes the first ever thorough characterisation of LiNbO\textsubscript{3} by RHEED, and has led to a working knowledge of the effects of heat treatment and 3keV argon ion bombardment cleaning on LiNbO\textsubscript{3} substrates. 550°C has been pinpointed as the likely threshold temperature for the activation of surface or near-surface diffusion.
REFERENCES


91


3.23 Dr. P.J. Dobson, Philips Research Laboratories, Redhill, Private Correspondence; now of University of Oxford, Dept. of Engineering Science.

3.24 I.T.L. Ltd., Castleham Road, St. Leonards-On-Sea, E.Sussex.


3.46 M. Abbott, "Computer assisted analysis of RHEED patterns", 3rd Year project report, 1988; further information available from C.W. Pitt, Dept. Electronic and Electrical Engineering, University College London, Torrington Place, London, WC1E 7JE.
3.49 Loughborough Consultants Ltd., commissioned work, unpublished.
3.50 Oxford Applied Research, Data Sheet: "Sputtered rates for 500eV Argon ions at 1mA/cm²", Crawley Mill, Witney, Oxfordshire, OX8 5TJ.
3.53 Calculated from data and equations in: B. Smith, "Ion Implantation Range Data for Silicon and Germanium Device Technologies" (Harwell).
CHAPTER 4
THE PROVISION OF OXYGEN IN Li-Nb OXIDE MBE:
AIMS, DEVELOPMENTAL WORK, SUMMARY OF RESULTS

4.1 INTRODUCTION

Previous work\cite{41} has shown that lithium-niobium-oxide MBE has a persistent problem with oxygen stoichiometry: the growth of oxygen-saturated layers was impossible in the inherited MBE system, all layers being oxygen deficient to varying degrees and requiring post-deposition thermal oxidation to bring them to (or close to) oxygen saturation. It will be seen in Ch. 5 that the problem is even worse for niobium oxide MBE: this could be due to factors such as the growth kinetics, or simply the greater proportion of oxygen that is needed (the relevant kinetics are discussed in a later section of this chapter). For these reasons, new approaches to the provision of oxygen were considered from the outset of this project. The first solution attempted was to simply increase the $O_2$:Nb flux ratio impinging on the substrate. Also, system modifications were executed, aimed at purification of the oxygen beam (to reduce carbon contamination in the film), and to stabilise oxygen flux. Later, alternative forms of oxygen were considered, such as ionic and atomic beams: the results of studies performed with a new atomic source form the latter part of the chapter.

4.2 MOLECULAR EFFUSION SOURCES

4.2.1 ORIGINAL OXYGEN SOURCES

Originally, the molecular oxygen was supplied by a simple aperture ("sonic nozzle"\cite{41}). The oxygen molecules entered the chamber at thermal velocities by simple molecular effusion. However, this type of beam proved to be highly divergent, obeying a $\cos \theta$ variation (see Fig. 4.1(a)). The need to increase the oxygen flux rate at the substrate without raising the oxygen chamber pressure led to the use of a microcapillary array inlet. Betts\cite{41} concluded that this gave a highly collimated beam, and installed a differential pumping line opposite the array in order to remove the bulk of the "unused" oxygen (the cause of serious difficulties during growth, Appx. 4.1). At the same time, the vacuum conductance between growth and evaporator regions was reduced in order to minimise oxygen overpressure in the vicinity of the evaporators.

4.2.2 EFFUSION SOURCE AND PUMPING: ASSESSMENT AND MODIFICATIONS

The "differential pumping line" concept was ineffectual in this system. Calculations show that, even if the line orifice were a perfect molecular sink, it could at best only halve
FIGURE 4.1 (a):

COMPARISON OF MOLECULAR FLUX DISTRIBUTIONS FROM VARIOUS GEOMETRICAL SOURCES

(i) IDEAL APERTURE (ii) SINGLE CANAL (iii) IDEAL CAPILLARY ARRAY

\[ N(\theta) \approx N(0) \cos \theta \]

source pressure, \( p_0 \)

\[ R_{\text{eff}} = a \sqrt{N_t} \]

\( a = \) radius of tubelets \( N_t = \) total no. of tubelets

FIGURE 4.1 (b):

SCHEMATIC DIAGRAMS OF ORIGINAL AND MODIFIED MICRO-CAPILLARY ARRAY ARRANGEMENTS

Original system Modified system
the pressure in the growth region. In fact, a reduction in chamber pressure of only 20% was observed when the line was opened with the oxygen beam pointing straight at it. The liquid nitrogen shrouds had a greater effect: they initially reduced the oxygen pressures by between 20% and 50%, but became less effective as pressure and run time were increased. Extensive cryo- or turbo-pumping would be required in the probe region to make higher growth pressures feasible at the substrate surface in the existing system.

A detailed study of the various modifications made by the author is given in Appx. 4.1. The main points are now presented.

(1) By making pressure measurements across the oxygen beam, it was found that the microcapillary array gave a more divergent beam than was supposed by Betts, especially at high pressures. A bellows system was therefore constructed (see Fig. 4.1(b)) to bring the array closer to the substrate and thereby increase beam uniformity and flux per unit area.

(2) In the inherited system, the reliable monitoring of oxygen had been problematic. There were no means of monitoring beam pressures directly, and a number of factors in the chamber could dramatically influence the oxygen pressure readings during a run: there was thus an urgent need for reliable flux calibrations, and for the measurement of the oxygen "backing" (or "feed") pressure (i.e. the pressure behind the array), termed \( p_o \). A Baratron sensor (capacitance manometer) was therefore installed behind the oxygen source (with a suitable "buffer" chamber for the diaphragm and array, Fig. 4.1(b)): this improved run to run reproducibility, and made possible a thorough check of the "effusion theory" applied to the array (Appx. 4.1). Background pressure measurement capabilities were retained and extended.

(3) An attempt was made to reduce the impurities (especially carbon-bearing species) in the oxygen beam, e.g. by using a purer source of oxygen and installing a flush facility on the gas line.

### 4.2.3 RESULTS WITH MODIFIED EFFUSION SOURCE

After the above modifications had been completed, three different methods were devised for estimating the molecular oxygen beam flux:

(a) The chamber pressure method of Appx. 4.1.3;
(b) Using the measured source pressure \( p_o \) in the effusion equations of Appx. 4.1.2;
(c) From a direct measurement of beam pressure with a calibrated mass spectrometer.
FIGURE 4.2 (a):
TYPICAL MASS SPECTRUM TAKEN ON AXIS OF CAPILLARY-ARRAY OXYGEN SOURCE

Spectra have been corrected for background vacuum species.
Spectra for original and modified arrays were similar: both had approx. 12% total impurities.

FIGURE 4.2 (b):
MASS SPECTRUM TAKEN ON AXIS OF ATOMIC RADICAL SOURCE

Dotted line: peak height after O$_2$ gas line left unpurged for 4 days.
Discharge "on".
The calculations and results are presented in full in Appx. 4.1. All methods concur to within a factor of three. The O₂ beam fluxes quoted in this thesis are generally as calculated from (a), unless otherwise stated.

The beam spectra for the gas issuing from the array were virtually identical before and after the bellows redesign. In both cases, the total impurities amounted to about 12% of the beam, though some of this "impurity" may have originated from the filament and ion cage of the mass spectrometer used for the measurement. A typical spectrum, corrected for vacuum background, is shown in Fig. 4.2 (a). The main improvement was in the 28 peak (N₂⁺, CO⁺). The mass 4 peak (He⁺) was due to leak-testing.

Despite the above modifications, it still proved impossible to deposit oxygen-saturated LiNbO₃ or Nb₂O₅ using molecular oxygen (see Ch. 5). The low sticking coefficient of molecular oxygen during growth led to a great deal of unreacted gas in the system: at very high oxygen beam pressures, this severely interfered with the operation of the evaporators, causing loss in emission (and hence flux), tripping of over-pressure protection circuits, and flux instabilities; probe and evaporator filament lifetimes were seriously reduced, and the beam collimation of the array was degraded. These factors prevented the use of oxygen pressures in excess of a certain value (Ch. 5). Run reproducibility had been vastly improved, and much larger O₂:Nb beam ratios could be maintained during growth; however, the oxygen deficiency problem had persisted to virtually the same extent as with the original array.

4.3 ATOMIC OXYGEN: A SOLUTION TO OXYGEN DEFICIENCY IN OXIDE MBE?

4.3.1 INTRODUCTION; Reasons for choosing an Atomic Source

It is well known that the full oxidation of metals in vacuo by molecular oxygen can be difficult. The work cited above, combined with the sticking coefficient curve of Ch. 5, strongly suggested that the use of molecular oxygen was unlikely to give oxygen-saturated films in the lithium-niobium system by MBE. (In Ch. 5 it will be shown that the best that could be expected using molecular oxygen was thin films (< 50nm or so) of lithium niobate with at least a few atomic % oxygen deficiency, or thicker films of NbOₓ with x < 2.)

It was decided that an alternative means of introducing oxygen into the growing crystal lattice might improve the situation. Most of the options considered could not easily (or cheaply) provide oxygen under ultrahigh vacuum conditions as uniform, collimated, low energy, controllable beams of high flux. Among the options shortlisted were a low-energy ion source, and a cold-cathode discharge source for generating free atomic radicals. The latter was preferred for the following reasons:
(1) ease of design and use, lower bulk, lower cost;
(2) no filament (the ion source would be prone to frequent filament burn-out);
(3) sputtering and ion-induced damage are associated with the use of
   (even low energy) ion sources;
(4) possible substrate charging problems with ion source
   (beam neutralisation requires a further filament);
(5) the use of atoms means that the O-O bond does not need to be broken at
   the growing surface;
(6) high sticking coefficients have been demonstrated for oxygen atoms
   during the oxidation of metals (see below).

Looking more closely at (6): there is substantial work in the literature reporting
enhanced oxidation of metals and semiconductors by atomic oxygen over its parent molecule.
For example, the sticking coefficient of molecular oxygen ($C_{\text{mol}}$) on silicon surfaces is only
0.02, even at 1500K, whereas that of the oxygen atom ($C_{\text{atom}}$) is close to unity\cite{2}. Also, the
oxidation probability of Mo by oxygen atoms is $10^3$ times greater than that of $O_2$\cite{3} under
conditions not very different to those used in the MBE system (650°C, 2 mTorr). In addition,
Clampitt\cite{4,5} demonstrated that thick layers of Cu and Ag undergo a substantial degree of
oxidation throughout their bulk, even near room temperature, when exposed to a beam
containing a few % of atomic oxygen. This work is discussed more fully later. On the basis
of these results, an atomic source was constructed for use in the MBE system in an attempt
to improve oxygen stoichiometry in situ. The principle and construction of the source are
described in Section 4.3.3.

4.3.2 AIMS OF WORK WITH ATOMIC SOURCE

(1) Design and commission an appropriate atomic oxygen source.
(2) Test source characteristics; find a suitable working regime for the UCL MBE system.
(3) Perform growth runs with the atomic source "on" and "off" (but under otherwise
   identical conditions) to determine whether or not the atoms enhance the oxygen
   content of the MBE-grown layers.

The results of (2) showed that the gun could not be operated in the MBE system at
high atomic flux rates. Attempts were therefore made to measure the oxygen atomic flux
emitted by the source at low discharge currents: this data helped to rationalise the results of
(3) [growth Runs 14 and 15], in which the composition of grown films remained virtually
unalterted when niobium oxide was deposited with and without the oxygen atomic flux (all
other conditions constant). The data obtained at low discharge currents might also indicate how
much greater an oxygen flow rate would be needed to grow the higher oxides. A full
discussion of these results is given in Section 4.4.
FIGURE 4.3 (a) SCHEMATIC OF DISCHARGE SOURCE

(b) PHOTOGRAPH OF SOURCE
4.3.3 CONSTRUCTION AND OPERATION OF THE ATOMIC SOURCE

The idea of using a source of atomic oxygen was arrived at in association with Oxford Applied Research Ltd.\(^{146}\), who were commissioned to design and build the entire unit (Model Ref. 1810, Fig. 4.3). A magnetically-confined, cold-cathode, Penning-like source was built, giving a practical, rugged device. The absence of filaments was an important consideration at the high oxygen pressures used (> \(10^5\) Torr beam pressure, with perhaps more than 10 times this pressure in the gun). A discharge was struck at high voltage (5kV) between a coaxial mesh anode and hemi-cylindrical cathodes; the latter were earthed. The oxygen atoms were generated in the resulting plasma. Cascade ionisation was enhanced by a crossed magnetic field provided by Co/Sm UHV-compatible magnets within an iron yoke. The cylindrical discharge illuminated a beam-exit aperture of 8mm \(\times\) 12.5mm, which was fitted with an electrostatic ion trap to prevent the escape of charged particles from the discharge (< \(10^8\) A was measured in the beam by a Faraday Cup when the source was operated at full power). All the discharge elements (apart from the magnets) were made from niobium to minimise contamination of the grown film by species sputtered inside the gun, and the discharge was initiated in ultra-pure oxygen, admitted via a leak valve arrangement.

The atomic flux was expected to depend on the discharge current, which in turn was determined by the oxygen flow rate through the source. The atoms had a line-of-sight path to the sample which, in the MBE system, was approx. 6cm from the front end of the source. The angular spread of the beam was quoted as being < 1° at this distance, giving a rectangular beam profile at the sample of 9mm \(\times\) 14mm for the atoms. However, our studies showed that this may be an underestimate (see later). The source therefore produced a slightly divergent beam of oxygen neutrals, mostly atoms and molecules (the molecules preponderant), with some of the neutrals in various excited (but not ionised) states. The atomic species in the beam shall henceforth be referred to simply as "the oxygen atoms", or as "free atomic radicals" in accordance with the manufacturer's literature\(^{146}\).

Fig. 4.2 (b) shows a mass spectrum taken on the axis of the atomic source at a similar beam pressure to the spectrum obtained for the array. Again, the background vacuum peaks were subtracted. Compared to the array, the impurities were greatly reduced, especially the mass 1 (H\(^+\)) and 44 (CO\(_2\)\(^+\)) peaks. The total impurity was < 4%, some or all of which may have been due to the interaction of the oxygen with the mass spectrometer filament, etc. The height of the 28 peak increased when the line was left for a time, unflushed. The carbon dioxide peak, though, was very small compared to the 32 peak (ratio was < 0.7%). The carbon observed in grown films, both before and after the atomic source was installed, therefore probably originated from other sources, notably the evaporator filaments and probe filament/ceramics, which caused large increases in the CO\(_2\) peak during growth. The probe filament assembly appeared to be the main culprit (see Ch. 5). Spectra obtained for the atomic source operated at higher pressures (e.g. the pressures used for Runs 14 and 15, below) were
very similar to Fig. 4.2 (b), and had comparable impurity levels. The spectra were hardly affected by switching the discharge "off": no change was observed in the 16 (O*, O₂*) peak height; the impurity peaks dropped, but only very slightly.

4.4 RESULTS OF MBE GROWTH RUNS WITH THE ATOMIC SOURCE: A PROBLEM!

The atomic source was designed to give a flux rate of > 2 x 10¹⁴ oxygen atoms/cm²/s, which was well above the estimated flux required for the growth of Nb₂O₅ (assuming unity sticking coefficient for the atoms). However, this flux rate was only obtained at the largest discharge currents, Iₐ (= 50mA). The maximum oxygen gas throughput that could be used in the MBE system during growth (while maintaining steady operation of the evaporators and a usable filament lifetime) gave ≈ 5 x 10⁶ Torr in front of the source (see Ch. 5). This corresponded to an Iₐ of about 3mA. If the atomic flux is proportional to Iₐ, then 3mA would correspond to an atomic flux rate of only ≈ 1.2 x 10¹³ atoms/cm²/s.

Now, Run 14 and 15 layers were grown under the following conditions:

RUN 14
- Molecular oxygen flux rate: 3.6 x 10¹⁴ O₂/cm²/s
- Niobium flux rate: 4.5 x 10¹³ Nb/cm²/s
- O₂:Nb Ratio: 80
- Substrate: 610°C, α-alumina
- NO OXYGEN ATOMS IN THE BEAM.
- Measured film composition (AES): NbO₁₂₂

RUN 15
- Molecular oxygen flux rate: 3.8 x 10¹⁴ O₂/cm²/s
- Niobium flux rate: 4.9 x 10¹³ Nb/cm²/s
- O₂:Nb Ratio: 77
- Substrate: 610°C, α-alumina
- OXYGEN ATOMS: 3 mA discharge
- Atom flux (first estimate) = 1.2 x 10¹³ O atoms/cm²/s
- Measured film composition (AES): NbO₁₂

Assuming the sticking coefficient of the oxygen molecules (Cₐₒ) is the same in each case, and that the sticking coefficient of the atoms (Cₐₐ) is unity, we can estimate the expected composition for Run 15. Cₐₒ for Run 14 was 0.0153, so that Run 15’s composition should be:

\[
[(0.0153 \times 3.8 \times 10^{13}) + (1.2 \times 10^{13})] + (4.9 \times 10^{13}) = 1.43 \quad \text{(i.e. } \text{NbO}_{1.43}\text{)}
\]  
(Eqn. 4.1)
Despite the low atomic oxygen flux rates, then, there should still be an increase in oxygen content detectable by Auger Electron Spectroscopy, AES (which is accurate to ± 5% or so). However, the compositions for Run 15 were about the same as those for Run 14. Growth conditions were very well defined for these runs - they were among the most reproducible ever performed in the system - so it is unlikely that the conditions were set up incorrectly. Also, for Run 15, one sample was placed so that only two thirds of it was exposed to that part of the beam containing atomic oxygen: AES analyses were performed at several points across the sample and no difference in composition was observed.

Putting aside for a moment the possibility that the assumptions made in the above calculation are not valid, the most plausible explanation for this null result is that fewer atoms than predicted were being produced at the low discharge currents used. It therefore became important to measure the atom flux delivered to the substrate in the 3mA to 5mA regime, rather than rely on a value extrapolated down from 50mA. This necessitated the work at Oxford Applied Research, which is now reported.

4.5 MEASUREMENT OF OXYGEN FREE RADICAL FLUX

4.5.1 INTRODUCTION

Sources similar to the one described in Section 4.3.3 have recently been used to oxidise cold Cu and Ag films; the resulting data has yielded estimates of the issuing atomic fluxes. The same facilities were commissioned to make atomic flux measurements on the UCL atomic source. Silver films were vacuum-deposited on the crystal of a quartz-crystal thickness monitor (Intellemetrics, Model IL002). The monitor head was placed on the axis of, and 1.5cm from, the source, thus intercepting the beam and recording the mass gain during oxidation. Both oxygen and hydrogen gas were available for the discharge, so that the silver could be oxidised or reduced as required. This gave a means of cleaning contamination from the surface and removing native oxide by cycling the sample through alternate oxidation and reduction runs. The reduction could also be employed as a means of verifying that real oxidation had taken place. Background pressures in this system were typically between $10^{-5}$ and $10^{-6}$ Torr. The experiments reported below were the first to be conducted at low atomic flux rates: all previous work had avoided low flux-rate measurement, mainly because various effects (such as instrumental drift and surface recontamination) make such experiments difficult. Further details of the technique can be found in the references.

4.5.2 CALIBRATION OF THE THICKNESS MONITOR SYSTEM

(a) Atomic flux. The thickness monitor had a calibration constant of: $1.00 \text{ Hz} = 0.1 \text{ nm}$
of material of unit density (this was derived from standard thickness monitor theory \(^{14,7}\) and checked by calibration). The constant was used to calculate the thickness of the silver films deposited. For the uptake of oxygen atoms, it yielded the figure:

\[
1 \text{ Hz/s} = 3.74 \times 10^{14} \text{ absorbed oxygen atoms/cm}^2/\text{s} \quad \text{(Eqn. 4.2)}
\]

(b) **Temperature Sensitivity.** A change of 2.5 Hz in the oscillation frequency of the thickness monitor crystal corresponded to a change in temperature of 1°C (measured). Since 1 Hz = 0.1 nm of material of unit density, then 1 nm = 4°C (unit density layer). Temperature effects are apparent in the graphs below; these were typically 10 → 50 Hz, so that temperature changes were not severe in these experiments (< 20°C).

### 4.5.3 MEASUREMENTS:

**VACUUM BACKGROUND & SURFACE-SATURATION EFFECTS**

A number of problems had to be appreciated in performing a flux-measuring experiment at low atomic flux rates in a low-vacuum system of this kind. The most important of these were that the thickness monitor was prone to drift, and that contamination effects could arise from vacuum background species. Neither of these would be significant at high flux rates, since they then account for a relatively small fraction (typically 5 → 10%) of the total incident flux on the crystal. In most cases, however, the layer of contamination on the surface of the metal film had to be removed before oxidation could proceed, even at high flux rates.

The background pressures were typically 5 x 10\(^{-6}\) Torr, which corresponded to an arrival rate of contaminants\(^{6,8}\) of approx. 3 x 10\(^{15}\) contaminants/cm\(^2\)/s, a value much larger than the atomic arrival rates (typically \(\approx 10^{14}\)/cm\(^2\)/s maximum). It follows that the sticking coefficients of the contaminant species were \(< 1\), since oxidation effects could be observed (see later).

The only means of estimating the rate of contamination was to observe the drift rate for a fresh metal film on the thickness monitor crystal at stable temperature and with the atomic source switched off. This was typically 0.7 Hz/min, but was subject to variations from run to run. This corresponded to a gain of 5 x 10\(^{12}\) contaminants/cm\(^2\)/s (assuming an average mass of 20 for contaminants, and that the drift was entirely due to contamination). It was supposed that, during oxidation, these species (mostly carbon- and hydrogen-based) would pick up, on average, about one oxygen atom each and consequently be released from the surface as volatiles. Initially, then, both the mass of the contaminant and the mass of the atomic radical were "lost" as far as the thickness monitor was concerned, giving an initial dip in the curve (as observed). Once the surface contamination had been "consumed" in this way, and oxidation of a clean surface had commenced, the layer would gain mass due to reaction of the
metal layer with the arriving oxygen atoms. However, contaminants from the vacuum background would continue to bombard the surface and could be responsible for removing some of the arriving atoms. It was estimated that atomic arrival rates of $\approx 5 \times 10^{12}$ oxygen atoms/cm$^2$/s would probably just be registered - rates less than this would be lost in the "drift". The correction to the atomic flux for the drift was, fortunately, usually small, so that if any of the assumptions above are false, the results are not unduly affected.

Two other effects to consider were: recombination on the metal/growing-oxide surface, especially at high flux rates; and diffusion-controlled surface saturation by atoms. The recombination effect could not be quantified in this system, but simple calculations of surface coverage showed it was probably not serious at the low flux rates. An important fact concerning the saturation effect was that the total time for a metal layer of given thickness to fully oxidise at a given (high) flux rate decreased rapidly with increasing substrate temperature$^{[4,4.5]}$. This observation was consistent with a diffusion-limited oxidation process occurring at the higher flux rates: it was supposed that, when the incident atomic flux rate exceeded a certain value (= rate of uptake of oxygen atoms from the surface by diffusion into the bulk at that temperature), then the oxidation rate was constant and largely independent of further increases in flux rate (hence the term "saturation" effect). Clearly, if dynamic monolayer adatom coverage was being approached, then further atomic arrival would have little effect on the rate of oxidation, and recombination effects would take over; only an increase in temperature (which speeds up diffusion from the surface into the bulk) could then bring the higher fluxes into play.

The contamination, recombination and diffusion-limiting effects all lead to underestimation of the oxygen-atom flux-rate, especially at the highest and lowest rates. Also, changes in power to the gun caused temperature changes in the thickness monitor crystal (even when water-cooled), giving rise to a transient response in the frequency: these can be seen in the graphs below. Slow changes in temperature gave rise to drift. It would be too involved to discuss fully the techniques used to filter the required information from the graphs, but the notes below and an inspection of the figures show the general features of the procedure.

**4.5.4 GRAPHS OF MASS GAIN VERSUS TIME: ATOMIC FLUX RATES**

The general shape of the oxidation curve (mass gain of layer, or $|$oscillation frequency$|$ of crystal, versus time) could be easily explained in the light of the above discussion. The reader should refer to Fig. 4.4.

1. *Oxygen gas "off"; atomic source "off":* background drift due to instrumental drift plus arriving contaminant matter.
2. *Oxygen gas (only) "on"* - to flush system and determine if molecular oxygen causes oxidation. Little or no effect observed.
Atoms "on" - initial drop due to ashing of surface contaminants and their removal from the surface as volatiles + the drop due to a rise in temperature of the crystal (crystal had a line of sight to the warm gun and discharge).

Temperature stabilised; contaminant layer removed - oxidation began.

Eventually, a maximum rate of oxidation was achieved - this was used as the best estimate of incident atomic flux. The drift slope in (1) or (7) was subtracted from the slope measured here to yield a corrected, "observed" oxygen flux rate. This was still probably an underestimate, however, due to the recombination and diffusion-limited processes discussed above.

Mass gain slowed; nearly all the metal was oxidised.

"Bulk saturation": oxidation process complete. The arriving atoms now either recombine or react with contaminants. The observed drift was therefore probably due to instrumental &/or temperature drift (though residual oxidation may also be occurring).

Atoms "off" - upwards blip in frequency curve due to crystal cooling. After a while, (1) returns. In many graphs, this drift was larger than (7), supposedly due to contaminants now staying on the surface.

Experience of many atomic oxidation runs confirmed this general behaviour. In some cases, the oxidised layer was reduced by using hydrogen in the source: this was done in order to ensure that a real oxidation had taken place (the expected shape of the reduction curve can be inferred from the information given for oxidation, see Fig. 4.4). A re-oxidation was sometimes then performed as a further check: the mass gain observed after the first oxidation could usually be retrieved. In most cases, these reductions and re-oxidations gave good results when the various drift factors were taken into account.

Typical graphs of mass gain (given as a frequency change) versus time are presented for the experiment described above (Figs. 4.5 and 4.6). The corrected maximum slopes of these graphs were used with Eqn. 4.2 to obtain corrected, "measured" atomic oxygen flux rate as a function of discharge current, $I_\alpha$. This data is tabulated in Table 4.1 and plotted in Fig. 4.7. In some of these experiments, $I_\alpha$ was changed during the course of the oxidation. Although rather difficult to achieve this in practice, it was a good way of improving the comparability of the data: different layers often behaved differently, and this procedure eliminated errors due to such variations. However, care had to be taken to perform the changes in $I_\alpha$ before the layer approached full oxidation.

The shape of Fig. 4.7 suggests that surface saturation effects only began to become important between 9 and 17 mA.
FIGURE 4.4: OXIDATION AND REDUCTION OF METAL/METAL-OXIDE FILMS DEPOSITED ON A THICKNESS-MONITOR CRYSTAL: PREDICTED GRAPH SHAPES OF OSCILLATION FREQUENCY versus TIME

OXIDATION OF SURFACE-CONTAMINATED METAL LAYER BY O ATOMS

REDUCTION OF CLEAN OXIDE LAYER BY H ATOMS

MASS GAIN, $\alpha(-\Delta f)$

$t$ = change in oscillation frequency of the quartz crystal which has been loaded with the layer

See text for discussion and annotation.

FIGURE 4.5: OXIDATION OF 810A SILVER FILM BY ATOMIC BEAM (discharge current = 10 mA)

$|\Delta f|$/Hz

"DRIFT"

A = O$_2$ GAS ON
B = O ATOMS ON
C = O ATOMS OFF
P = maximum slope

0 10 20 30 40 50 60

$\alpha(-\Delta f)$

time/min.
FIGURE 4.6: OXIDATION OF 570Å SILVER FILM BY ATOMIC BEAM (discharge current varied)

A, B and C are as for Fig. 4.5

P, Q, R and S are maximum slopes for oxidation at 10, 9, 6 and 4 mA respectively.
FIGURE 4.7: ATOMIC-OXYGEN FLUX RATE VERSUS DISCHARGE CURRENT FOR NEW OXYGEN SOURCE

- Ag film, 29.5 nm thickness; 16°C (approx.)
- Ag 81.2 nm 16°C
- Ag 13.6 nm 16°C
- Ag 69.1 nm 16°C
- Ag 85.2 nm 16°C
- Ag 56.9 nm 16°C

References 4.5 & 4.6:
- Ag film, 14 nm thickness; 16°C
- Ag 29 nm 16°C
- Cu 19 nm 16°C
- Cu 19 nm 90°C

OXYGEN-ATOM FLUX RATE (10^12/cm²/s)

\[ \frac{I_d}{mA} \]
TABLE 4.1: ATOMIC OXIDATION DATA FOR SILVER AT ROOM T.

<table>
<thead>
<tr>
<th>Silver Layer Thickness (Å)</th>
<th>$I_d$ (mA)</th>
<th>Corrected, max. slope (Hz/s)</th>
<th>O flux rate ($10^{19}$/cm²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Layer 1</td>
<td>136</td>
<td>2.2</td>
<td>0.018</td>
</tr>
<tr>
<td>Layer 2</td>
<td>295</td>
<td>10.0</td>
<td>0.235</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.4</td>
<td>0.035</td>
</tr>
<tr>
<td>Layer 3 †</td>
<td>569</td>
<td>9.0</td>
<td>0.230</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.0</td>
<td>0.111</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.0</td>
<td>0.0058</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10.0</td>
<td>0.303</td>
</tr>
<tr>
<td>Layer 4</td>
<td>852</td>
<td>9.4</td>
<td>0.203</td>
</tr>
<tr>
<td></td>
<td></td>
<td>17.2</td>
<td>0.303</td>
</tr>
<tr>
<td>Layer 5</td>
<td>691</td>
<td>9.4</td>
<td>0.171</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.0</td>
<td>0.075</td>
</tr>
<tr>
<td>Layer 6</td>
<td>812</td>
<td>10.0</td>
<td>0.375</td>
</tr>
</tbody>
</table>

† Sample was 25% closer to the source.

4.6 DISCUSSION OF FLUX RATE RESULTS; THRESHOLD EFFECT

4.6.1 THRESHOLD EFFECT AT SMALL DISCHARGE CURRENTS

The atomic oxygen flux rate data in Fig. 4.7 is plotted as a function of the discharge current, $I_d$; this includes points at 50mA calculated from the work by Clampitt[44,45]. The general shape of the curve at high atomic flux rates is consistent with the surface saturation effect discussed earlier. It is also noticeable, however, that the flux appears to tail off at low $I_d$ (< 5mA or so). The reliability of the atomic flux data (especially near the origin) must be viewed with caution; but, given that the proposed curve is correct, two possible explanations are proposed to explain this effect:

(a) some atomic flux is "consumed" by bombarding contamination, as described in Section 4.5.3 (this effectively redefines the origin of the graph);

(b) a "threshold" (or flux-limiting) effect for atomic generation is operating at low oxygen throughputs.

A "threshold" effect adequately explains both the observed shape of the graph and the null result of Run 15. The contamination theory is less convincing. There are four reasons for this.
The shape of Fig. 4.7 near the origin is more like a "tailing off" than a straight line with a negative intercept (representing atomic flux removed by contaminant species). Of course, it may be that some combination of the two effects is occurring.

An "intercept" can be estimated by extrapolation of the graph, giving a value in the region of $2 \rightarrow 4 \times 10^{13}$ O atoms/cm$^2$/s. This is much larger than the value calculated from the drift rate in Section 4.5.3.

If the contamination hypothesis is accepted, the estimated "true" flux for Run 15 in the MBE system was $3 \times 10^{13}$ atoms/cm$^2$/s or greater, more than twice the value estimated in Section 4.4. It is unlikely that this atomic flux would not give an observable increase in oxygen content of the Run 15 layers (the atomic sticking coefficient would have to be remarkably low, $< 0.02$).

A plausible mechanism has been found for the threshold effect (see Section 4.7 and Appx. 4.2).

A further contribution to the null result of Run 15 comes from an observed dependence of atomic flux per unit area on source-sample distance. The flux rates measured above should be extrapolated to the MBE growth position (source-sample distance = 6cm): a drop in flux/cm$^2$ of 40% could be caused by this effect.

### 4.6.2 RE-EVALUATION OF RUN 15

When $I_d$ is $2 \rightarrow 3$ mA, the atomic flux (as estimated from the oxidation experiments) is $= 4 \times 10^{12}$ O atoms/cm$^2$/s. This flux is unlikely to give an observable difference in oxygen content between Runs 14 and 15, as measured by AES. The maximum change in the layer composition would be: NbO$_{1.20}$ $\rightarrow$ NbO$_{1.24}$ (which includes a correction for the loss in flux/cm$^2$ with source-sample distance). This change could be swallowed up in the estimated error bar for the AES measurement ($5 \rightarrow 10\%$), and still leaves leeway for flux underestimation. It may therefore be concluded that the only likely explanations for the null result of Run 15 are:

(a) An unexpectedly low sticking coefficient for O (C$_{O_d}$) during growth;

(b) A non-linear relationship between $I_d$ and atomic flux, in which the flux tails off at low $I_d$. (This was termed the threshold effect.)

It might prove possible to confirm (b) more directly, by repeating the flux measurement experiments in a UHV system for which the low $I_d$ data would not be complicated by contamination effects. Such experiments could not be performed, but a mechanism for the threshold effect is discussed in Appx. 4.2.
As regards possibility (a), \( C_o \) would have to be less than about 0.14 in Run 15 in order for the compositional change of the layer to fall within the Auger error bar. Given the high reactivity of Nb to oxygen (see Ch. 5), this seems rather unlikely at the temperatures used during MBE growth (> 600°C), especially as sticking coefficients tend to increase with temperature in this range\(^{62-45}\) and, at 600°C, enhanced diffusion should also improve oxygen uptake. However, although the oxidation of metal layers at room temperature by oxygen atoms has been demonstrated, this work involved Ag and Cu layers, and no experiments were performed with Nb. It would therefore be foolish to discount altogether the possibility of a low atomic sticking coefficient during MBE on the basis of data acquired from bulk oxidation experiments conducted in different metals under different conditions. It is clear from the oxidation graphs, however, that the concomitant molecular oxygen in the "atomic" beam did not cause appreciable oxidation of the Ag at the temperatures used, while the atomic species in the beam did (nor was the oxidation by the atoms impaired by the molecular oxygen in any obvious way). The above work therefore shows, at the very least, that free atomic oxygen radicals can bring about appreciable oxidation in situations where molecular oxygen cannot.

### 4.7 CONCLUSIONS REGARDING THRESHOLD MECHANISM

The processes occurring in the gun are complex (Appx. 4.2). The source and plasma are not sufficiently understood to permit complete assessment of the production of atomic oxygen. For example, quantitative predictions of the threshold effect would require that the energy spectrum of the electrons in the atomic generation region be accurately known; the precise effects of the magnetic field on the electron trajectories would also have to be determined. However, all qualitative considerations in this chapter (and in Appx. 4.2) lean towards a threshold effect; the existing quantitative data is in support. The "threshold" effect is, in fact, merely a result of the low efficiency with which atoms are produced in the plasma at low discharge currents. It is evident that the gun must be run at high pressures (i.e. low discharge voltage, high discharge current) for efficient atomic production.

### 4.8 FURTHER INVESTIGATIONS INVOLVING THE ATOMIC SOURCE

#### 4.8.1 INTRODUCTION

The above experiments showed that the niobium oxide grown in the MBE system using the new atomic source would not be expected to show an increase in oxygen content. This was because there was too low an atomic flux in the beam. The only option available at this late stage of the project was to perform oxidation experiments with the atomic source ex situ, to see if high oxygen atom flux rates could enhance the oxidation of layers already grown by MBE. It was encouraging to find that, from these "static" experiments, some insight could be gained into the kinetics controlling the uptake of molecular and atomic oxygen in niobium oxide.
4.8.2 EXPERIMENTAL DETAILS; RESULTS

The oxygen radical gun was used to oxidise part of a layer (900Å of NbO$_2$) grown in Run 15, with the rest of the layer shielded by Ta foil. During this oxidation, a thickness monitor was also placed in the beam to register temperature changes - the sample was not allowed to exceed an estimated temperature change of 40°C, and chamber pressures were maintained at about $10^{-4}$ Torr throughout. After 30 min. at > 65mA, the layer had discoloured slightly, from a metallic reflective grey to a brown-yellow tinge. The atomic flux at 65mA was in the "surface saturation" regime; this large current was chosen because it gave the least heat dissipation in the gun, which was then operating in the high-efficiency 500V plateau (see Fig. A4.2.2). The beam pressure, however, was only about three times that at 20mA.

The AES depth profiles for shielded/unshielded parts of the layer are shown in Fig. 4.8: the part of the layer exposed to the beam increased in thickness from 910Å to 960Å (measured by Talystep), a factor of 1.05. This corresponds to a calculated increase in oxygen content of about 14%. The measured increase in oxygen content was about 7% (averaged out over the entire layer) with less oxidation having occurred deeper in the layer (probably a diffusion effect). There was also a smearing-out of the Li surface impurity; a few atomic per cent of Si and K were found to depths of nearly 100Å or so, but they then stopped abruptly. X-ray analyses showed that the crystal structure and quality of the bulk of the layer had remained largely unchanged, but the patterns were slightly degraded.

4.8.3 COLD OXIDATION BY ATOMS: DISCUSSION OF RESULTS

The above results are consistent with a significant bombardment of the layer by energetic radicals. This would explain the slight degradation of the X-ray patterns and the observed implantation of the K and Si impurities; it also helps to make sense of the excessive expansion factor (it is known that partial/complete amorphisation of LiNbO$_3$ is accompanied by a drop in density$^{[49]}$, and the same may be true of the niobium oxides). However, the increase in oxygen content throughout the layer cannot be explained in terms of direct implantation of energetic oxygen neutrals: the penetration depths of oxygen ions in LiNbO$_3$ are only 10Å and 80Å at 600eV and 5keV respectively$^{[49]}$, and the values for neutrals (of the same energy) should be similar. It is far more likely that the extra oxygen at greater depths arrived there by diffusion, as in the case of the thick Ag layers oxidised at room temperature.

4.8.4 KINETICS OF OXYGEN INCORPORATION FOR NIOBIUMOXIDES

The hypothesis at the end of Section 4.8.3 requires further scrutiny; it also opens up some important aspects regarding the kinetics of oxygen incorporation into MBE-grown layers.
FIGURE 4.8:
DYNAMIC AUGER DEPTH PROFILES FOR AN NbO_{1.2} LAYER BEFORE AND AFTER EXPOSURE TO THE OXYGEN ATOMIC BEAM

Note the increased thickness of "processed" layer (probably due to oxygen uptake). X-ray analysis showed no signs of structural change in the layer after atomic oxidation.

(Data from Loughborough Consultants Ltd.)
It is known that a saturated native oxide forms readily on the surface of Nb metal and its various lower and sub-oxides when exposed to molecular oxygen at room temperature (see Ch. 5). Even under vacuum conditions, molecular oxygen has been shown to oxidise Nb metal and the sub-oxides at room temperature, forming a skin of native oxides (including the pentoxide) to a depth of about 50Å. It seems unlikely, then, that the difficulty experienced in growing fully-oxygenated layers by MBE using molecular oxygen is due to inadequate reactivity or an inability to break the O-O molecular bond.

It is important to note that the oxidation of Nb by molecular oxygen is not extensive near room temperature: the sticking coefficient of O$_2$ on clean Nb(110), though initially quite high (0.55), falls rapidly to a very small value as monolayer coverage is approached. Grundner showed that, near room temperature, the diffusion of O$_2$ into the Nb lattice is negligible (at 10$^5$ Torr): in fact, the oxidation is governed by a Cabrera-Mott process in which the Nb moves in a field-assisted process. (The limited oxidation of Nb by O$_2$ at room temperature can be compared with the fact that molecular oxygen had no observable effect on the Ag or niobium oxide layers in the Oxford Applied Research system.) However, as temperature is increased to some critical value, the onset of oxygen diffusion through the lattice causes oxide growth to become rapid and unlimited (“bulk” oxidation occurs, obeying the parabolic law). For Nb, this critical temperature appears to be $> 400^\circ$C (in oxygen at 1 atmosphere, see Ch. 5). Bosov stated that the capture of oxygen by the surfaces of niobium and niobium monoxide may well be limited by the rate at which oxygen can diffuse away from the surface into the "bulk" or near-surface regions (the flux rate regime he considered was close to those typically used in the MBE system). So, under MBE-growth conditions, for which Nb metal is continuously arriving, the diffusion processes associated with the molecular oxygen may be too slow, even at 600°C, to cause full oxidation of the growing material.

Section 4.8.3 showed that the atomic oxygen beam species were able to bring about significant oxidation of a niobium oxide layer throughout its bulk, while molecular oxygen had no effect. Ag and Cu layers behaved similarly. But was this really due to an enhanced diffusivity for the atoms, or was it merely a result of using a more reactive form of oxygen? It is known that unsaturated oxides are produced for metals such as Nb and Ta even when reactive evaporation and reactive sputtering processes are employed; the highest niobium oxides grown by sputtering have had compositions somewhere between Nb$_2$O$_3$ and NbO$_2$; r.f. oxidation of Nb metal produces, at best, = NbO$_{2.4}$. It seems reasonable, then, to assert that the problem of oxygen deficiency in MBE-grown layers is more closely related to bulk/near-surface diffusion and the stability of precursor structures than to the reactivity of the arriving oxygen.

Further confirmation for this can be gleaned from the plot of O$_2$ sticking coefficient (for MBE) versus O$_2$:Nb beam ratio (see Ch. 5). This shows that the arrival of further
molecular oxygen does not significantly enhance oxidation once a certain flux ratio is already in use. Now, a monolayer of Nb or O adatoms is typically \( 1.3 \times 10^{15} \) atoms/cm\(^2\). In Run 15, therefore, the flux rates corresponded to 0.05 Nb monolayers/s and 4 molecular oxygen monolayers/s: moderate increases in the oxygen arrival rate would not be expected to enhance the superficial processes. It is supposed that the available surface sites were already glutted with oxygen; only faster diffusion into the bulk could then speed up oxidation. The production of lower oxides by MBE is not, then, merely the consequence of a small sticking coefficient for molecular oxygen - the fact that, and the manner in which, the sticking coefficient is flux-dependent rules this out. Diffusion may, indeed, be playing a dominant role.

4.8.5 ATOMIC OXIDATION: SUMMARY

The results of the above experiments suggest that molecular oxygen is unable to oxidise the stable lower oxides of Nb under vacuo; NbO and NbO\(_2\) may therefore be the highest "bulk" oxides achievable by MBE. NbO is an expected, and dominant, precursor formed under low-pressure conditions (\( \approx 10^5 \) Torr of O\(_2\))\(^{4.11}\). It is only when pressure, temperature and time are increased (\( > \) a few Torr, \( > 400^\circ\)C, several hours) that the pentoxides form: the required surface bombardment by oxygen is then present, the diffusion conditions are propitious, and the temperature is sufficiently high to allow the required phase transformations/lattice rearrangements to take place. The important question is: can oxygen atoms overcome all these conditions in situ?

The interplay of bulk and surface dynamics (including surface diffusion, and diffusion from the surface, through the growing oxide, into the bulk of the layer) is an important consideration in MBE oxide growth. In contrast to the molecules, we have found that O atoms are able to oxidise metals such as Ag, Mo, and Cu, and even NbO (with its skin of saturated oxide) to a considerable depth, even at room temperature. This either indicates that the excited atoms are far more mobile and/or reactive than the molecules in the metal/oxide lattices, or that the process of bulk oxidation is different (and enhanced) when the atomic beam is used. Layers taken from Run 15 were partly oxidised by the atomic beam near room temperature, giving some support to the hypothesis that the oxidation of NbO in vacuo may be a diffusion-controlled process (NbO layers are fairly stable in air, though not at the surface).

We cannot be certain what ramifications the results of the previous sections have for MBE growth conditions: the substrate temperature is higher, and the oxide lattice is assembled from molecular/atomic beams rather than being generated by oxygen incorporation into an existing structure by a thermal process. Thermal oxidation and MBE-growth are both complex processes, especially in a system where a number of oxidation states can occur; conclusions based on one type of oxidation process would not be expected to apply directly to the other. It is clear, however, from the results of Ch. 5 and by inspection of the sticking coefficient
curve, that molecular oxygen will not yield saturated oxide films in MBE at tolerable pressures. But, if the growth of the higher oxides in vacuo is, indeed, hampered by the slow diffusion of molecular oxygen, there is strong evidence to suggest that this factor would be alleviated by using a suitable atomic beam. With higher atomic flux rates, then, it would not seem unreasonable to expect improved oxidation for layers grown in the MBE system using the new radical source. It is unfortunate that the atomic flux rates used in Run 15 were too low to permit direct confirmation of this; neither was there sufficient time or means to use Nb films in the ex situ atomic oxidation experiments.

The growth of Nb$_2$O$_5$ by MBE may also be inhibited by the stability of precursor oxides (such as NbO). The fact that NbO$_{1.2}$ could be partly oxidised at room temperature by an oxygen beam containing a small % of atoms is encouraging: the NbO stability factor, if it exists, clearly did not prevent at least some oxidation by atoms. However, it cannot be firmly concluded from this result that there is no barrier to the formation of a pentoxide structure when an atomic beam is employed.

4.9 FURTHER WORK; SOLUTIONS TO EXISTING PROBLEMS

Assuming a sticking coefficient of unity for the atoms, a Nb flux rate such as that used in Run 15 would require approximately $1.4 \times 10^{14}$ O/cm$^2$/s to approach full oxygen stoichiometry. If contamination effects are assumed small, this would need $I_a$ in the region of 10–15 mA. Growth runs should therefore be performed with the atomic source operating at higher discharge currents in the MBE system, thus avoiding the problem of low atomic generation efficiency. Atomic flux rates would then be high enough to eliminate the possibility that extra incorporation of oxygen had merely fallen within Auger detection limits. Furthermore, the flux "lost" due to beam spreading, sticking coefficient $<< 1$, etc. could be better tolerated.

Unfortunately, $I_a >$ a few mA plunges us back into oxygen overpressure problems. One solution is to redesign the MBE system to accommodate much larger molecular/atomic oxygen beam pressures (see Ch. 5). Another solution is to increase the atomic generation efficiency for a given beam pressure of oxygen, for example by welding a Nb-foil "pepper-pot" orifice across the front end of the atomic gun. The best atomic generation efficiency was obtained as $I_a$ approached = 50mA (corresponding to the 600V "plateau" of the source, see Appx. 4.2, Fig. A4.2.2): to achieve this would need an increase in gun pressure of about x10. The open:closed ratio of the pepper-pot would therefore need to be 1:10. This would raise the O$_2$ pressure inside the gun into the regime where atomic generation efficiency is enhanced, while leaving the overall emergent flux unchanged. However, the 1:10 ratio would make beam uniformity difficult; there might also be clogging or erosion problems. Even this solution, therefore, is not trivial, and some design work is needed.
Microwave discharge sources may be another possibility, since these give a large % of atoms in the beam, but operating pressures are currently far too high (1 Torr or so[4,20]). Another option is electron injection into the existing discharge plasma, but a filament would probably be unsuitable, so that a radioactive (β) source would be needed.

Towards the end of the project, emphasis was returned to the deposition of LiNbO₃ by MBE. This work is presented in Ch. 5. An improvement in the molecular oxygen sticking coefficient (Cₘₒ) was found to occur when Li flux was used. Insufficient Li-Nb-O growth runs were performed to allow any firm conclusions to be made regarding the viability of LiNbO₃ growth by MBE: the advances made in flux rate measurement should, however, now make it possible to perform a more detailed exploration of the roles of Li and oxygen in Nb-Li oxide deposition. This is without doubt the most important area of further research.

A modest input in the future would, then, open up the investigation of several potentially rewarding areas of research. In addition, the lessons learned in lithium-niobium oxide MBE might suggest possible solutions to problems encountered in contemporaneous areas of research: for example, the oxygen-deficiency nut is yet to be cracked in exciting areas such as the vacuum-growth of high-Tc superconductors[4,21] (see also Ch. 5).

4.10 SUMMARY

Oxygen deficiency has been identified as one of the major problems associated with the growth of Nb and Nb-Li oxides by MBE. Various modifications were performed to the MBE rig and (molecular) oxygen source in an attempt to increase the maximum O₂:metal flux ratio achievable in the system, and to avoid the routine operation of the MBE unit close to its performance limit. Oxygen flux reproducibility was greatly improved. However, layers still did not exhibit full oxygen stoichiometry, even when grown at the new performance limit.

An alternative form of oxygen was therefore sought, and a free atomic radical source built. Ex situ experiments showed that oxygen was taken up at low temperatures (< 70°C) by many metals, and even by the monoxide of Nb, when supplied as a combined O + O₂ beam from this source; molecular oxygen alone had no such effect. The null results of MBE growth-runs performed with the atomic source (Run 15) were most probably due to insufficient atomic production at the low discharge currents used for those experiments ("threshold" effect). The limitation here was again the maximum pressure allowable in the system during growth. However, the ex situ experiments did give further insight into the kinetics of the oxidation process in the Nb-Li-O system (these may be added to those deduced in Ch. 5 from the growth runs and post-deposition oxidation experiments).
A modified MBE system which allows the atomic source to be run at higher discharge currents would clarify the issue considerably, and might reasonably be expected to give niobium oxide layers containing a far greater percentage of oxygen. The drastic system changes required to accommodate the higher throughput/pressures of oxygen could not be brought about in this project. It is suggested that the deposition of Nb and Nb-Li oxides in such a modified MBE system using an improved oxygen radical source would be a promising line of future research. Some interim modifications to the gun have been suggested towards this end.

Further growth studies involving Li are strongly recommended.

REFERENCES

4.7 IL002 or IL004 thickness monitor manual, Intellemetrics Ltd., 4 North Avenue, Clydebank Business Park, Glasgow, G81 2LA.
4.11 M. Grundner and J. Halbritter, "XPS and AES Studies on Oxide Growth and Oxide Coatings on Niobium", J. Appl. Phys. 51 (1980) 397 et seq.


4.21 See references cited in Ch. 5.
CHAPTER 5

MBE GROWTH OF THIN-FILM NIOBIUM AND NIOBIUM OXIDE

5.1 ABSTRACT

The results and discussions reported in this chapter represent the first systematic study of the deposition of niobium and niobium oxide layers on z-cut LiNbO₃ and sapphire substrates by MBE. Single crystal and oriented polycrystal niobium oxide layers were grown on +z-cut LiNbO₃ substrates. A new variant of the monoxide (NbO-6C fcc) and an entirely new phase of niobium oxide (hex-\(\pi\), NbO₁₂₅) were grown and characterised. The potential advantages and limitations of MBE for growing the higher oxides, such as Nb₂O₅, were established. Niobium metal layers were grown on z-cut LiNbO₃. The deposition of excellent quality niobium oxide on z-cut sapphire was demonstrated, providing an optical waveguiding structure of large differential refractive index. Crystallinity and compositional data are presented for all the above layers. The post-deposition oxidation of oxygen-deficient films to the pentoxide was studied in detail, and equipment requirements for the in situ growth of Nb₂O₅ are proposed.

5.2 DEPOSITION STUDIES: BACKGROUND INFORMATION

5.2.1 CHOICE OF SUBSTRATE; GROWTH CONDITIONS

The reasons for growing niobium metal and niobium oxide layers on LiNbO₃, sapphire and silicon substrates were explored in Ch. 1. Y-cut LiNbO₃ might, in several ways, be considered preferable to z-cut LiNbO₃ as a substrate for Nb₂O₅ deposition: a larger difference in n exists in the former case, and there are advantages associated with resulting acousto-optic devices (see Ch. 1). However, growth studies were conducted on z-cut LiNbO₃. This is because completed RHEED studies of the simpler z-cut surface provided a good understanding on which to base a reliable interpretation of the structure of deposited layers. Z-cut LiNbO₃ was also of greater interest for making use of the electro-optic interaction in novel and efficient "vertical" modulator devices (see Ch. 6). Layers were also deposited on z-cut sapphire.

Z-cut LiNbO₃ and sapphire substrates were prepared as described in Chs. 2 and 3 and the References\(^{51-53}\). After loading, these were subjected to examination using 38.3kV RHEED (see Fig. 5.1 and Ch. 3). Substrate temperatures were usually selected between 610°C and 660°C, which includes the range for which homoepitaxial growth of LiNbO₃ has been demonstrated. Early on in the project, oxygen and niobium flux rates were selected according to the limited available sticking coefficient data (Betts\(^{53}\)) so as to give (expected) compositions approaching Nb₂O₅; at that time, some error was possible in the estimation of flux rates (see Ch. 2). Later in the project, flux rates were selected according to the sticking coefficient curve

121
deduced from the runs, and flux rate estimates were much more reliable. Layers were grown over a wide thickness range (100Å → 1.2μm). Growth on z-cut sapphire provided a greater refractive index difference for optical waveguiding purposes, and also gave information on the role and source of lithium in the growth process on LiNbO₃ substrates (traces of lithium appeared in most niobium oxide films).

Ion cleaning was not used if substrate surfaces gave good RHEED patterns (and SIMS spectra) after the wet-etch plus heat cycle: usually, good single-crystal layers could be grown without recourse to ion-cleaning. (In some cases, low ion doses were administered as required, and as described in Ch. 3, to remove excessive contamination as observed by RHEED or SIMS; the SIMS unit, however, was not always available to monitor impurity coverage). It is convenient for the purposes of discussion to differentiate the layers broadly into two categories: films grown at higher O₂:Nb flux ratios, greater than ~ 10, and films grown at flux ratios of less than ~ 10. In early work, these flux ratios (and the chamber pressures) were only considered trustworthy to within a factor of about 5: this range was considered typical of the uncertainties in the absolute measurement of local pressures/flux rates in vacuum systems of this kind. Later improvements in pressure and flux measurement showed (Appx. 4.1) that the estimates were, in fact, quite accurate: to within a factor of 2.

5.2.2 EX SITU ANALYTICAL TECHNIQUES

For all the layers described in this chapter, the bulk internal structure of the films was probed using ex situ inclined-beam X-ray photography and X-ray texture (static and rotation) photography[53] (Fig. 5.2). Corroborative X-ray data was often sought using diffractometer and/or powder diffraction techniques[53]. Composition profiles were compiled, both before and after post-deposition oxidation, with dynamic AES, using ion-milling to obtain depth data. Ion-beam-induced decomposition effects were accounted for by reference to standards subjected to identical conditions in the Auger rig: Nb, NbO, NbO₂, Nb₂O₅ and LiNbO₃ were among the many standards used. These calibrations gave an assurance in the Nb and O compositions of 5 atomic % or better. Other compositional analyses agreed well with the Auger work: for example, layers of average composition NbO₁.₃ (as assessed by dynamic AES) gave a result of NbO₁.₇ when analysed by Rutherford Back-Scattering (RBS), and NbO₁.₁ (± 30%) with quantitative XPS. The RBS result was expected to be an over-estimate because of the oxide substrate on which the films had been grown. The Auger analysis parameters are given in the relevant figures; the XPS work was performed at Loughborough University on a VG ESCALAB machine, with X-ray energy 1486.6eV, anode voltage 15kV, and anode current 20mA; the RBS analysis was performed at Harwell (Ion Beam Analysis Unit; ref: HVL/VAX CAMAC ADC7, VRBS546) using 2MeV He⁺.
FIGURE 5.1: TYPICAL 38.3keV RHEED DATA FOR AN EPITAXIAL, NbO-6C f.c.c. LAYER GROWN ON Z-CUT LITHIUM NIOBATE BY MBE

SUBSTRATE
LiNbO₃ (001)

OVERLAYER
NbO-6C (111)

FIGURE 5.2: A SELECTION OF X-RAY AND RHEED DATA FOR POLYCRYSTALLINE NIOBIUM OXIDE LAYERS GROWN ON Z-CUT LITHIUM NIOBATE AND SAPPHIRE BY MBE

(a) X-ray texture photograph for a 4100Å layer of NbO₀.₉ grown on z-cut LiNbO₃. Angle of inclination of x-ray beam = 20'. Rotation axis = LiNbO₃ [001]. The lines indicate a layer of polycrystalline NbO-6C fcc with a strong (111) orientation.
FIGURE 5.2: (b) Inclined-beam, x-ray photographs taken in a cylindrical powder diffraction camera\[5.3, 5.35\].

(i) Same sample as for Fig. 5.2 (a), above. Growth T = 650°C,
(ii) Photograph taken under identical conditions to (i) for a 1.15\(\mu\)m layer of NbO\(_1.15\) grown on z-cut sapphire. Growth T = 650°C.

Ring sections due to polycrystalline overgrowth. Inclination angle = 15°;
Scale: 1mm = 1° in 2θ.

\[\begin{array}{c}
\text{substrate spots} \\
(111) (200) (220) (311) (222) (331) (420) \\
\text{NbO-6C fcc indices}
\end{array}\]

\(z\)-cut LiNbO\(_3\)

\(z\)-cut sapphire

\(\text{50 mm}\)

The NbO-6C fcc rings are present, as in (i) above. Most of the extra lines are due to the tetragonal NbO\(_2\) phase (see text).

(c) 38.3keV RHEED data for the mixed-oxide layer that gave the x-ray photograph shown in Fig. 5.2 (b) (ii).

\(z\)-cut sapphire \(<210>\) azimuth

The ring radii are consistent with the presence of two oxide phases in the overlayer: NbO-6C fcc + NbO\(_2\) (tetragonal\[5.3, 5.35\]).

The cylindrical x-ray cameras for the powder and texture photography are described in refs. 5.3 and 5.35. Photographs (a) and (b) were obtained at GEC Hirst Research Centre, with the help of Dr. C. Dineen and W.G. Freeman. Monochromated CuK\(_\alpha\) radiation was used throughout.
Several other ex situ analysis techniques were employed, but these shall be dealt with as they arise.

5.3 NbO\textsubscript{4} LAYERS GROWN ON z-CUT LiNbO\textsubscript{3} SUBSTRATES

The grown films were examined optically under a microscope and by scanning electron microscopy. They were dark grey in colour, uniform, smooth, and with a shiny metallic appearance. Talystep studies confirmed that the layers were smooth and uniform. Layer thickness was measured by quartz thickness monitor (in situ) and Talystep (ex situ). RHEED and X-ray data obtained for thicker films (up to 1.2 \textmu m in thickness, and necessarily grown at higher niobium flux rates, up to \( \sim 1 \text{ Å/s} \)) showed that these layers tended to grow oriented polycrystalline with some random polycrystalline material. Thinner films (up to \( \sim 0.2 \text{ μm} \), and grown at lower Nb flux rates, \(< 0.4\text{Å/s}\)) gave RHEED patterns characteristic of single-crystal material with a well-defined epitaxial relationship to the substrate (Fig. 5.1).

From X-ray data, a modified form of the " NbO-6C" cubic structure (NbO-6C f.c.c.) was postulated for the thicker layers grown at low O\textsubscript{2}:Nb ratios (see Section 5.5.1). A typical set of X-ray results is tabulated in Table 5.1. The rings observed in inclined beam X-ray photography of the thicker films indicated some random polycrystallinity, but there was moderate orientation along NbO-6C f.c.c. \( <220> \) and strong orientation along NbO-6C f.c.c. \( <111> \) (see Figs. 5.2). The structure was confirmed by the 38.3 keV RHEED results, in which the observed ring radii for polycrystalline NbO\textsubscript{1.6} films gave the expected f.c.c. sequence up to \( N = 14 \).

The thinner films gave spot X-ray patterns in apparent agreement with the thicker films in terms of lattice parameter, but less data was obtainable; some of the thin layers grown at high O\textsubscript{2}:Nb ratios had different structures to NbO-6C f.c.c., yet to be fully identified. Direct confirmatory evidence of epitaxy for the thin films stemmed from the RHEED studies (see Fig. 5.1), and from Weissenberg X-ray photography (this gave the in-plane structural relationships for the overlayer): this data was very similar to the examples given in Section 5.4 for niobium oxide growth on sapphire.

The layer reported in Table 5.1 was analysed using ellipsometry, yielding the results: \( n \geq 2.31, \ k = 2.02 \) (at 633 nm). Upon oxidation to the pentoxide, the value of \( n \) might be expected to fall, but not by very much. Near-surface Nb oxidation-state was assessed ex situ using XPS: this showed that a thin (\( \sim 30\text{Å} \) ) layer of Nb\textsuperscript{5+}-type material was present on top of Nb\textsuperscript{5+}-type material. When oxidised in an oxygen atmosphere at 450°C for about 1 hour, the entire probed region became Nb\textsuperscript{5+}. Thus a thin Nb\textsubscript{2}O\textsubscript{5} layer (produced by atmospheric oxidation, see Ch. 4) was covering essentially NbO-type material, and post-deposition annealing in \( \text{O}_2 \) was effecting a change in Nb oxidation state by uptake of oxygen. Layers oxidised in the
furnace were seen to become clear, and X-ray analysis confirmed that structural changes were involved. For further discussion of post-deposition oxidation, see Section 5.7. No evidence of any other niobium bonding state was found at any time.

Dynamic AES composition profiles were consistent with XPS results; these indicated that, in most cases, the films were relatively free of contaminants, a result confirmed by dynamic SIMS analyses. Some films contained traces of carbon, probably originating from carbon-bearing species such as CO and CO₂ in the vacuum background and present in smaller quantities in the molecular oxygen source. Occasionally, carbon was observed at the film-substrate interface, at slightly higher levels than in the film.

The thicker films were usually grown at low O₂: Nb ratios, due to the higher Nb flux rates required to gain appreciable layer thickness in a given time (the maximum oxygen flux rate was limited by overpressure problems). Compositionally, the O: Nb ratio in these films was in the range 1.1 → 0.8. Early films were not entirely uniform in composition: the non-uniformities correlated well to variations in the growth beam fluxes, implying that improved flux stabilisation was desirable, but also that the film composition could be controlled. Improved flux control gave good compositional uniformity (as assessed by dynamic AES and SIMS, see Section 5.4). Small quantities of lithium (< 1%) were also present in the bulk of the films with generally much more lithium in the top few monolayers: this impurity originated from the probe, chamber walls, and adjacent Li electron-beam evaporator. Layers grown at the highest O₂: Nb flux ratios generally contained a greater percentage of oxygen, up to ≈ NbO₁.₅, and possessed a structure different to NbO-6C f.c.c. (see Section 5.4 for further discussion).

Microscopic examination showed some evidence of strain-induced defects in the layers, but a low level of film perforation. There were indications of adherence problems for layers grown on substrates that had given poor RHEED patterns prior to growth, or that had not been meticulously prepared (e.g. by careful ion cleaning, if needed). The oxide layers were electrically conducting, the d.c. resistivity depending on oxygen content and varying from 8.4 × 10⁶ Ωm to 2 × 10⁸ Ωm as the film composition changed from NbO₆.₈ to NbO₁.₄. The lowest sheet resistance measured for an oxide layer was ≈ 30 Ω per square, though this parameter, of course, depends on film thickness (which was 0.41 μm in this case).

5.4 NIOBIUM OXIDE GROWTH ON Z-CUT SAPPHIRE BY MBE

During the course of the growth work on z-cut sapphire, two new, single-crystal phases of niobium oxide were identified. One of these was the NbO-6C f.c.c. phase also observed on z-cut LiNbO₃; the other was a hexagonal phase of approximate composition NbO₁.₂₅.
FIGURE 5.3: 38.4keV RHEED DATA FOR A 1200Å EPITAXIAL
LAYER OF NbO-6C f.c.c. GROWN ON Z-CUT SAPPHIRE BY MBE

FIGURE 5.4: INCLINED-BEAM X-RAY OSCILLATION PHOTOGRAPH
FOR A 1200Å NbO-6C f.c.c. FILM GROWN ON Z-CUT SAPPHIRE

Inclination angle of x-ray beam: 19.5°; Radiation used: CuKα (nickel-filtered).

The computer simulation is for a film of NbO-6C f.c.c. (i.e. NbO-6C with the
vacancies randomised) oriented with its [111] axis normal to the substrate
surface, and with a₀ = 4.24Å. All graduations are in mm; camera radius =
28.65mm; rotation axis = sapphire [00.1]. Spot indices and (bracketed)
multiplicities are also given. The cited references contain a full
account of the camera arrangement and x-ray technique. Fig. 5.3 shows RHEED data
for this layer. (X-ray data was obtained at the Crystallography Unit, UCL, with
the help of Dr. H.J. Milledge).
**TABLE 5.1:** X-ray investigation of an NbO-6C f.c.c. layer on z-cut LiNbO₃
Beam glancing angle of incidence = 15° (nominal); CuKα radiation (Ni-filtered)

<table>
<thead>
<tr>
<th>N = h² + k² + l²</th>
<th>Intensity of line</th>
<th>f.c.c. line indexing</th>
<th>2θ (°)</th>
<th>dₒ₀₀/Å¹</th>
<th>Lattice parameter aₒ = dₒ₀₀.Nᵞₒ/Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>Very strong</td>
<td>(111)</td>
<td>36.55</td>
<td>2.46</td>
<td>4.26</td>
</tr>
<tr>
<td>4</td>
<td>Strong</td>
<td>(200)</td>
<td>42.55</td>
<td>2.12(5)</td>
<td>4.25</td>
</tr>
<tr>
<td>8</td>
<td>Medium</td>
<td>(220)</td>
<td>61.70</td>
<td>1.50</td>
<td>4.24</td>
</tr>
<tr>
<td>11</td>
<td>Weak</td>
<td>(311)</td>
<td>74.00</td>
<td>1.281</td>
<td>4.25</td>
</tr>
<tr>
<td>12</td>
<td>Weak</td>
<td>(222)</td>
<td>78.05</td>
<td>1.224</td>
<td>4.24</td>
</tr>
<tr>
<td>16</td>
<td>Too weak to measure</td>
<td>(400)</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>19</td>
<td>Very weak</td>
<td>(331)</td>
<td>105</td>
<td>0.972</td>
<td>4.24</td>
</tr>
<tr>
<td>20</td>
<td>Medium-weak</td>
<td>(420)</td>
<td>108.7</td>
<td>0.949(0)</td>
<td>4.244</td>
</tr>
</tbody>
</table>

**Average = 4.24**

**Notes:**
1. ¹ Calculated using Bragg Law.
2. The above data was obtained from an inclined-beam X-ray photograph of a polycrystalline layer. X-ray texture photography also showed these lines (plus those too weak to measure above) in an fcc sequence, and up to N = 24.
3. The above work was performed at GEC, Hirst, East Wembley, with the aid of Dr. C. Dineen.
5.4.1 NIOBIUM OXIDE GROWN AT LOW O$_2$:Nb RATIOS

Such films usually had the "NbO-6C f.c.c." structure, though only limited X-ray data was obtainable if the films were too thin (< approx. 700Å). The RHEED pattern from a single-crystal, epitaxial layer of NbO on z-cut sapphire (α-alumina) grown at a low O$_2$:Nb flux ratio (= 8) is shown in Fig. 5.3. The growth temperature was 640°C, and the layer was 1200Å thick. It was oxygen deficient compared with NbO and had a composition of ≈ NbO$_{0.9}$. AES, XPS and SIMS were variously used to deduce composition and impurity levels: major impurities were carbon (< 1%), molybdenum (< 0.5%, from the evaporation crucible), and lithium (< 1%, shown to be due to auto-doping from probe and chamber). Fig. 5.4 shows indexed inclined-beam, X-ray data for this layer. The good crystal quality of the overgrowth is evident from the size and shape of the film spots, and from the fact that well-defined, high-order reflections were obtained. All X-ray spots from the film could be indexed on the assumption of a layer of "NbO-6C f.c.c.", oriented exactly as described in the next section. The RHEED patterns of Fig. 5.3 are also fully consistent with such an orientation. The computer simulation and observed X-ray pattern were in excellent agreement, and there was no evidence of spots due an ordered vacancy (NbO-6C) structure. The reader is also referred to Table 5.1.

5.4.2 NIOBIUM OXIDE GROWN AT HIGH (& VERY HIGH) O$_2$:Nb RATIOS

The crystalline structure of the thin layers (grown at low and moderate growth rates) tended to be the least imperfect. Inclined-beam X-ray photographs of thicker layers grown at moderately high O$_2$:Nb flux ratios revealed extra features not observed for the NbO-6C f.c.c. layers grown on z-cut LiNbO$_3$/sapphire under conditions of low O$_2$:Nb flux ratio. The precise relationship of the extra lines to the layer structure was not always clear, but their presence was consistent with Brauer's observation$^{[54]}$ that additional features begin to appear in the X-ray powder pattern of NbO as the oxide composition moves from NbO$_{1.0}$ to NbO$_{1.25}$. In fact, the strongest lines of the NbO$_2$ tetragonal phase reported by Terao$^{[55]}$ were all observed as weaker, extra lines in an inclined beam X-ray photograph of a sampled layer of this kind (Fig. 5.2). Most, but not all, of the additional lines could be accounted for in this way (Appx. 5.1).

Layers grown at very high O$_2$:Nb ratios (= 80) on z-cut sapphire at 610°C were composed of an altogether new and definable crystal phase. Typical X-ray and compositional data are shown in Figs. 5.5 and 5.6. Very low growth rates were used, leading to thin films (typically 900Å). They were not composed of NbO-6C (f.c.c. or otherwise), nor did they possess any of the dioxide structures. Auger composition profiles showed that the layers contained more oxygen than NbO-6C, typically NbO$_{1.2}$ → NbO$_{1.25}$, and that good compositional uniformity had been achieved. The layers were epitaxial and good single-crystal, as indicated by 38.3 keV RHEED, inclined-beam X-ray oscillation photography, and Weissenberg X-ray photography. The RHEED patterns were rather streaky, and similar in appearance to Fig. 5.1.
FIGURE 5.5: X-RAY DATA FOR A 910Å LAYER OF NbO$_1$.25 (HEX-$\alpha$ PHASE) GROWN ON Z-CUT SAPPHIRE BY MBE

(a) An inclined-beam x-ray oscillation photograph set for the 8th layer line ($18.15^\circ$) of the NbO$_1$.25 hex-$\alpha$ phase (hexagonal unit cell: $a = 2.97\AA$; $c = 19.5\AA$). The x-ray beam, camera arrangement and rotation axis are otherwise as for Fig. 5.4. The computer simulation shown beneath is for a single-crystal film of the hex-$\alpha$ phase oriented as described in the text.

(b) An example of a Weissenberg photograph for the above sample. In this case, the camera was set for the 6th layer line of the hex-$\alpha$ phase ($13.7^\circ$).

(All data obtained at the Crystallography Unit, UCL)
FIGURE 5.6: COMPOSITION PROFILE THROUGH A NIIOBIUM OXIDE LAYER AS DETERMINED BY DYNAMIC AUGER

**ATOMIC PERCENT OF GIVEN ELEMENT**

<table>
<thead>
<tr>
<th>AIR</th>
<th>MONOXIDE: % Nb, O</th>
<th>DIOXIDE: % O</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**DEPTH (Å)**

- OXYGEN
- NIIOBIUM
- ALUMINIUM

Sputtering ion beam: Ar+, 1 keV, 40μA/cm²
Electron probe beam: 3 keV, 0.6μA into approx. 0.04 mm²

X-ray data for this layer was presented in Fig. 5.5
(Data from Loughborough Consultants Ltd.)
A detailed analysis of this new phase, termed "hex-\(\pi\)", is given in Section 5.5. Further data is due to be published elsewhere, and a preliminary report has already appeared\(^{[56,57]}\).

### 5.4.3 Comments on Growth Work

An interesting fact that emerged towards the end of these studies was the remarkable structural similarity that existed in many cases between corresponding niobium and tantalum oxides, particularly between the niobates and tantalates\(^{[58]}\). This may be of use to future work in the field, since the tantalate structures have been well characterised\(^{[58]}\).

Terao’s work has confirmed that niobium dioxide can be grown under vacuum growth conditions. It should therefore have been possible, with high enough \(O_2:Nb\) flux ratios, to grow at least the dioxide in this MBE system. In fact, the preceding paragraphs contain significant evidence to support the claim that dioxide structures were actually grown. Terao’s results also suggest that the approximate pressure range in which the pentoxide would be expected to begin to form is \(10^2\) to \(10^3\) Torr, although this applies to bulk growth conditions.

In an attempt to increase the oxygen content of the niobium oxide layers, and achieve at least \(\text{NbO}_2\), a series of layers were grown at the highest \(O_2:Nb\) ratios possible, with and without the new oxygen radical source. Z-cut sapphire substrates were used in this work. Results were presented, and dealt with thoroughly, in Ch. 4.

### 5.5 Structural Models for the New Niobium Oxide Phases

There are at least 32 registered forms of niobium oxide, \(\text{NbO}_x\) \((1 < x < 2.5)\)\(^{[59]}\), some of which are polymorphic; numerous intermediate oxides have also been identified during phase transformations; various sub-oxides \((x < 1)\) have been characterised (see references in Section 5.7). A number of these oxides are only formed under particular/peculiar growth conditions, such as very high pressure; the fact remains, however, that the niobium-oxygen system is extremely complex. In scouring the literature for the oxide phases described below, the lithium-niobium oxides were also investigated, including the \(\text{LiNb}_3\text{O}_8\) phase reported in thermal treatments of \(\text{LiNbO}_3\)\(^{[5,10]}\).

#### 5.5.1 Model for \(\text{NbO}-6C\) fcc Grown on z-Cut LiNbO\(_3\) & Sapphire

The results of Sections 5.3 and 5.4 made it possible to propose a model for the epitaxial growth of a new form of niobium monoxide on z-cut LiNbO\(_3\) and sapphire substrates. Only one oxide in the literature fitted the observed X-ray, RHEED and compositional data for
the layers grown at low and intermediate \( \text{O}_2: \text{Nb} \) flux ratios. The selected candidate was \( \text{NbO}^{6}\text{C} \) (cubic; \( a_0 = 4.21\text{Å} \)). It has an \( \text{NaCl} \)-type unit cell, but with ordered vacancies at \((0,0,0)\) and \((1/2,1/2,1/2)\), so that the number of formula units per unit cell, \( Z = 3^{13,4,5,11,13} \). AES confirmed that the compositions of these layers were centred on that of \( \text{NbO}-6\text{C} \).

\( \text{NbO}-6\text{C} \) has a primitive cubic lattice; however, the X-ray line sequence of the analysed material was manifestly f.c.c. (please refer to \( N \) values in Table 5.1). The following hypothesis explains this observation: in the MBE-grown \( \text{NbO} \) material, the \( \text{Nb} \) atoms were randomly distributed on the available lattice and vacancy sites, leading to a statistical 75% occupation of each f.c.c. \( \text{Nb} \) lattice site. It is possible that the sub-lattice (oxygen) occupation was randomised in a similar manner, though this would not be immediately apparent from X-ray data. Bulk disordering of this kind is a common occurrence in other material systems (e.g. Cu-Au alloys\textsuperscript{13}). The "randomised" oxide had a lattice parameter of 4.24\text{Å}, and was termed by the author: "\( \text{NbO}-6\text{C} \) f.c.c.". The ordered \( \text{NbO}-6\text{C} \) oxide is widely reported as a bulk-grown niobium oxide\textsuperscript{13,5,12,5,14,15}; however, to the knowledge of the author, this randomised variant has not been reported elsewhere.

A very strong \( (111) \) orientation was indicated by the X-ray data; detailed analysis of X-ray and RHEED photographs (see Sections 5.3 & 5.4) confirmed that the \( \text{NbO}-6\text{C} \) f.c.c. material grew with a \( (111) \) face parallel to the \((00.1)\) face of the \( \text{LiNbO}_3 \). These two faces have a 0.8% lattice mismatch, considering occupied \( \text{Nb} \) sites (the mismatch for sapphire \((00.1)\) is approx. 8%). There is also a 1:1 correspondence in \( \text{Nb} \)-site occupancy for these faces when appropriate in-plane directions are aligned and the \( \pm c/6 \) out-of-plane \( \text{Nb} \) atoms are included in the \( \text{LiNbO}_3(00.1) \) section (Fig. 5.7 (a)). The expected RHEED rod-spacings for each azimuth were calculated: this was done by inspection of in-plane lattice row separations in the appropriate \( \text{NbO}-6\text{C} \) f.c.c. lattice nets; results were checked using tabulated reciprocal lattice sections for cubic crystals\textsuperscript{15,16}. The expected spacings were in direct agreement with the observed RHEED data of Figs. 5.1 and 5.3. The weaker, half-interval rods, in Fig. 5.1, suggest a 2 \( \times \) 2 periodicity in the \((111)\) surface: this could be accounted for by a reversion to ordered vacancies on that surface (i.e. a return to the \( \text{NbO}-6\text{C} \) structure; see Fig. 5.7 (b)).

The above results have been used to deduce the lattice relationships that hold for MBE-growth of \( \text{NbO}-6\text{C} \) f.c.c. on \( z \)-cut \( \text{LiNbO}_3 \):

\[
\begin{align*}
\text{LiNbO}_3 & : \text{parallel to (111)} & \text{NbO}-6\text{C} \\
(00.1) & : \text{parallel to (111)} & \text{f.c.c.} \\
(\text{trigonal}) & & \\
\text{x axis, [10.0]} & : \text{parallel to [11\overline{2}]} & (\text{cubic}) \\
\text{y axis, [12.0]} & : \text{parallel to [\overline{1}10]}
\end{align*}
\]

133
This also holds for the growth of NbO-6C f.c.c. on z-cut sapphire. In addition, the relationship is identical to that proposed by Betts[5,3,17] for MBE-grown Li$_3$NbO$_4$ on z-cut LiNbO$_3$, and by Nunomura[518] for r.f.-sputtered MgO on z-cut LiNbO$_3$. The growth of lattice-matched cubic niobium oxide on z-cut LiNbO$_3$ appears to follow the same pattern, probably by virtue of the match in trigonal symmetry and the equivalence of cationic occupation sites.

5.5.2 Model for Growth of New Hex-π Phase on z-Cut Sapphire

On the basis of the available X-ray (Fig. 5.5) and RHEED data, a unit cell could be established for this oxide. The crystal symmetry of the oxide was hexagonal, and the cell parameters were:

$$a = 2.97\text{Å}; \quad c = 19.5\text{Å}.$$  

This phase of niobium oxide is not reported elsewhere in the literature: it was given the name "hex-π". The epitaxial relationship for the growth of hex-π on z-cut sapphire was:

In-plane:
- sapphire $<11.0>$ axis parallel to hex-π $<10.0>$

Film normal:
- sapphire [00.1] axis parallel to hex-π [00.1]

When the lattice nets for the appropriate planes are superimposed, there is a +7% lattice mismatch (hex-π larger), and a 1:1 correspondence in Nb occupation sites. The RHEED streak spacings for substrate and overlayer gave an observed in-plane lattice mismatch of +5.0%. Flux rate data for these runs predicted 8 (±1) Nb atoms per unit cell.

In Weissenberg photography, both the camera and the layer move in such a way as to give information on the in-plane periodicity of the layer (this is done by associating spots in the Weissenberg sequence of the film with spots arising from the substrate). The Weissenberg data of Fig. 5.5 was of very high quality for the layer thicknesses sampled (900Å). From these photographs, the hexagonal symmetry of the layer was clear: the {216} reflection had a multiplicity of 12, as required for a hexagonal crystal when $h \neq k \neq 0$. In both the inclined-beam and the Weissenberg X-ray photographs, the overlayer spots were not much larger than spots produced from the extended single-crystal substrate. This indicated that the layers were probably structurally coherent (i.e. single-crystal); the fact that spots were obtained at large angles gave affirmation to this conclusion. Also, a complete set of equi-inclination Weissenberg photographs about the c-axis indicated that there may have been systematic absences [compare the X-ray photographs of Fig. 5.5 with the computer simulation in Fig. 5.5 (a)]: these may help to define a specific space group for this phase.
FIGURE 5.7:

(a) Surface lattice nets for LiNbO$_3$ (001) and NbO-6C f.c.c. (111). Only the niobium atoms are shown (black circles): for these, the projected sites are concurrent for the two faces. All the niobium atoms are in-plane for the NbO-6C fcc (111) surface. However, the LiNbO$_3$ (001) projection includes Nb atoms which are slightly out of plane: the out-of-plane displacement is given in units of $c_H/12$ next to each Nb site in the diagram ($c_H$ for LiNbO$_3 = 13.867\,\text{Å}^{(5,36)}$).

\[ \text{LiNbO}_3 \text{ y}_H \text{ axis } \langle 010 \rangle, \]
\[ \text{NbO 6C f.c.c. } \langle 211 \rangle \]

\[ \text{LiNbO}_3 \text{ y axis } \langle 120 \rangle, \]
\[ \text{NbO 6C f.c.c. } \langle 110 \rangle \]

\[ \text{LiNbO}_3 \text{ x}_H, \text{ x axes } \langle 100 \rangle, \]
\[ \text{NbO 6C f.c.c. } \langle 211 \rangle \]

(b) Ordered vacancy arrangement for the NbO-6C (111) surface (open circles represent vacancies). The unbroken and dashed constructions illustrate the $X_2$ periodicity observed for each of the RHEED azimuths of Fig. 5.1.

\[ \times 2 \]

\[ \text{NbO 6C } \langle 211 \rangle \]

\[ \times 2 \]

\[ \text{NbO 6C } \langle 110 \rangle \]
Layers of niobium metal were deposited on z-cut LiNbO$_3$ between 620°C and 670°C. They were found to be relatively free of most elements except for a few % carbon and oxygen (with traces of molybdenum and lithium, < 0.5%). Now, at elevated temperatures, niobium is reactive towards oxygen and oxygen-bearing gas species such as CO$_2$[519-521], oxygen diffuses rapidly through the metal[5,5,520], and carbon atoms are readily accommodated into its lattice[5,15]; Nb forms a stable carbide in vacuo[5,19], NbC having a similar structure and lattice parameter to the monoxide[5,19]. Hence the carbon and oxygen impurities probably stem from the high levels of carbon-bearing vacuum species (such as CO$_2$) released for these particular runs during the operation of the electron-bombardment substrate heater (though it is also possible that some oxygen had diffused in from the substrate). An alternative means of substrate heating, with low outgassing and having no carbon-bearing components, should therefore reduce the major impurities of these films.

Both RHEED (in situ) and inclined beam X-ray analysis (ex situ) were employed to analyse the structure of the layers. The presence of oriented, polycrystalline niobium having the bulk b.c.c. structure was confirmed. However, a detailed analysis of the X-ray arcs suggested a unit cell distortion of about 5%, to partially accommodate the 10% in-plane lattice mismatch between the (001) LiNbO$_3$ substrate and the growing (110) Nb planes. This (110) growth mode for MBE-deposited Nb was apparent from RHEED and X-ray studies independently, and is rather unusual for metallic deposition on trigonal and hexagonal substrates: Claassen[5,22], for example, reports the more usual (111) growth of Nb metal on z-cut sapphire (in this case, involving a 3D registry between the two crystal lattices).

Layer quality tended to vary depending on growth conditions, and layers grown on ion-cleaned substrates showed a greater degree of polycrystallinity (Fig. 5.8). The crystalline structure of the metal layers was imperfect, probably owing to the mismatch strain, but a fair degree of order and orientation was apparent from the X-ray analysis and from the blurred spot/arc patterns observed with 38.4 keV RHEED. Some layers were very well oriented: at best, the X-ray features for these layers had a spread corresponding to a ± 3° misorientation.

The d.c. sheet resistance was measured at approximately 16 Ω per square for 800Å Nb films, giving a resistivity of 1.2 x 10$^{-6}$ Ωm: this was encouraging as a preliminary result for applications as buried sheet electrodes (see Ch. 6), but was a factor of 5 → 10 times higher than the value expected for a pure 800Å Nb film. The discrepancy may have been due to the oxygen impurity. SEM showed that the layers were continuous and uniform.
FIGURE 5.8: 38.3keV RHEED PATTERNS FOR AN 800Å LAYER OF NIOBIUM METAL GROWN ON Z-CUT LiNbO₃

LiNbO₃ <120> azimuth = Nb <100> azimuth

FIGURE 5.9: PLOT OF INITIAL LAYER COMPOSITION AGAINST MEASURED EXPANSION WHEN CONVERTED TO THE GAMMA-PENTOXIDE

O/Nb ratio in as-grown film

Expansion factor upon conversion to pentoxide (= thickness after oxidation : as-grown thickness)
5.7 POST-DEPOSITION OXIDATION STUDIES

5.7.1 INTRODUCTION; REVIEW OF LITERATURE

All MBE-grown films were oxygen deficient relative to NbO₅, including those grown at the maximum oxygen pressures permissible for controlled and steady operation of the MBE system (≈ 5 x 10⁻⁶ Torr local O₂ pressure at the substrate, ≈ 4 x 10¹⁵ oxygen molecules/cm²/s, corresponding to O₂:Nb = 100). Low O₂:Nb ratios gave rise predominantly to the NbO₁₋₆C f.c.c. structure, with some tendency towards NbO₂ at the highest ratios (Fig. 5.2). In order to obtain NbO₅ material suitable for optical and acoustic characterisation, a series of experiments were performed to determine the behaviour of monoxide layers when subjected to ex situ oxidation in a furnace. The results agree well with published work.

Terao²⁵ shows that the final product(s) of the oxidation of niobium metal, or of the niobium sub-oxides and lower oxides, depends both on the temperature and oxygen pressures employed. Certainly, the transformations that occur in air/O₂ at atmospheric (or reduced) pressure are rather different to those that occur under vacuo. A good account of this may be found in the references²⁵⁻²¹, which also include details of the formation of various pentoxide phases. Terao indicates that, under vacuum growth conditions (< 10⁻⁵ Torr), several lower oxides may be grown: the highest of these is the tetragonal dioxide, NbO₂ (a = 4.837Å, c = 2.998Å). Lower oxygen pressures result in the formation of the cubic monoxide: the conditions prevalent in the MBE system appear to lie predominantly in this pressure regime.

Unfortunately, there is sometimes confusion in the literature as to the precise structure and properties of some of the oxides, and authors employ diverse nomenclature. The reader is referred to the paragraphs below, and to the references²⁵⁻²¹ for a representative description of the niobium oxide system, and of the transformations that occur both in air and at reduced pressures. Some good, recent review papers are cited in Ch. 1. To rationalise the nomenclature, this thesis recommends Terao's system as the most appropriate.

The principal phases of NbO₅ formed by heating Nb, or its lower oxides, in air/O₂ may be referred to as the low-, medium-, and high- temperature forms. Terao²⁵ named these hex-δ, gamma, and α respectively, where hex-δ is either a precursor to NbO₂²⁵⁻²ⁱ or else a poorly-crystallised form of gamma²⁵⁻²⁴. The transformation "hex-δ → gamma" takes place through relatively small changes in the atomic distribution, while "gamma → α" occurs via a significant rearrangement of both kinds of atoms. Two distinct intermediate forms, the gamma' and β oxides, have also been identified in this transformation²⁵⁻²⁶. The gamma, β and α niobium pent oxides were identified and characterised by Brauer²⁴ as early as 1941, and were named T, M and H respectively. Holser²⁷ correctly referred to the "T" form as such, but Terao named it the "L" form. Terao also referred to an α' form, stable only at elevated temperatures. Goldschmidt²⁸ performed structural and stability studies on many of these
oxides: he named the gamma and \( \alpha \) forms of Terao as \( \alpha \) and \( \beta \) respectively, and the \( \beta \) form of Terao was described as being merely an intermediate oxide closely related to the \( \alpha \) form of Terao. It is, therefore, the gamma and \( \alpha \) pentoxides of Terao that are of greatest interest to this work. The available data on these oxides is summarised in Table 5.2.

5.7.2 POST-DEPOSITION OXIDATION OF NbO\(_x\) LAYERS: RESULTS

The monoxide of niobium may be converted to the gamma-form of the pentoxide in an oxygen atmosphere and at temperatures as low as 400°C\(^{5,19,5,20}\). The change in specific volume, however, is great (= 1.87), inducing cracking of the film above a certain critical thickness (unspecified in the literature)\(^{5,19}\). Using the available crystal data, the change in volume per niobium atom was evaluated for each transformation (Table 5.2): when one is dealing with the oxidation of a layer of niobium/niobium oxide of fixed Nb content and known thickness, this is of greater use than the change in specific volume.

MBE-grown layers of niobium oxide were oxidised in dry oxygen in a quartz-tube furnace. Warm-up times were approximately 1.5 hours, and the layer was kept at the oxidation temperature for between 2 and 5 hours. Results for this work are included in Table 5.2. The calculated relative volume per Nb atom for the transformation "NbO \( \rightarrow \) gamma-Nb\(_2\)O\(_5\)" is 1.74 (if \( Z \) is assumed = 12, as early authors claim\(^{19,24}\)). This compares favourably with the measured change in thickness (for NbO-6C f.c.c. films on LiNbO\(_3\) and sapphire) of approximately 1.7. However, Terao\(^{5,20}\) contests the density measurements of previous workers and estimates \( Z = 14 \): this data has been included in Table 5.2. The expansion factor of the layers upon conversion to the gamma pentoxide was surprisingly reproducible (Fig. 5.9), so much so that the increase in thickness could be reliably used to estimate initial layer composition.

Layers whose initial thickness exceeded \( \approx 0.4 \) \( \mu \)m showed a marked tendency to roughen and crack upon ex situ oxidation in a furnace; the film even flaked away from the substrate in some cases. The thickest layers (up to \( \approx 1.2 \) \( \mu \)m) were necessarily grown at reduced O\(_2\):Nb ratios, and therefore also required the largest uptakes of oxygen. The value of the critical cracking thickness would be expected to depend on many factors, such as layer stress, composition and crystallinity; also, film-flaking may be aggravated by the use of substrates that are not atomically clean prior to deposition. Flakes obtained from the oxidation of thicker layers (grown both at high and low O\(_2\):Nb ratios) were crushed and subjected to X-ray powder diffraction analysis: the results were in excellent agreement with the X-ray data reported by Goldschmidt\(^{5,28}\) and Terao\(^{5,5}\) for the monoclinic gamma-Nb\(_2\)O\(_5\) with cell parameters:
\[ a = 7.31(7) \text{ Å}; \quad b = 15.72(8) \text{ Å}; \]
\[ c = 10.74(9) \text{ Å}; \quad \beta = 120^\circ 30'. \]

(Note that this structure is closely approximated by a simpler, orthorhombic unit cell with cell parameters: \( a = 6.174 \text{ Å}, b = 3.658 \text{ Å}, \) and \( c = 3.932 \text{Å} \).)

There are several niobium oxides (particularly the hex-\( \delta \) form) that possess similar X-ray structures to that obtained for the flakes. However, there was sufficient unique, identifying information in the flake powder diffraction patterns to permit a confident assignment to the gamma structure. Only one significant X-ray line was not indexable in Terao’s study of the gamma phase - this can be attributed to the strongest line (the (201) reflection, \( d = 2.734 \text{Å} \)) of the "NbO\(_2\)" tetragonal structure\(^{[5.5]}\). There was also evidence for this line in the author’s X-ray studies.

The thinner, single-crystal films of NbO-6C f.c.c. (< 1500Å) were successfully converted to gamma-Nb\(_2\)O\(_5\) without cracking. Baking in a furnace at 420°C for < 3 hours in a dry \( \text{O}_2 \) atmosphere caused the layers to become clear and effected a complete transformation. The quoted transformation/oxidation temperature (\( \approx 400^\circ \text{C} \)) was also confirmed in these experiments. X-ray analysis indicated that, upon oxidation in the furnace, the layers became more disordered. In the worst cases, single-crystal films became poorly-oriented polycrystalline (see Fig. 5.10, which also gives evidence for the presence of an oriented film of polycrystalline gamma-Nb\(_2\)O\(_5\)). X-ray orientation (Weissenberg) studies performed on oxidised layers (deposited on z-cut sapphire) suggested that the gamma-Nb\(_2\)O\(_5\) orthorhombic (111) plane of the crystallites was parallel to the (001) sapphire plane. The orientation of the crystallites for oxidised layers on z-cut LiNbO\(_3\) was very similar.

No detailed information was available on atomic positions within the unit cell for gamma-Nb\(_2\)O\(_5\)\(^{[5.29]}\). An investigation of the possibility of lattice-matched planes between LiNbO\(_3\)/sapphire and gamma-Nb\(_2\)O\(_5\) has been published by the author elsewhere\(^{[5.30]}\).

### 5.7.3 PHASE CHANGES IN NIOBIUM PENTOXIDES; PROBLEMS

From the point of view of device stability, a possible drawback of the gamma-pentoxide is the slow, partial, time-temperature dependent conversion in air to the \( \alpha \) form. Available data\(^{[5.19.5.28]}\) indicates a 10% conversion after \( \approx 1000 \) hours at 600°C, or after a number of years at room temperature. The \( \alpha \) form appears to be more stable than the gamma form, and might therefore be considered preferable in device manufacture. A long treatment of gamma layers at temperatures > 700°C should give total conversion. However, this temperature may not be compatible with other device processing requirements; also, the transformation is accompanied by a significant structural change and a further increase in specific volume (Table 5.2).
<table>
<thead>
<tr>
<th></th>
<th>Nb</th>
<th>NbO-6C f.c.c.</th>
<th>NbO₂[^a]</th>
<th>gamma-Nb₂O₅[^b]</th>
<th>gamma-Nb₂O₅[^d]</th>
<th>α-Nb₂O₅[^e]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unit cell type:</td>
<td>Cubic b.c.c.</td>
<td>Cubic f.c.c.</td>
<td>Tetragonal†</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td></td>
<td>c₀ = 5.976</td>
<td></td>
<td>c = 10.749</td>
<td>b = 15.728</td>
<td>b = 15.72</td>
<td>b = 3.824</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>β = 120°30'</td>
<td>β = 120°42'</td>
<td>β = 120°10'</td>
<td></td>
</tr>
<tr>
<td>Cell Volume (Å³):</td>
<td>36.17</td>
<td>76.23</td>
<td>1118</td>
<td>1066</td>
<td>1062</td>
<td>1359</td>
</tr>
<tr>
<td>Z (see text):</td>
<td>2</td>
<td>3[^f]</td>
<td>32</td>
<td>14[^g]</td>
<td>12</td>
<td>14[^h]</td>
</tr>
<tr>
<td>Nb atoms/unit cell[^i]:</td>
<td>2</td>
<td>3[^i]</td>
<td>32[^i]</td>
<td>28</td>
<td>24</td>
<td>28[^i]</td>
</tr>
<tr>
<td>Volume /Nb atom (Å³):</td>
<td>18.08</td>
<td>25.41</td>
<td>34.95</td>
<td>38.07</td>
<td>44.26</td>
<td>48.54</td>
</tr>
<tr>
<td>Relative volumes per Nb atom[^j]:</td>
<td>0.712</td>
<td>1.000</td>
<td>1.38</td>
<td>1.50[^l]</td>
<td>1.74[^l]</td>
<td>1.91</td>
</tr>
<tr>
<td>Relative volumes per unit mass[^l]:</td>
<td>...</td>
<td>1.00</td>
<td>1.37</td>
<td>...</td>
<td>1.87</td>
<td>2.68</td>
</tr>
</tbody>
</table>

[^a]: Reference 5.37; [^b]: Reference 5.5; [^c]: Reference 5.26; [^d]: Reference 5.38; [^e]: Reference 5.9, File No. 35-789;
[^f]: Statistical occupation of available Nb sites gives Z = 3; [^g]: Reference 5.24; [^h]: Quoted Z, or calculated using density data in j;
[^i]: Value measured for the oxidation of NbO-6C fcc layers to gamma-Nb₂O₅ on z-cut LiNbO₃ and sapphire substrates was approx. 1.7;
[^j]: Reference 5.19. Additional Footnotes: †This phase forms a tetragonal superstructure; *NbO is defined as = 1.
1.2 μm, polycrystalline layer of NbO-6C fcc + NbO$_2$ (tetragonal phase) deposited on z-cut sapphire. (3cm oscillation photograph, rotation axis = sapphire [110]). Layer composition = NbO$_{1.15}$.

Selected indices: A = NbO$_2$ (110); B = NbO-6C fcc (111); C = NbO$_2$ (211); D = NbO-6C fcc (220).

The presence of the two phases was confirmed by Texture photography.

Powder diffraction photograph for layer (a) after oxidation in dry O$_2$ at 420°C for 6 hrs. The phase is identifiable as gamma-Nb$_2$O$_5$. Selected indices are given: E = (001); F = (111); G = (002); H = (220).

Oxidation product for layer presented in Fig. 5.4 after heating in dry O$_2$ for 3 hrs. at 420°C. The oxidised layer was intact on the z-cut sapphire substrate. (3cm oscillation photograph, rotation axis = [100]).

Arc indices: I = gamma-Nb$_2$O$_5$ (111); J = gamma-Nb$_2$O$_5$ (110).

CuK$_\alpha$ (nickel-filtered) radiation was used throughout. All photographs were taken in the same camera. The quoted gamma-Nb$_2$O$_5$ indices are for the orthorhombic unit cell. (Data was obtained at the Crystallography Unit, UCL, with the help of Dr. H.J. Milledge).
Layers of gamma-Nb$_2$O$_5$ were processed at 800°C for 20 hours in dry O$_2$ in order to convert them to the α form (in accordance with Goldschmidt’s results$^{28,29}$). The total volume change (referred to NbO = 1) was approximately 2.0: this compares well with the predicted value of 1.91 in Table 5.2. However, the process also resulted in a reduction in layer quality: significant surface roughening/cracking was observed using Talystep; X-ray patterns showed a further degradation in crystal quality; optical losses were increased (see next section).

5.7.4 OPTICAL WAVEGUIDING IN PROCESSED LAYERS

Optical waveguiding was achieved in the gamma-pentoxide layers. In all cases, He-Ne wavelengths were employed; prism and end-fire techniques were used to launch a guided mode. The theory and practice of optical waveguiding experiments are dealt with fully elsewhere$^{31-33}$; in this case, a computerised, automated waveguiding rig was used to deduce β/k and loss for the layers$^{33}$.

The waveguides tended to be lossy, with a large proportion of the loss being in-plane scatter (due to the crystallite boundaries). Most guides were single mode, and gave both TE and TM modes$^{31}$. The thickness of the layer and the coupling angle were used in established slab waveguide equations to yield, among other data, the refractive index, n, for the material constituting the waveguide$^{33}$. One (rather lossy) waveguiding gamma-pentoxide layer gave:

$$\beta/k = 2.0097 \text{ (TE mode)} ; 1.8265 \text{ (TM mode)}$$

$$n = 2.350 \quad ; \quad 2.345$$

The refractive index is usefully high (see Ch. 1), but the large loss makes the material unsuitable for practical devices.

All n values were reduced, and losses increased, upon conversion to the α form. A fairly typical result was:

**Gamma form**

Refractive index:

$$n_{\text{TE}} = 2.36 ; \quad n_{\text{TM}} = 2.26$$

Loss:

$$12 \text{ dB/cm} \quad ; \quad 10 \text{ dB/cm}$$

which, when converted to the α form, gave:

**Alpha form**

Refractive index:

$$n_{\text{TE}} = 2.22 ; \quad n_{\text{TM}} = 2.16$$

Loss:

$$> 25 \text{ dB/cm for each polarisation.}$$

Ellipsometry was often used to confirm the refractive index results. Agreement was good.
The lower $n$ and higher loss observed for the $\alpha$ form detracts from its usefulness in waveguide device applications. The difference in $n$ observed in different directions for the oriented layers, both by ellipsometry and guided wave probe, may be indicative of birefringence.

5.8 SUGGESTED FUTURE WORK; DISCUSSION; KINETICS.

The symmetry and niobium occupation site relationships have been examined for NbO$_6$C f.c.c. and gamma-Nb$_2$O$_5$ on z-cut LiNbO$_3$ and sapphire (see Fig. 5.7 and ref. 5.30). Further research is needed, aimed at the direct growth of Nb$_2$O$_5$ by MBE on the z-cut and y-cut faces of LiNbO$_3$ [the use of y-cut substrates may yield further information on the growth kinetics, and gives a more useful combination for acousto-optic applications (Ch. 1)].

Epitaxial layers of niobium oxide grown by MBE were structurally of high quality, but optically opaque. Post-deposition, ex situ oxidation retained a suitably high refractive index, but (owing to layer degradation) gave rise to inhibitive optical scatter. Successful deposition of pentoxide material in situ must now be achieved if MBE-grown layers of niobium oxide are to be of practical use in optical waveguide applications. As it stands, however, the MBE system may be limited to growing the monoxide or dioxide of niobium: the reasons for this are practical (system over-pressure) and thermodynamic in origin (see Ch. 4).

One approach to the growth of niobium pentoxide in situ would be to employ much higher O$_2$:Nb ratios. The trend in the variation of film composition with incident O$_2$:Nb beam flux ratio suggests that the present maximum O$_2$:Nb ratio (= 100) would have to be increased by a factor of at least 10 in order to grow the pentoxide. This corresponds to local O$_2$ pressures at the substrate of between $5 \times 10^3$ and $5 \times 10^4$ Torr (with the lowest, reliably-measured Nb flux rate, $= 0.05$Å/s). This proposed threshold O$_2$ pressure for the formation of the pentoxide is within the range quoted earlier for bulk growth (as suggested by Terao$^{15-51}$). The temperatures that have given the single-crystal growth of NbO-6C f.c.c. and hex-\(\pi\) in this work are close to (or above) those required for the formation of pentoxides in air: this, at least, augurs well for future attempts at MBE-grown pentoxide.

However, we saw in Ch. 2 that severe problems are encountered when high ambient pressures of oxygen are used during MBE growth. Drastic system modifications would have to be brought about to permit the growth pressures quoted above (this is discussed further in Ch. 6). In addition, the quoted Nb flux rate corresponds to a rather small growth rate (< 200 Å/hr.). Fortunately, there are alternative approaches to that of raising O$_2$ growth pressure: the challenge is to develop an oxygen source which gives a form of oxygen (e.g. free atomic radicals, or ions) for which the oxygen sticking coefficient and/or surface residence time are increased; it may also be of benefit to seek growth regimes that are more favourable to
oxygen uptake (for example, reduced growth rates and temperatures may, in fact, shift the
growth towards NbO₂ and Nb₂O₅[142]). Such work, if successful, would pave the way to
realising a full oxide growth capability in an MBE system: i.e. control over oxygen
stoichiometry of grown layers from Nb to Nb₂O₅, coupled with precise control over layer
thickness, interfaces and purity. Some progress was made towards this goal in Ch. 4, where
the development of these ideas, and results of initial investigations using a free oxygen radical
source, were presented: the required specification seems to be an O:O₂ ratio in the beam of
the order of 5% (for an assumed O sticking coefficient of 1/2).

The reduction of fluctuations in the flux rates gave superior compositional control in
the films, and may also help to improve epitaxy/film quality, especially for thicker layers. The
niobium oxide system is complex and many of the oxides are closely matched in terms of
composition and/or structure: tight process control might, then, also prove crucial in inducing
a specific oxide phase to grow in preference to all others, particularly if the desired phase is
favoured only over a narrow range of conditions by virtue of lattice-matching, symmetry,
beamflux, occupation site or thermodynamic considerations. For example, the tendency,
oberved by Betts[153], for lithium niobate to grow with the cubic Li₃NbO₅ structure on y- and
z-cut LiNbO₃ and z-cut sapphire substrates may be linked to the favourability of the cubic
growth mode of niobium monoxide on crystal surfaces possessing the particular symmetry and
structure of these substrates: growth of a different structure (e.g. rhombohedral LiNbO₃ or a
monoclinic niobium pentoxide) may well require that a narrow range of conditions be met (see
Fig. 2.3). If MBE is to be applied successfully to this oxide system, good control (and
reproducibility) is needed for all the factors that can influence growth (see Ch. 2).

Further optimisation of growth parameters and process control is now needed to
improve the growth of thick oxide and niobium metal layers. Pure, single crystal layers of
niobium metal have interesting applications[522]; however, the high binding energy and solubility
of niobium for oxygen, nitrogen, carbon and hydrogen would require that the ambient pressure
be minimised during its deposition on heated substrates[534]. MBE is therefore a promising
choice, if a vacuum process is to be employed to grow epitaxial niobium layers of controlled
purity, uniformity and thickness.

Electrically-conducting, epitaxial layers of niobium metal or niobium oxide, grown by
MBE, were envisaged as having applications as efficient, buried, field electrodes. The aim was
to construct an epitaxial, electro-optic modulator device as a vertical waveguide structure, with
enhanced efficiency resulting from the strong interaction between the LiNbO₃/Nb₂O₅ and the
applied electric field. The results of this chapter (and of theoretical studies performed by
Robinson[533]) show that such layers are not suitable: alternatives are now being sought (see
Ch. 6).
The sticking coefficient of O$_2$ ($C_{\alpha\beta}$) during the MBE-growth of the niobium oxides was calculated from the known beam fluxes and layer compositions (see Fig. 5.11). $C_{\alpha\beta}$ was defined as:

$$C_{\alpha\beta} = (O: Nb \text{ in film}) + (2 \times O_2: Nb \text{ in beams})$$

(Eqn. 5.1)

The sticking coefficient of O$_2$ ($C_{\alpha\beta}$) during the MBE-growth of the niobium oxides was calculated from the known beam fluxes and layer compositions (see Fig. 5.11). $C_{\alpha\beta}$ was defined as:

$$C_{\alpha\beta} = (O: Nb \text{ in film}) + (2 \times O_2: Nb \text{ in beams})$$

(Eqn. 5.1)

The general trend of the graph is: as the O$_2$:Nb beam flux ratio is increased, the fraction of the O$_2$ beam incorporated into the layer drops nearly as fast (i.e. $C_{\alpha\beta}$ drops). The overall effect is a slowing increase in the oxygen content of the film with increasing incident O$_2$:Nb flux ratio. The O$_2$ sticking coefficient per niobium atom was enhanced by the simultaneous presence of Li flux: the limited available data is included in Fig. 5.11 (further discussion is deferred to Ch. 6).

The above discussions show that it may now be beneficial to return the emphasis to LiNbO$_3$ growth. The lower O$_2$:metal ratio in LiNbO$_3$ (compared with Nb$_2$O$_5$) could help to ease the oxygen deficiency problem. Limited work of this kind was performed by the author: Li-Nb oxide material was deposited by MBE on LiNbO$_3$ and SiO$_2$ substrates at low and intermediate O$_2$:Nb flux ratios. The results of this work did not add significantly to the previous work by Betts$^{[53]}$, except in two respects: firstly, reliable sticking coefficient data for Li-Nb oxide growth on LiNbO$_3$ substrates was obtained (as described above); secondly, Auger depth profiles for layers grown on SiO$_2$ demonstrated that good control over composition and uniformity was possible (see Fig. 5.12; part (b) is for the Nb:Li flux ratio approximately doubled). However, oxygen deficiency was still apparent. Further work is now required, as described in Ch. 6.

It remains to be seen if improved in situ oxygen stoichiometry (Ch. 4) could ever entirely obviate the need for post-deposition oxidation in a furnace: this, at present, causes the thick layers to suffer from cracking and other detrimental effects; the thin layers suffer a degradation in crystal quality. The rate at which post-deposition oxidation is made to occur may have a bearing on this, and deserves further investigation.
FIGURE 5.11: STICKING COEFFICIENT DATA FOR NIOBIUM OXIDE
AND LITHIUM-NIOBIUM OXIDE GROWTH BY MBE

\[ \Delta = \text{niobium oxide growth} \]
\[ \diamond = \text{growth in presence of Li}\]
\[ (\text{average Li flux } < 3.6 \times 10^{14} \text{ Li atoms/cm}^2/\text{s}) \]

Substrate temperature range: 610°C - 650°C;
z-cut LiNbO₃ and sapphire substrates were used.

A = result quoted by Betts¹³.¹⁴
(corrected for new oxygen calibrations)

\[ C_{O_2/Nb} = \frac{O_2 : Nb \text{ ratio in grown film}}{(O_2 : Nb \text{ ratio in beams}) \times 2} \]

\( \text{NbO}_x: \ x < 1 \quad x = 1 \quad x > 1 \)
\( x \neq 1.25 \text{ to } 1.4 \quad \llap{|}_x \llap{-\text{Layer composition}} \)
(a) Lithium-niobium oxide layer grown on thermally-oxidised silicon; (b) Layer deposited under similar conditions, but with a greater Nb/Li flux ratio.

Electron and ion beam parameters as for Fig. 5.6.
(Data from Loughborough Consultants Ltd.)
5.9 SUMMARY

Epitaxial, thin films of single-crystal niobium oxide were successfully grown on z-cut LiNbO$_3$ and sapphire by MBE, a technique which, to the authors' knowledge, has not been applied to this material system elsewhere. The structure of single- and poly-crystal films grown at low O$_2$:Nb flux ratios (up to $\approx 10$) was that of a new variant of NbO-6C with randomised vacancies in the bulk of the layer: this was termed "NbO-6C f.c.c.". This phase was grown on both types of substrate. At high O$_2$:Nb ratios (approaching 80) a new form of niobium oxide, "hex-$\pi$", was grown on z-cut sapphire, with a composition close to NbO$_{1.25}$. The epitaxial relationships have been determined for both of the above phases as grown on their appropriate substrates: the stated growth modes are entirely consistent with all observed structural and compositional data. Intermediate O$_2$:Nb ratios produced, in thick layers, a mixed oxide phase consisting of NbO-6C f.c.c. + NbO$_2$ (tetragonal phase). Important sticking coefficient data was deduced for MBE growth of Li-Nb oxides using molecular oxygen.

All films developed a thin "skin" of Nb$_2$O$_5$ on the surface upon exposure to the atmosphere. Ex situ oxidation procedures were developed for the films, leading to oriented polycrystalline gamma-Nb$_2$O$_5$ on z-cut sapphire and LiNbO$_3$. Optical waveguiding was achieved in these layers, but scattering losses were high. Further progress towards the growth of device quality material by MBE may hinge on the future solution of the oxygen deficiency problem.

REFERENCES

5.5 N. Terao, Japan. J. Appl. Phys. 2 (1963) 156.  
5.7 British Crystallographic Association, Spring meeting, 28-31 March, 1988, Warwick.  
5.8 Dr. H.J. Milledge, The Crystallography Unit, Dept. of Geological Sciences, University College London, Gower Street, London, WC1E 6BT (Private Correspondence).  
5.9 The JCPDS 1985 Powder Diffraction File; Inorganic Phases (The International Centre for Diffraction Data, 1601 Park Lane, Swarthmore, PA 19081), Alphabetical Index, p. 532.  

149


5.29 The Inorganic Crystal Structure Data File (Bergerhoff) at the SERC Chemical Databank System, Daresbury, England.


5.32 R.A. Betts, Ref. 5.3, Ch. 6.


CHAPTER 6

SUMMARY AND APPRAISAL OF REPORTED WORK

Summary of novel contributions to the field;
Successes and shortcomings of MBE for the Nb-Li-O system;
Suggestions for future work.

6.1 SUMMARY:
WORK PERFORMED: NOVEL CONTRIBUTIONS TO THE FIELD

Molecular Beam Epitaxy is a crystal-growth technique rarely applied to oxide systems. Previous work in the Nb-Li-O system\textsuperscript{[64]} had involved the deposition of very thin LiNbO\textsubscript{3} layers at low growth rates homoepitaxially and on sapphire. There was little more than an existence theorem for the growth of single crystal LiNbO\textsubscript{3}. Owing to system limitations, the conditions and fluxes under which the desired layers were produced were not known to any useful accuracy and could not be reliably reproduced. Little was understood regarding the growth kinetics and sticking coefficients of the beam species, and the effects of various pre-deposition substrate preparations had been only partly monitored. The work, though, made a useful platform from which to launch more detailed studies in this oxide system; it also isolated a number of problems that would have to be solved in order to make further progress.

This thesis has concentrated on the deposition of niobium oxides on LiNbO\textsubscript{3} and sapphire substrates by MBE: to the knowledge of the author, there is no other report of MBE-grown niobium oxides in the literature. The aims were to grow epitaxial niobium oxide for device applications, and to explore the MBE growth kinetics; the latter study was not only for niobium oxide in its own right, but also in order to clarify the role of the niobium oxide lattice in lithium niobate growth by MBE. As a result of this work, the roles of Li and Nb in the Nb-Li-O MBE-growth process were deconvolved to some extent. Some Li-Nb oxide deposition was performed, but was not pursued in great detail: Betts\textsuperscript{[64]} had already established the approximate growth regimes for these oxides, and the niobium oxide work proved to be sufficiently complex to absorb the research effort.

Chapter 1 explored the potential applications for MBE-grown oxides in this materials system, highlighting the advantages and drawbacks of MBE as a deposition technique. Certainly, the growth of such oxides by MBE was deemed to be a novel approach. Chapter 2 established the main limitations of the inherited system. The most important of these were:

1. Lack of control over growth parameters;
2. Low growth rates;
3. Oxygen deficiency.
(1) and (2) were technological problems, and were largely overcome. (3) was less tractable, and is discussed later. The problems associated with the growth of Li-Nb oxides in an MBE system were addressed (e.g. the simultaneous operation of a gaseous, a volatile and a refractory source). This development work led to reproducible growth runs in the system for the first time, with precise control over beam fluxes, substrate temperature, and substrate preparation.

The theme of equipment development was continued in Chapter 3, where the new 50keV RHEED unit was described. The problems arising from the use of insulating substrates, such as surface charging, were overcome. The detailed empirical and theoretical study of the reciprocal lattice of LiNbO₃, as performed by RHEED, is without precedent. The mean inner crystal potential was deduced for LiNbO₃, and an upper limit was measured for the average sampling depth of 38.3keV electrons in amorphous Nb. Wet-etch etch rates and 3keV Ar⁺ etch rates were measured. Surface studies on the effects of various ion-cleaning conditions and doses, and of typical heat treatments, were also completed: an Ar⁺ dose of circa $10^{16}$/cm² amorphised z-cut LiNbO₃ surfaces in vacuo, but reconstitution was achieved above 600°C. Using an Al-backed phosphor screen, RHEED patterns were obtained during electron bombardment heating. The RHEED and Auger studies gave the first true indication that surface composition and crystal structure could be largely recovered following a typical predeposition clean. Also, the main problems with the substrate preparation procedure were pinpointed, e.g. residual ion damage (which influenced subsequent epitaxy) and carbon contamination.

Chapter 4 described the development of the oxygen source used for oxide growth. This began with performance testing of, and modifications to, the microcapillary array, and ended with the use of an oxygen "free atomic radical" source relying on a magnetically-confined plasma discharge for its operation. The appendices contain the theory, extended by the author, for the performance of both types of source: in each case, comparison was made between theoretical predictions and observed performance. A "threshold" mechanism was postulated to explain the apparent lack of atomic oxygen generated by the discharge source at low discharge currents. The available quantitative data was largely in support of a mechanism of the type described. In addition, the vacuum system was calibrated for reliable flux measurement, both for molecular and atomic oxygen. The problems and limitations of using molecular oxygen for layer growth were investigated in depth.

Chapter 5 contained the bulk of the growth studies. This dealt mainly with the deposition of niobium oxide of various compositions, and of niobium metal, by MBE. The modified MBE system described in Ch. 2 gave good control over growth parameters and, for the first time, gave repeatable growth runs for a wide range of O₂:Nb beam flux ratio. In most cases, niobium oxide layers could be grown of predetermined composition, structure and thickness, and with good thickness uniformity. The O₂:Nb beam ratio was varied between about 2 and 100, and the limits of the system's capabilities were explored. The first layers having a thickness in excess of 1 micron were also deposited.
A number of new and mixed-oxide structures of composition between NbO$_{0.8}$ and NbO$_{1.4}$ were grown: these included thin, single-crystal layers of a new variant of niobium monoxide (termed NbO-6C fcc) and an entirely new phase of niobium oxide ("hex-\(\pi\)). Thick, polycrystalline layers were also grown, composed either of NbO-6C fcc or of an NbO-6C fcc + NbO$_{2}$ mixed phase. A great deal of RHEED, X-ray, Auger, XPS, SIMS, ellipsometry, and resistivity analysis was brought to bear on the layers. X-ray data yielded the epitaxial relationships of the single-crystal layers of hex-\(\pi\) and NbO-6C fcc to their respective substrates. The cubic growth mode observed by Betts$^{61}$ for the deposition of Li$_{3}$NbO$_{4}$ by MBE was repeated (as far as the symmetry relationships were concerned) in the MBE-growth of niobium monoxide: these two structures have marked similarities, and this result may be relevant to understanding the dominance of the Li$_{3}$NbO$_{4}$ phase in the growth of lithium niobate by MBE.

However, the work of Chapters 4 and 5 also brought us face to face with the limitations of the system. The most serious problem encountered was that of oxygen deficiency. A quantitative assessment of the problem led to the conclusion that it was unlikely that the pentoxide could be grown in a conventional MBE system using molecular oxygen; hence, in Chapter 4, alternative forms of oxygen with enhanced sticking coefficient/mobility were sought. Because of oxygen deficiency, post-deposition oxidation of the layers was needed to achieve optical transparency. The effects of such oxidation on the crystal structure were studied, and are now largely understood: the threshold temperature for oxidation in a furnace was found to be circa 410°C, and the final structure was that of the gamma-pentoxide. The alpha-pentoxide was also obtained, by higher temperature processing in the furnace. The post-deposition oxidation invariably caused a degradation of crystal quality; also, if the initial film thickness exceeded a critical value, layers tended to roughen and crack upon oxidation. Optical waveguiding was achieved in many of the oxidised layers, but with large losses (8→20 dB/cm). The best oxidised, intact, waveguiding layers that could be obtained were oriented polycrystalline: grain boundary scattering probably accounts for most of the loss in these waveguides, which were usually monomode, occasionally bimodal. It was also found that a critical thickness existed for the niobium oxide layers, above which they tended to grow polycrystalline rather than single crystal. So, one of the primary aims of the project was partly achieved: the growth of thicker layers (in this case, of niobium oxide) that might be suitable as multimode waveguides; however, low-loss, single-crystal films of this kind were not obtained.

Significant progress was made in understanding process kinetics. The RHEED studies indicated that the temperature threshold for the mobility of surface species was about 550°C (concurrent with the epitaxial temperature for MBE-grown Li-Nb oxides, determined by Betts$^{61}$). Also, epitaxy was shown to be very sensitive to substrate processing and growth conditions. Furthermore, the growth runs yielded sticking coefficient data for molecular oxygen as a function of the O$_{2}$:Nb beam ratio used during MBE. This work shed light on the oxygen
deficiency problem, and enabled an estimate to be made of the required fluxes for Nb$_2$O$_5$ growth by MBE. The sticking coefficient of O$_2$ was found to be dependent on Li flux - it was higher than for corresponding runs involving niobium and oxygen only. However, the sticking coefficient in the presence of Li was, at best, only doubled (see Fig. 5.11): therefore, even using the lowest Nb flux rates could achieve no better than about LiNbO$_3$, in this apparatus. This gives an adequate explanation of why oxygen-saturated layers have never been grown in the MBE system using molecular oxygen. The work with the various oxygen sources indicated that the acquisition of molecular oxygen by the growing surface during MBE was difficult, and gave clues as to possible reasons for the oxygen deficiency (e.g. the uptake of O$_2$ may be a diffusion-controlled process). There was also evidence to suggest that atomic oxygen will be more mobile and reactive than molecular oxygen during oxide MBE.

The work has been exploratory, and pursuit of various goals and devices has led to a number of interesting offshoots. For instance, early on in the project, vertical modulator heteroepitaxial structures were envisaged$^{[62]}$ (epitaxial sequence: substrate/ buried electrode/ buffer/ LiNbO$_x$/ buffer/ upper electrode): epitaxial niobium (or NbO) was to be the efficient, buried, field electrode, and niobium pentoxide was to form the buffer layers. As a result, niobium metal and niobium oxide films were deposited on (00.1) LiNbO$_3$. Subsequent research showed this device configuration to be too lossy$^{[63]}$; in compensation, however, the growth studies have extended the understanding of these materials, and new crystal phases have been grown. Alternative vertical modulator devices involving LiNbO$_3$ and SOS are now being investigated (see Section 6.3).

6.2 AN IMPROVED MBE SYSTEM
FOR THE DEPOSITION OF Nb-Li OXIDES

The main shortcomings of the project were: (a) that oxygen deficiency in the grown layers was not overcome; and (b) that LiNbO$_3$ growth was not investigated in depth. However, an understanding was achieved of the equipment and substrate preparation requirements for the growth of oxygen-stoichiometric Nb$_2$O$_5$ or LiNbO$_3$ by MBE. Several aspects of MBE growth and surface dynamics were explored, and the oxygen deficiency problem was investigated. On the basis of these results, suggestions may now be put forward for an improved and viable oxide-growth MBE system.

(1) Substrate preparation is of considerable importance. A low energy, high current-density source for ion-cleaning would be preferred, to help avoid residual surface damage which appears to inhibit epitaxy, especially of the rhombohedral LiNbO$_3$ phase. If 3keV Ar$^+$ is used, ion doses should be kept well below $10^{15}$cm$^{-2}$ (at this voltage, there is a case for avoiding ion cleaning altogether). Reliable and optimised SIMS is also needed, for surface impurity coverage data and to identify substrates that will give carbon-contaminated interfaces. Auger may be
preferred on the grounds that it causes less disruption to the surface; it would also be a less sensitive but more quantifiable technique, and could thus give compositional data.

(2) The present process control is adequate, but should ideally be improved further: this would help to achieve the precise conditions required for a particular oxide phase to grow (e.g. rhombohedral LiNbO$_3$ as opposed to cubic).

(3) Provision should be made for in situ RHEED during growth (see next section).

(4) At present, the highest achievable O$_2$:Nb ratio is about 100; this will have to be increased to at least 1000 to enable the growth of Nb$_2$O$_5$. For a growth rate of 0.1Å/s, this corresponds to a local oxygen pressure of more than about 10$^4$ Torr at the substrate. It is difficult to design an MBE system that can operate under these pressure conditions. An increase in oxygen uptake efficiency may therefore be desirable, requiring that an alternative oxygen source be found.

The plasma discharge source of Ch. 4 was not entirely suitable, but there was much data to suggest that using oxygen atoms might enhance the oxygen content of the grown layers. An improved source with efficient local differential pumping and operating with a good O$_2$ to O conversion efficiency (> 2%, preferably 5%) might do the job whilst allowing MBE conditions to prevail. The source would have to supply at least 1.6 x 10$^{14}$ O/cm$^2$/s for a Nb flux of 0.1Å/s (5.6 x 10$^{13}$ Nb/cm$^2$/s). The theory of Ch. 4 would be of use in designing such a source, and in understanding its operational characteristics. An oxygen ion source might also be tried, in which energy and angle of incidence could be varied, but the ions would need to be of very low energy to avoid resputtering, and charge neutralisation of the beam might be needed. In the last year, oxygen-deficiency problems in vacuum-deposited, high-$T_c$ oxide superconductors (using molecular oxygen) have been eased by the use of ionisation near the substrate$^{[16]}$: this might be applicable to MBE. An alternative is to seek a hybrid process, something akin to the adaptation of MOCVD to LPCVD - in this case, we may need low pressure MOMBE, though the availability and suitability of precursor materials for this materials system is problematic.

(5) Other system modifications are needed, as follows: an alternative to electron bombardment heating (to avoid having a hot filament near the substrate, and to facilitate RHEED during processing); a more efficient load lock (to improve wafer throughput); a Knudsen multisource cell for the Li (to improve Li flux control and reduce interference with the Nb evaporator). In addition, the technique would benefit from automation and feedback control (e.g. for flux stabilisation and control). A possible retrofit with solid oxygen sources should also be catered for.
6.3 SUGGESTIONS FOR FUTURE WORK

These have been mostly dealt with at the end of each individual chapter. The most important are now summarised.

(1) This thesis has investigated several aspects of growth and surface kinetics pertinent to the MBE-deposition of Nb-Li oxides. Further work is now needed to understand the process even more fully. Research should be undertaken to investigate:

(i) the kinetics of layer nucleation and initial growth;
(ii) surface mobility of reactants;
(iii) sticking coefficient and surface residence times for O radicals & other relevant species.

Data for (iii) could be obtained from a Modulated Beam Mass Spectrometry (MBMS) setup, using beams of O₂, O, Li and Nb under a variety of substrate conditions. In particular, reliable values for the sticking coefficient of O atoms (preferably during MBE growth) would be very useful in refining the estimate of required oxygen atom flux as given in Section 6.2. To investigate the initial stages of epitaxy, RHEED monitoring during growth would be invaluable.

(2) Further work is needed to improve the oxygen stoichiometry of MBE-grown Nb-Li oxide layers. For example, the system could be modified to cater for higher fluxes of O and/or O₂ during growth; alternatively, excited states of oxygen could be tried. However, Stall has suggested another approach, which uses solid oxygen sources. He argued that during the MBE-growth of alumina using molecular oxygen, the kinetics of the reaction between Al and O₂ at the growing surface was the rate-limiting factor (i.e. the surface residence time of the O₂ was much less than the typical reaction time for Al and O₂, so that the O₂ mostly desorbed before it could react); hence, very slow growth rates or very high pressures of O₂ would be needed to grow Al₂O₃ by MBE. This is effectively the same conclusion as that arrived at in Chs. 4 and 5 for the deposition of Nb-Li oxides by MBE using O₂. Stall’s approach was to use separate effusion cells to evaporate Al and As₂O₃ onto a heated substrate. As₂O₃ met the following essential requirements: it sublimed congruently; it had a long surface residence time compared with O₂; it reacted with the Al at the substrate surface to produce alumina and volatile by-products. Although the layers were not suitable for waveguide applications, oxygen deficiency in the grown material was largely overcome without having to resort to high oxygen pressures. It may be possible to apply this technique to the vacuum growth of Nb₂O₅ and LiNbO₃.

(3) The conclusions drawn from the niobium oxide studies, taken together with the work by Betts and the author’s own efforts with LiNbO₃ growth, carry sufficient weight to be acted upon. However, now that the NbOₓ system has been extensively studied by MBE and good growth-run reproducibility has been demonstrated, further deposition of Li-Nb oxides is
desirable, in order to confirm and clarify the role of Li in MBE overlayer growth. Some work with Nd or Cr doping would also be interesting for optical emission waveguide devices\cite{6,7,68}. Work should also be extended to other substrates, such as silicon (for which growth studies have already begun\cite{62}) and LiTaO$_3$. Alternative materials should also be grown, such as KNbO$_3$.

The main impetus for (2) and (3) is to be able to deposit, by MBE, Nb$_2$O$_5$ and LiNbO$_3$ layers that are suitable for device applications. For example, in the case of LiNbO$_3$, a novel waveguide structure is being looked into that involves a Si/LiNbO$_3$/Si vertical sandwich for IR propagation on sapphire or LiNbO$_3$ substrates: calculations show that very thin layers (circa 400→1000 Å) of electro-optic material give efficient 5V modulation in a device whose length is only a few hundred μm or so\cite{63} (hence large bandwidth). The silicon acts as electrode material and also contributes to the IR confinement, and no buffer layers are needed. Successful deposition of epitaxial layers that can be employed in structures such as these opens up exciting hybrid opto-electronic device possibilities: e.g. the integration of optically-active interconnect and switching elements with silicon and SOS\cite{62,63} (here, the good acoustic and optical properties of the oxides can be combined with the semiconductor capabilities of the substrate, such as lasing, detection, and electronics). MBE could meet the requirement for a heterogeneous single-crystal deposition technique with a high degree of film control.

However, given the results presented in this thesis, what are the prospects for MBE in terms of depositing Nb oxide and Nb-Li oxide material suitable for device applications, and are there credible reasons for adopting an MBE approach?

6.4 PROSPECTS FOR MBE AS A VIALBLE DEPOSITION TECHNIQUE IN THE Nb-Li-O SYSTEM

As far as the Nb-Li-O system is concerned, the work described above enables us to reasonably assess the prospects of MBE for the controlled growth of the higher oxides in this system.

Oxygen deficiency has been a persistent problem in the growth of Nb oxide and Li-Nb oxide material by MBE: it leads to severe optical loss and conducting layers, and makes necessary ex situ oxidation. In an attempt to grow niobium pentoxide in situ, O$_2$:Nb ratios were pushed to the limits of system capability (approx. 100) but the highest oxide achieved was a mixed-phase containing the dioxide (overall composition < NbO$_{1.4}$). Unfortunately, there was insufficient time to perform a detailed study of Li-Nb oxide growth. (Such work was not conducted in parallel with NbO$_3$ deposition because Li contamination of grown layers occurred whenever the Li gun had recently been in use). Nevertheless, some growth runs were performed with Li flux present: these showed that although the O$_2$ sticking coefficient was
improved in the presence of Li flux, even the lowest growth rates would yield ≈ 7% oxygen-deficient LiNbO₃ material in the present MBE system. Higher growth rates worsened the problem. Oxygen deficiency remains, therefore, the major obstacle to the growth of Nb oxides and Li-Nb oxides using the present MBE rig.

It is unlikely, then, that the MBE system as it stands will be able to yield single-crystal waveguides, either of Nb₂O₅ or rhombohedral LiNbO₃. For thinner layers of MBE-grown material, the proven control over growth conditions has given unprecedented reproducibility in crystal phase, quality, thickness, and composition. For thicker layers, the degradation of crystal quality that results from post-deposition oxidation weakens the case for MBE-grown waveguides; in addition, the growth of single-crystal niobium oxide by MBE appears to be limited by a critical thickness condition, though this should be less of a problem in homoepitaxial and lattice-matched systems (e.g. the growth of LiNbO₃ on LiTaO₃ or LiNbO₃).

In the light of these comments, it must be asked whether the MBE technique offers any genuine competition to its main rivals: in particular, r.f. sputtering is now enjoying a degree of success for epitaxial LiNbO₃ deposition on sapphire⁶-⁷ and for the controlled deposition of low-loss amorphous Nb₂O₅ waveguides⁶-¹⁰. However, in r.f. sputtering, the species have much higher energies than in MBE, and incorporation of plasma impurities can be high: this gives MBE the prospect (at least in principle) of an edge on sputtering for the growth of pure, single-crystal material. The MBE technique also lends itself easily to the growth of graded and multiple layers, and of doped material. The surface analyses and process monitoring associated with MBE can give excellent layer control and provide considerable potential as a research tool. The growth of thin-film LiNbO₃ by r.f. sputtering still has a long way to go, particularly in terms of controlling layer stoichiometry, achieving low optical loss and in actually demonstrating electro-optic properties in the layers. As for niobium oxide, no single-crystal growth has been reported by this method. It should also be remembered that, despite the cited difficulties, excellent single crystal layers possessing the NbO-6C fcc, hex-π, LiNbO₃, and Li₃NbO₄ structures have been grown by MBE under suitable conditions.

6.5 CONCLUDING REMARKS

The outlook for oxide deposition in general is favourable: the market is expanding and novel device structures are being sought. The concept of oxide layer growth by MBE has been a neglected one, probably owing to the cost involved and the specialised problems associated with the provision of oxygen and the monitoring of insulating substrates and overlayers. MBE offers a number of advantages, such as a proven capability for single-crystal growth, excellent control over layer composition, thickness and purity, the ability to grow multilayer or graded composition structures, and a flexible dopant capability.
The work presented in this thesis has led to a good understanding of the problems that must be overcome in order to grow oxides in the Li-Nb-O system by MBE. Growth regimes have been examined in a quantitative manner, kinetics data has been acquired along the way, and two new phases of niobium oxide have been grown epitaxially. The demonstration of suitable substrate preparation procedures and in situ analyses for Nb-Li-O MBE, and the information culled from the various attempts at achieving an oxygen source that can give oxygen-saturated layers, may be of considerable use to oxide MBE generally. It may also be possible to apply the acquired expertise to areas in which similar problems exist, and for which MBE may hold some of the answers (e.g. in the fabrication of niobium oxide Josephson junctions, or for high-T<sub>c</sub> superconductor devices, where the epitaxial growth of defect oxides is of particular interest). In the light of this, and given the growing importance of the superconducting oxides, the concept of oxide growth by MBE may not yet be defunct; in fact, it may have a great deal to offer.

To the author's knowledge, no other workers have reported MBE-grown niobium oxides, so the research input to this field has been relatively minor. Further research could pay dividends, especially as Nb<sub>2</sub>O<sub>5</sub> and LiNbO<sub>3</sub> have already found niches in electro-optic and SAW devices, and the applications seem set to continue and expand, at least in the near to middle term. However, the impact that would be made by MBE in this field depends on whether or not the work described in this thesis can be extended to the growth of single crystal, oxygen-saturated layers of waveguiding thickness and of desired crystal phase. The advantages of MBE could then bear fruit in specialist areas of thin film growth, and also allow growth kinetics to be better explored.

The low throughput and high cost of MBE may, however, be a disincentive to device production by this technique and could seriously put off prospective research institutions. MBE of Nb-Li oxides will probably be assigned to the realm of expensive, "wildcat" research. Even if pursued, oxide MBE will not leave the research bench for the production floor as quickly as its main rival, sputtering: this is because of the overwhelming disparity in the deployment of resources and the fact that r.f. sputtering is beginning to show some promise for the deposition of epitaxial Li-Nb oxide layers. However, further research into the MBE growth of these oxides is important, as this would determine the viability (or no) of the process for a vast range of useful material combinations, and would help to gauge the future of the technique in research philosophy. The work reported in this thesis will be of general use to any institution embarking on oxide MBE in the Li-Nb-O (or a similar) materials system. It is hoped that this brief sally into the field will encourage further work in the area.
REFERENCES:


6.3  H. Robinson and C.W. Pitt, Optics Communications, to be published. Also: M. Petrucci and H. Robinson, private communication.


APPENDIX 2.1

LIMITATIONS OF SIMS
FOR QUANTITATIVE ANALYSIS OF COMPOSITION

(a) The sputter yield of a given ion is highly dependent on a variety of factors (e.g. the chemical environment of the constituent (sampled) atoms, and the mass and energy of the sputtering specie): there is not, therefore, a one-to-one correspondence between the relative sputter yields of the constituents of a crystal surface and its stoichiometry. To obtain a surface composition usually requires reference to a standard (see (h)).

(b) The sputtered species are often molecular ions (e.g. NbO\(^{+}\)); it is difficult to relate the abundance of these directly to an absolute composition.

(c) The peak heights, as displayed by the SIMS unit, depend not only on the sputter yields, but also on a host of instrumental parameters: these are associated with the filtering and detection of the sputtered ions and the electronic processing of the resulting signal. Some of them are subject to variations with time. If any crucial parameter is altered during a run, then the resulting spectra are not strictly comparable to those obtained earlier, or in any previous run (though, of course, approximate comparisons may still be made).

(d) A number of other factors can influence relative peak heights in the spectra: for example, sample position and orientation, and the accumulation of surface charge from the sputtering beam. Also, the detector can have "memory" effects. The gain decay of the channeltron electron multiplier with time is not linear with mass, and secondary effects such as "preferential axis sputtering" (in which anomalously high sputter yields are obtained along particular crystallographic directions\(^{[14]}\)) can be at work. No such factors were monitored or investigated previously in this system: consequently, any quantification of SIMS spectra given in earlier work is to be doubted. Some of the above effects have now been observed (e.g. see Fig. 2.4).

(e) The SIMS electronics give a non-linear output as the signal approaches a certain ("saturation") value. Quantitative interpretation of large peaks (such as Li\(_{7}^{+}\)) should be viewed with particular caution.

(f) According to Wittmaack\(^{[24], p.675}\), "preferential sputtering" by the SIMS probe beam occurs at the beginning of a SIMS analysis on the fresh surface of a multicomponent system, even for "low damage" (or "static") SIMS; this is due to the different escape probabilities associated with each of the sputtered species. The effect should be prominent for LiNbO\(_{3}\), where the constituents have widely differing masses, and might account for the dominance of the Li\(_{7}^{+}\) peak over peaks such as Nb\(^{+}\) and NbO\(^{+}\) in the initial SIMS spectra of LiNbO\(_{3}\).
substrates (though it may also be a result of the quadrupole system sensitivity). A steady state is only achieved after approximately one monolayer of material has been sputtered away, whereupon the peak heights become steady, and can be regarded as being related to the "bulk" composition in some way. An order of magnitude calculation suggests that at the etch rates involved\textsuperscript{[A2.1.1]}, steady-state times for LiNbO\textsubscript{3} could be up to several hours or more: this has been observed as a shift in relative peak heights during early stages of SIMS. The etching effect is also evident from the gradual reduction of surface impurity peak heights with time.

(g) The SIMS ion-beam spot size (approx. 0.8 cm diameter) means that some secondary ions originate from the clip holder and substrate table.

(h) As a result of the above problems, little work has been done in relating SIMS spectra directly to absolute surface composition\textsuperscript{[2,3]}. The only practical means of circumventing at least some of these difficulties, in particular (a) to (e) above, is to calibrate the equipment for the substrate material being used and for a given composition: this would require that a LiNbO\textsubscript{3} sample of known composition be cleaved in vacuo to establish a "fingerprint" spectrum\textsuperscript{[2,3]} for the particular instrumental parameters used; subsequent compositions may then be derived comparatively. It is difficult, in our system, to perform this experiment. In any case, the literature shows that vacuum-cleaved surfaces are often non-representative of bulk composition/impurities: in particular, LiNbO\textsubscript{3} surface stoichiometry shows a complex dependence on the thermal and chemical history of the particular sample\textsuperscript{[2,1,A2.1.2]}, also, argon ion bombardment and electron irradiation influence carbon and oxygen levels on the surface.

Further work would be required to understand these problems in greater depth and to optimise the use of SIMS. Clearly, SIMS is a valuable and informative surface analytical tool; despite the above difficulties it can, when used with care, give vital data on impurity coverage\textsuperscript{[2,1]} and useful comparative data on compositional changes. Its limitations and reliability are now better understood.

References:


A2.1.2 V.H. Ritz and V.M. Bermudez, "Electron-Spectroscopic Studies of LiNbO\textsubscript{3} and LiTaO\textsubscript{3} Surfaces", Phys. Rev. B \textbf{24} (1981) 5559-5575.
A full treatment of the scattering of electrons by a periodic crystal lattice is a complicated, quantum mechanical problem. The intensity of electrons scattered into a given direction takes the form of an integral\(^1\). If some simplifying assumptions are made (e.g. elastic scattering; wavefunction inside scatterer = incident wavefunction), then this integral takes the form of the Fourier Transform of the scattering potential (equivalent to the Fourier Transform of the crystal lattice itself). This, when evaluated, is found to maximise in certain directions, which are taken to correspond to those of the diffracted beams.

However, it is far more convenient to make use of an established mathematical construction to predict the diffracted beam directions: in the RECIPROCAL LATTICE, each lattice point represents a set of crystal planes (the distance of a reciprocal lattice point from the origin of reciprocal space is proportional to the inverse of the separation of the planes it represents, and its direction is that of the normal to those planes). The incident electrons are represented by a vector \( AB \), such that: \( |AB| = 1/\lambda_{\text{electron}} \), \( B \) is the origin of reciprocal space, and the direction of \( AB \) in reciprocal space is the same as that of the electron beam in real space (see Fig. 3.7 (b)). We shall refer to reciprocal space vectors as k-vectors: these are closely related to wavevectors, or momentum vectors. Now, if the scattering event is elastic, then all possible scattered electron k-vectors must lie on a sphere (radius = \( 1/\lambda \) centred on \( A \): this is termed the Ewald Sphere\(^1\). The Ewald Sphere and reciprocal lattice constructions in k-space are such that if the Ewald sphere intersects a reciprocal lattice feature, then this gives the real-space direction of a possible diffracted beam (i.e. a "reflection") and also indicates which crystal planes give rise to it. For "simple" diffraction conditions\(^1\), the construction gives results in direct agreement with the predictions of the more advanced (and less manageable) theories\(^1\). The diffraction directions thus obtained can be related to real-space distances on the fluorescent screen via simple geometry. The Bragg Law algorithm of Ch. 3 yields the surface periodicity of the crystal.

For high-energy electrons (\( \geq 10\text{keV} \)) the radius of the Ewald sphere is sufficiently large to allow the intersection with reciprocal space to be approximated by a plane, provided that only a small angular range is sampled at the screen. However, an appreciation of the slight curvature of this sampling "plane" is still needed to fully understand the RHEED patterns (for example, to explain the Laue Circle\(^1\) often observed for well-ordered surfaces, see Fig. 3.6).

Although the Ewald sphere construction is based on a simplified approach to electron diffraction, it usually provides an adequate interpretation of RHEED data. RHEED features which are not easily predicted or explained using this construction can often still be dealt with
within the framework of reciprocal space. Such features include: reciprocal lattice "rods"; Kikuchi lines; diffuse background scattering; intensity enhancements due to forward diffuse scattering; intensity distributions centred on reciprocal lattice points; and effects due to surface disorder\cite{A3.1.2}. Many examples of the above may be found in the cited literature of Ch. 3, along with more detailed accounts of the Ewald sphere approach and the advanced theory.

References:

A3.1.1 D. McKie and C. McKie, "Crystalline Solids" (Nelson, 1974).
ALUMINIUM-BACKED PHOSPHOR SCREEN FOR RHEED

The performance of RHEED phosphor screens can be considerably improved by coating the vacuum face with a thin, metallic (usually aluminium) layer. The thickness and finish of the layer are arranged to make it opaque to low energy electrons and visible light, but highly reflecting to light and virtually transparent to the primary electron beam. Contrast is improved, charging effects are reduced, and the efficiency of conversion of electron beam energy into light is increased (e.g. phosphorescence that would otherwise escape to the vacuum side is reflected back).

For the UCL screen\textsuperscript{[A3.2.1]}, an organic (cellulose-based) "blanket" layer was first floated onto the granular phosphor surface: this ensured that the subsequently evaporated metal was planar, continuous, and mirror-like. The cellulose layer was then baked away, and the metal layer earthed, to leave a thin, conducting, aluminium mirror in intimate contact with the phosphor. Electron range and transmission data\textsuperscript{[A3.2.2,A3.2.3]} were used to predict the thickness of aluminium required, and different thicknesses around this value were tried. About 2000Å was adequate, being virtually transparent to 20keV electrons, and opaque to light: thus, electrons associated with the RHEED patterns were not significantly affected, but background haze due to stray light in the system was eliminated; patterns were sharper and brighter, and the 2keV electrons from the probe heater no longer caused screen white-out, so that RHEED could be performed during substrate heating for the first time (for typical results, see Fig. 3.11).

References:

A3.2.1 Work performed by Bob Airy, Imperial College, London.
A3.2.2 D.W. Epstein and L. Pensak, "Improved Cathode-Ray Tubes with Metal-backed Luminescent Screens", RCA Rev. 7 (1946) 5-10.
CALCULATION OF ELECTRON PENETRATION DEPTH, D

(Extracts from documents RED1 and RED2[3,29].)

(a) Variation of sampled depth in RHEED with electron energy.

\[ D = \text{penetration depth perpendicularly into sample}; \]
\[ \Sigma = \text{electronic inelastic mean free path}; \]
\[ \theta = \text{angle of grazing incidence of electron beam}; \]
\[ E = \text{electron accelerating potential in volts}; \]
\[ \lambda = \text{electron wavelength}. \]

Assumptions: (i) No refraction; (ii) Specular reflection;
(iii) Average distance travelled by electrons in sample = \( \Sigma \).

A simple geometrical construction is used to estimate \( D \):

From which: \[ D = \left( \frac{\Sigma}{2} \right) \sin \theta \] \hspace{1cm} (Eqn. A3.3.1)

Now: \[ \Sigma \propto E^{1/2} \] \hspace{1cm} (Eqn. A3.3.2)

holds for electrons with \( E < 10 \text{keV}^{[329]} \), and should be approximately true for \( E = 40 \text{keV} \).

For reflections to occur from crystal planes (hkl):

\[ \lambda = 2 \cdot d_{(hkl)} \sin \theta \] \hspace{1cm} (Eqn. A3.3.3)
Therefore, for a reflection from a given set of planes:

\[ \lambda \propto \sin \theta \]  
(Eqn. A3.3.4)

so that, at higher electron energies, smaller angles of \( \theta \) are used.

Now:

\[ \lambda \propto E^{1/2} \]  
(Eqn. A3.3.5)

Eqn. A3.3.5 is for non-relativistic electrons, but will apply with only 3% error to 50keV electrons.

Substituting Eqn. A3.3.2 and Eqn. A3.3.4 into Eqn. A3.3.1, then substituting Eqn. A3.3.5 into the resulting equation gives:

\[ D = \text{constant} \]  
(Eqn. A3.3.6)

Eqn. A3.3.6 is an approximation, and only applies to specular reflections from a given set of planes within the assumptions made. However, this result leads us to believe that \( D \) should not vary very much as electron energy is increased from 5keV to 40keV: i.e. although \( \Sigma \) increases, \( \theta \) decreases so that the normal penetration remains approximately constant.

(b) Calculation of \( D \)

Seah\(^{\text{327}}\) gives the empirical formula:

\[ \Sigma = 0.72 (\alpha E)^{1/2} \]  
(Eqn. A3.3.7)

where: \( \alpha = \) monolayer thickness (in nm) for the crystal;
\( E = \) in electron volts, as before;
and \( \Sigma = \) given in monolayers.

Taking the niobium sublattice to define the "monolayers", and considering z-cut LiNbO\(_3\):

\[ \alpha = c_a/6 \]  
(Eqn. A3.3.8)

where: \( c_a = \) c-axis lattice parameter for LiNbO\(_3\) in nm (see Ch. 3), which is divided by 6 because there are that many niobium "sheets" spaced perpendicularly to the z-axis in one unit cell of LiNbO\(_3\).

At 5keV, this gives:

\[ \Sigma = 25 \text{ monolayers of niobium} = 60 \text{ Å} \]

168
Using Eqn. A3.3.1 with a typical value of θ (= 10°) yields:

\[ D = 5 \, \text{Å} \]

At 40keV, we get:

\[ \Sigma = 170 \, \text{Å} \quad (\theta \text{ is typically } 3°) \]

and:

\[ D = 4 \, \text{Å} \]

Results are summarised below:

---

**TABLE A3.1:**

**RHEED DATA FOR LiNbO₃ (Σ and PENETRATION DEPTH)**

<table>
<thead>
<tr>
<th>Substrate</th>
<th>RHEED energy /keV</th>
<th>Σ /Å</th>
<th>θ /°</th>
<th>D /Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiNbO₃</td>
<td>0.5</td>
<td>7[^1][^2]</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>22[^a]</td>
<td>10</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>60[^b]</td>
<td>10</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>170[^b]</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>35[^c]</td>
<td>10</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>150[^c]</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>Silicon[^25]</td>
<td>40</td>
<td>360</td>
<td>2</td>
<td>6</td>
</tr>
</tbody>
</table>

[^a]: Calculated from the previous entry using the equation in Seah[^27] which relates Σ to electron energy.
[^b]: Calculated from the empirical formula given by Seah.
[^c]: Estimated from electron escape depths, as obtained from XPS energy loss intensity data for LiNbO₃[^29].

The above D values for LiNbO₃ compare favourably with those for a variety of other materials under similar conditions[^6,325]: as an example, typical data for silicon (which has a similar average atomic weight per atom to LiNbO₃) is given in the table.
In the crystal lattice of LiNbO₃, the oxygen ions occupy low symmetry positions, forming distorted octahedra. These low symmetry configurations give rise to "general reflections", which conform to the constraint:

\[-h + k + l = 3n\]  \hspace{1cm} (Eqn. A3.4.1)

where \(n\) is an integer, and \(h, k, l\) refer to the Miller indices of the reflection in question. The Nb and Li ions occupy higher symmetry positions, known as "special positions": these give rise to reflections that are subject to the same constraint as general reflections, but with a further condition that \(l\) must be even:

\[l = 2m\]  \hspace{1cm} (Eqn. A3.4.2)

For LiNbO₃, we would expect the special reflections to dominate in an X-ray diffraction experiment (the niobium elastic scattering cross section is much larger than that of oxygen or lithium). For general reflections, however, the extinction distance, \(\Gamma\), must be calculated in each case to determine if the intensity is likely to be observable (\(\Gamma\) is related to the structure factor). In Fig. 3.8 (a), for example, the general reflection (003) is not expected, because it has a very large \(\Gamma\); (213), however, has a sufficiently small \(\Gamma\) for it to be an observable reflection. In Figs. 3.8 (b), (c) & (d), only the special reflections participate, since all the general reflections have exceedingly large extinction distances. In Fig. 3.8 (e), all general reflections are also special, because \(l = 0\) for all reflections. In this way, by systematically considering the structure factor for each reflection, the expected reciprocal lattice sections of Fig. 3.8 were built up.
APPENDIX 3.5

MEAN INNER POTENTIAL ($\psi_0$) CALCULATION FOR LiNbO$_3$

Using the formula on p. 242 of Vainshtein's text$^{[3,7]}$:

$$\psi_{\text{mean}} = \frac{\sum_{\text{molecule}} (48 \times (\text{Volt.Å}^3) \times f_a(0))}{\Omega}$$

where:

- $\psi_{\text{mean}} = \psi_0$;
- $\Omega = \text{molecular volume (Å}^3\text{)}$;
- $f_a(0) = \text{atomic scattering factors (for electrons) of atoms in molecule as sin} \theta/\lambda \rightarrow 0 \text{ (absolute units)}$;
- $(\text{Volt.Å}^3)$ are the units of the constant, 48.

Using tabulated values$^{[3,7,12]}$ of $f_a(0)$ for Li, Nb and O gives:

$$\psi_0 = 48 \sqrt[4]{\frac{f_{\text{Nb}}(0) f_{\text{Li}}(0) f_{\text{O}}(0)}} V = 16 \text{ Volt for LiNbO}_3$$

**Note:** $\Omega$ is calculated from: $\Omega = 1/N$

where $N$ is given by:

$$\rho = N m_\text{e} A,$$

$N = \text{number density of molecules (m}^{-3}\text{)}$; $m_\text{e} = \text{mass of nucleon (kg)}$;

$A = \text{LiNbO}_3$ molecular weight = 148; $\rho = \text{density} = 4627 \text{ kgm}^{-3}$$^{[3,18,3,39]}$.

Thus:

$$N = \frac{4627/(148 \times 1.66 \times 10^{27})}{m^3} = 1.88 \times 10^{28} \text{ m}^3$$

giving: $\Omega = 1/N = 53 \text{ Å}^3$, as quoted above.
Appendix 3.6

COHERENCE LENGTH CALCULATIONS

Authors of RHEED work do not always quote the coherence lengths ($\delta z_{coh}$ or $\delta x_{coh}$) for their electron beam; but when they do, calculations are rarely shown and conclusions tend to differ. This type of confusion in the literature often stems from misconceptions as to the precise meaning of coherence length. Also, simplified equations cannot reliably be used for its evaluation in every case: each RHEED configuration must be considered individually.

As a first-order approach, the coherence width and length are approximated by:

\[ \delta z_{coh} = \lambda (2\beta_\parallel [1 + \delta E/2E])^{1/2} \]

(Eqn. A.3.6.1A)

\[ \delta x_{coh} = 2E\lambda/\delta E \]

(Eqn. A.3.6.1B)

where: $\delta E$ = energy spread of electrons; $\beta_\parallel$ = angular spread of beam (radians);
$z$ is parallel, and $x$ perpendicular, to the electron $k$-vector;
$\lambda$ = electron wavelength; $E$ = electron energy.

Note that, generally, the coherence length and width will differ, leading to a coherence "strip" on the surface of the crystal, usually elongated along the beam. Neave quotes a coherence strip of width 40Å and length 1000Å (at 10keV and 2° grazing incidence). Eqns. A.3.6.1 yield 50Å and 900Å respectively at 38keV for the UCL system - these are plausible results (typical values are 100→300Å and 1000Å respectively). The $\delta E/E$ factor was negligible: the filament electron energy distribution was less than about 1 eV, so that the major contribution to $\delta E$ was from the ripple on the H.T. supply, measured at only about 4V (a fairly typical result). The main contribution to broadening was thus from $\beta_\parallel$, the angular spread of the beam.

As a check, a calculation was made of the relative broadening of RHEED features due to the $\delta E$ and $\beta_\parallel$ factors using the Ewald sphere construction: this was done by allowing the pertinent range of sphere radii and beam directions respectively. The results showed that the $\delta E$ factor was relatively unimportant, but the $\beta_\parallel$ factor could account for about half of the width of the streaks observed in Fig. 3.6. The length of the streak was less helpful, since the contribution to streaking from the coherence length factor was swamped by effects such as refraction, disorder, and thermal diffuse scattering.
A meaningful estimate of coherence width can be gained by obtaining a RHEED pattern from a good-quality, Si single crystal, and estimating the coherence width directly from the streak broadening. The streaks were slightly narrower in width (and length) to those obtained for good LiNbO₃ substrates, and gave 80Å as a lower limit on \( \delta x_{coh} \).

The last word, however, should be had by Beeby\(^{[A3.6]}\), who shows that it is only the dimension of the electron wave packet which is important in determining the coherence area. The calculation of the spatial extent of a wave packet for a particular experiment is exceedingly difficult: values of \( \delta x_{coh} \) derived from the energy and angular divergence of the primary beam alone may therefore not be valid.

References:

A3.6.2 Ref. 3.14.
A3.6.5 Ref. 3.10.
APPENDIX 4.1: MOLECULAR EFFUSION SOURCE FOR OXYGEN

A 4.1.1 INTRODUCTION

This work is included as an appendix to Ch. 4, and gives a summary of quantitative analyses conducted on the microcapillary array. Betts[4.4.1] attempted to minimise the oxygen overpressure in the deposition chamber by replacing the sonic nozzle arrangement with such an array. The array system was redesigned by the author, and later replaced by the free atomic radical source. Here, the validity of the theory applied to the array, and the efficacy of the modifications, are discussed.

A 4.1.2 THEORY

The molecular flux profile from an ideal aperture[4.4.2] obeys a cosθ variation as shown in Fig. 4.1 (a) (i). It is easy to obtain a high flux intensity in the forward direction from such a source, but a large percentage of the flux is off-axis. In order to directionalise the beam, a canal of the same cross-section as the ideal aperture may be used. For the same source (backing) pressure ($p_a$), these two arrangements give the same oxygen flux per unit solid angle in the forward direction (for which: $θ = 0$, and flux/sterad = $N(θ)$). However, the canal has the advantage that the total flux is reduced by the factor $G[4.4.3]$, where:

$$ G = \frac{8R}{3L} \quad \text{(Eqn. A4.1.1)} $$

where: $R =$ radius of aperture or canal; $L =$ length of canal.

The theory requires that $p_a$ be sufficiently low for the effects of inter-molecular collisions inside the canal to be negligible, i.e.:

$$ \Lambda \gg L, R \quad \text{(Eqn. A4.1.2)} $$

where: $\Lambda$ is the mean free path, given by[4.4.4]:

$$ \Lambda = \frac{kT}{(2\pi \sigma p_a)^{1/2}} \quad \text{(Eqn. A4.1.3)} $$

for which $p_a$ is in Pa, $k$ is the Boltzmann constant, $T$ is the gas temperature in Kelvin, and $\sigma$ is the collision cross-section for oxygen molecules. The value of $p_a$ at which Eqn. A4.1.2 begins to break down we shall term $p_c$. 

174
For the single canal, values of $p_0$ in excess of $p_c$ were needed to obtain sufficient oxygen flux for MBE growth experiments: under these conditions, the beam collimation was poor. The same $N(0)$ could be obtained more compactly by substituting the canal for an array of narrow capillary tubes$^{[4.1.1 \rightarrow 4.1.3]}$ of radius $a$ and length $l$ (Fig. 4.1 (a) (iii)). In terms of $N(0)$, the array is equivalent to one canal of radius $R_{eff}$ and length $L_{eff}$ given by:

$$R_{eff} = (N_t \cdot a^2)^{1/2}$$  \hspace{1cm} (Eqn. A4.1.4)

and

$$L_{eff} = l \cdot (R_{eff} / a) = l N_t^{1/2}$$  \hspace{1cm} (Eqn. A4.1.5)

where: $N_t$ is the number of capillary tubes in the array.

The real advantage of the array over the single canal is that far greater source pressures can be used (by a factor $L_{eff}/l$) before effusion breaks down, because the condition for effusion (Eqn. A4.1.2) now becomes:

$$\Lambda \gg l, a$$  \hspace{1cm} (Eqn. A4.1.6)

The beam profile at the substrate is also more uniform than that of the single canal, and there is less off-axis flux. The array selected for the MBE system had the following dimensions:

- $l = 2 \times 10^3$ m; $a = 5 \times 10^{-6}$ m; Approx. open area of array = 50%;
- Open array diameter = 1.5 cm (multiply by 1.5 for bellows);
- $N_t = 1.1 \times 10^6$ (multiply by $1.5^2$ for bellows arrangement);
- Source to substrate distance = 15 cm (with the bellows, this became 6.1 cm).

The beam flux may be calculated using the following relationships, taken variously from Betts$^{[4.1.1]}$, Maissel and Glang$^{[4.1.4]}$ and the references cited above:

$$N(0)_{aperture} = n_o \cdot v \cdot a^2 / 4 \text{ molecules/s/sterad}$$  \hspace{1cm} (Eqn. A4.1.7)

$$N_{total} = \pi \cdot N(0)_{aperture} \text{ molecules/s}$$  \hspace{1cm} (Eqn. A4.1.8)

for which:

$$v = (8kT/\pi m)^{1/2}$$  \hspace{1cm} (Eqn. A4.1.9)

where: $m$ is the molecular mass, and $n_o$ is the particle density/m$^3$ behind the array/source, given by:

$$n_o = p_o'/kT = 131.6 \cdot p_o''/kT$$  \hspace{1cm} (Eqn. A4.1.10)

$'$ In N/m$^2$; $''$ In Torr.
Now, the total flux for a single capillary tubelet in the array is simply that from an ideal aperture of the same radius multiplied by the factor $G$ (as described above). Using Eqn. A4.1.7 in Eqn. A4.1.8 and multiplying by Eqn. A4.1.1 gives:

$$N_{\text{total}}_{\text{tubelet}} = G \cdot N_{\text{total}}_{\text{aperture}}$$

$$= 2\pi \cdot n_o \cdot \nu \cdot a^2 / 3l \text{ molecules/s} \quad \text{(Eqn. A4.1.11)}$$

When Eqn. A4.1.11 is multiplied by $N_o$, it gives the total flux/s from the array. Dividing by the array area gives flux/cm²/s. If Eqn. A4.1.10 is then substituted into the resulting equation, it becomes possible to relate source pressure to the total flux/cm²/s from the array:

$$N_{\text{total}}_{\text{per cm² of array}} = 1.2 \times 10^{15} / \text{s} \times p_o \quad \text{(Eqn. A4.1.12)}$$

with $p_o$ now in mTorr.

A 4.1.3 IMPROVED CALIBRATION OF ARRAY & OXYGEN BEAM FLUX

In Betts' work, the oxygen beam pressure (and hence molecular flux) was estimated from the background oxygen pressure. This was measured with a small mass spectrometer or ionisation gauge occupying a consistent position within the chamber but at some distance from the substrate (and not in the beam). Such uncorroborated data was unreliable and inaccurate: the ambient oxygen pressure was strongly influenced by many factors (gettering by the EG5 evaporators and evaporated metals, which could reduce the ambient pressure in the evaporator region by up to a factor of 4, and in the substrate region by typically 30%; outgassing of guns, chamber walls, etc.; liquid nitrogen shroud warm-up or drop in pumping efficiency; and so on). Also, it was not known precisely how the background and beam pressures were related. The resulting errors made it difficult to control oxygen flux; consequently, good compositional uniformity or reproducibility in the grown films was not achieved.

The molecular oxygen flux rates quoted throughout this thesis have been arrived at by careful calibration experiments. A given growth pressure was set, then all the pump valves on the system were closed. The chamber pressures were subsequently monitored as a function of time using calibrated ionisation gauges and mass spectrometers, and the experiment repeated for a number of growth pressures. Typical plots are shown in Fig. A 4.1.1 (b). The slopes of these graphs ($dp_{\text{chamber}}/dt$) per unit growth pressure were remarkably similar ("background" contributions due to outgassing, etc. were small, but were corrected for). The more general form of Eqn. A4.1.10, when differentiated with respect to time, gave the total molecular flow/s through the array as a function of rate of change of chamber pressure (the chamber volume was known, 0.12m³). Assuming a collimated beam, and knowing the exposed area of the
bellows array, then gave the measured oxygen beam flux calibration constant: $3.5 \times 10^{14} \text{O}_2/\text{cm}^2/\text{s per mTorr of } p_o$. This is within a factor of about 3 of the calculated constant of Eqn. A4.1.12: $1.2 \times 10^{15} \text{O}_2/\text{cm}^2/\text{s per mTorr of } p_o$ ($p_o << p_c$). The agreement is good under the circumstances. The discrepancy can easily be accomodated by pressure and beam-flux measurement errors, or by capillary anomalies such as tube non-linearity or an anomalous scattering function for the tube walls (other workers using effusion sources have found more off-axis flux than predicted by theory, especially at large distances from the source\textsuperscript{[A4.1.5]}. The oxygen beam fluxes quoted in this thesis were generally derived using the measured calibration constant.

As a further check, O\textsubscript{2} partial pressures in the beam were measured with a calibrated mass spectrometer: these agreed to within a factor of two with the beam pressures calculated\textsuperscript{[A4.1.4]} from the beam flux rates. For example, a beam flux of $3.6 \times 10^{15} \text{O}_2/\text{cm}^2/\text{s}$ gave a calculated beam pressure of about $5 \times 10^6$ Torr; the measured oxygen pressure was about $2 \times 10^6$ Torr slightly off-axis, and $6 \times 10^6$ Torr on-axis (i.e. in the beam). These agreements further justify confidence in the quoted oxygen fluxes and array theory. All subsequent runs were monitored for $p_o$; in conjunction with the other pressure sensors, this gave good oxygen flux control (see Ch. 2 for a quantitative assessment).

Further confirmation of the theory is given in Fig. A4.1.1 (a). As $p_o$ was increased from $<< 10^3$ Torr, a pressure regime was eventually reached ($= p_c$) for which the condition of Eqn. A4.1.6 was no longer met (i.e. a move from $\Lambda >> l$, $a$ to $\Lambda = l$, $>> a$). This is known as a "Mode I $\rightarrow$ Mode II transition"\textsuperscript{[A4.1.6]}. The equations governing the flow distribution inside and beyond the canal then become highly complex, but the trends for Mode I $\rightarrow$ Mode II are easily summarised: the beam width begins to increase with $p_o$; and (since the expression for total gas flow remains unaltered) the proportion of flow in the forward direction decreases\textsuperscript{[A4.1.7]}. These detrimental effects essentially limit the source pressures at which the array may be used to $< p_c$. Fig. A4.1.1 (a) shows the pressure monitored by a mass spectrometer tuned to the 32 peak and placed a few degrees off-axis of the array, as $p_o$ is varied. There is strong evidence for the above transition: it corresponds to the kink in the graph at about $1.3 \times 10^2$ Torr. Now, Eqn. A4.1.3 predicts that $\Lambda = l$ when $p_o = 10^2 \rightarrow 5 \times 10^2$ Torr: the observed transition point lies within the predicted range. Note also that the values of $p_o$ used in the highest O\textsubscript{2}:Nb runs were $= 10$ mTorr, which is only just short of the transition pressure. Simple effusion theory was expected to begin to break down, and the beam diverge, if source pressures were further elevated.

A 4.1.4 COMPARISON WITH INHERITED SYSTEM

The above results represent a major step forward from previous work in this system\textsuperscript{[A4.1.1]}. In the inherited system, $p_o$ was not measured; its value was estimated by assuming
a perfectly collimated beam, and converting the estimated beam flux/cm²/s to a flux per sterad
at θ = 0 (i.e. N(0)). The expression in Marton[^A4.1.3] was then used to relate N(0) to pa\textsuperscript{2/3}.
This method was dubious: each capillary tubelet is so small, and its flux so directional, that the
solid angle over which the expression for N(0) actually holds is very much less than that
occupied by the substrate in front of the array. Hence the use of N(0) to estimate the flux
at the substrate is neither convenient nor valid; each tubelet delivers virtually its entire flux
to the nearby substrate.

Furthermore, for the array, the beam should be well collimated in Mode I: the
parameter "θ\textsubscript{ta}" (the calculated beam half-width[^A4.1.8]) was small, typically < 1° (0.4° for the
bellows array). Although there may have been some beam spreading due to other factors[^A4.1.8]
(such as tubelet misalignment) it still held that off-axis pressure measurements (such as those
used by Betts) would give rise to significant errors when used as a basis for beam flux estimates.
Using the approach given in this appendix gave fair agreement between the
calculated and measured calibration constants for the flux issuing from the array; there was
also good agreement between the measured beam pressures and those estimated from pa\textsuperscript{2/3}. This
showed that the method of Section A 4.1.2, which used the total flux from the array tubelets,
was an improvement on previous theory. In addition, reproducible and reliable measurement
of oxygen flux was obtained for the bellows array for the first time. Similar calibrations were
later performed for the radical source, giving comparable, if not better, reproducibility and
accuracy.

REFERENCES

A 4.1.1 R.A. Betts, PhD thesis (see ref. 4.1).
A 4.1.2 N.F. Ramsey, "Molecular Beams" (Oxford Univ. Press, 1956).
A 4.1.3 L. Marton (Ed.), "Methods of Experimental Physics"
A 4.1.4 L.I. Maissel and R. Glang, "Handbook of Thin Film Technology"
A 4.1.5 Dr. Gordon Lovis, Vacuum Generators Ltd., Maunsell Road, Castleham
   Ind.\textsuperscript{1} Estate, St. Leonards-On-Sea, E. Sussex (Private Communication).
A 4.1.6 J.A. Giordmaine and T.C. Wang, "Molecular Beam formation by Long
A 4.1.7 Marton, pp. 164/165.
A 4.1.8 Giordmaine and Wang, p. 470.
FIGURE A4.1.1: CHARACTERISATION DATA FOR THE MICROCAPILLARY (BELLOWS) ARRAY

(a) GROWTH CHAMBER PRESSURE AND OFF-AXIS BEAM PRESSURE AS A FUNCTION OF $p_0$ (SOURCE PRESSURE); OXYGEN GAS USED THROUGHOUT

(b) TYPICAL PLOTS OF CHAMBER PRESSURE versus TIME FOR VARIOUS GROWTH PRESSURES

$t = 0$, pump valves shut

$P_0$/mtrr

$O_2/Nb = 100$

$10^{-7}$ torr

$10^{-6}$ torr

$10^{-5}$ torr

$10^{-4}$ torr

$10^{-3}$ torr

$10^{-2}$ torr

$10^{-1}$ torr

$10^0$ torr

$10^1$ torr
APPENDIX 4.2: DISCHARGES IN OXYGEN

A 4.2.1 INTRODUCTION

A mechanism will be proposed for the postulated "threshold" effect of Ch. 4. This requires a detailed discussion of magnetically-confined D.C. discharges struck across molecular oxygen. However, the theory of discharges in gases is highly complex: Chapman\textsuperscript{[4.2.1]} warns that state-of-the-art understanding of D.C. and R.F. discharge plasmas is by no means complete, and doubt remains as to what species are present and what their roles are in maintaining the plasma. Further work is needed on the quantification of specie energy distributions and relative abundance. As far as the atomic oxygen source of Ch. 4 was concerned, the pressures in the discharge region were not known accurately; the situation was further complicated by the presence of confining magnetic fields. For these reasons, it must be stated that any "conclusions" drawn here are at best tentative, unless substantiated by favourable comparison with reliable experimental results.

A 4.2.2 GUN OPERATION; DESCRIPTION OF D.C. DISCHARGE

To begin with, certain parameters require definition:

\[ p = \text{gas pressure in the discharge region;} \]
\[ V = \text{energy (in electron-volts) of the electron initiating} \]
\[ \text{the process under consideration;} \]
\[ V_d = \text{voltage between anode and cathode;} \]
\[ I_d = \text{discharge current (electron current collected at anode).} \]

In a D.C. gas discharge, where \( p \) is above 10→20 mTorr and the voltage in excess of a few hundred volts, the glow discharge is usually self-sustaining, and consists of the Crooke's Dark Space (CDS), Negative Glow (NG), and Positive Column (PC) regions\textsuperscript{[4.2.2,3]}. For most small systems, such as in the atomic source, the PC is not present, and the NG extends to the anode. Thompson's experiments with discharges in oxygen\textsuperscript{[4.2.3]} showed that the plasma consisted entirely of the NG up to about 5 mTorr (this type of discharge is usually also of the so-called "abnormal" type\textsuperscript{[4.2.4]}). Visual observations of the atomic source during operation were consistent with the discharge being of this type. It is believed that the NG is effectively a conducting region: it contains mostly neutrals, but also electrons and ions with typical energies of a few eV or less\textsuperscript{[4.2.1]}. This means that virtually the entire applied voltage drop will appear across the CDS, across which electrons from the cathode are accelerated. There are thus three types of electron in the NG of a self-sustained discharge.
(a) "Fast electrons" (or "primaries"). These largely originate from the cathode, where they are produced by secondary emission processes such as ion bombardment. It has been verified\textsuperscript{[A4.2,5]} that a large proportion of primaries entering the NG possess a substantial fraction of the energy acquired in being accelerated across the CDS. Thompson\textsuperscript{[A4.2,3]} reported fast electrons in oxygen discharges having at least one third of the cathode potential (his discharge conditions were typically 1000 V, 15 mTorr).

(b) "Secondary" electrons - these are mostly produced by collisions between the primaries and the source gas species, and have energies typically of a few eV.

(c) "Ultimate" electrons, which have become thermalised in the plasma. These generally have the highest number density.

The energy distribution of electrons in such a plasma is, therefore, highly anisotropic.

Which family of electrons is responsible, then, for the ionising (and, by inference, atom-generating) collisions in the source? Some quarters hold that D.C. discharges are maintained by the thermal electrons, which can gain sufficient energy to cause ionisation by occasional excursions into the tail of the Maxwell-Boltzmann distribution\textsuperscript{[A4.2,5]}. But this hypothesis is by no means verified: Chapman\textsuperscript{[A4.2,8]} is at pains to point out the inconsistencies in the available data, and the considerable evidence identifying the primary electrons as the discharge-sustaining agent. Thompson\textsuperscript{[A4.2,3]} found that although the fast electrons were the least numerous in his oxygen plasmas, they were by far the main ionising specie in the NG region.

A 4.2.3 EFFECT OF MAGNETIC FIELD

The discharge in the atomic source was subjected to a powerful magnetic field (Fig. 4.3 (a)). Those electrons not moving parallel to the magnetic field would describe helical trajectories around the magnetic field lines on their way to the anode. Because of the enhanced path-lengths, the discharge could be maintained down to pressures $< 10^{-5}$ Torr in a well-designed system (compared with only 10 mTorr or so in a non-magnetic D.C. discharge).

Now, the pressures in the discharge region of the atomic source were estimated at typically a few mTorr or less: this gave\textsuperscript{[A4.2,3]} an inelastic mean free path of about 8 cm for 200 eV electrons. This may seem large, but the magnetically-enhanced path lengths would cause the fast electrons to become the predominant ionising (and atom-generating) species in the source\textsuperscript{[A4.2,4]}, even at low pressures. In this mode of operation, a Penning-type discharge was obtained\textsuperscript{[A4.2,4]}.
A 4.2.4 OXYGEN PLASMAS: PROCESSES OCCURRING THEREIN

Thompson[^4] discussed thirty-six separate plasma collision phenomena in oxygen discharges, and his list was by no means exhaustive. However, the literature also shows that at the voltages typically used in this work, ionic-impact generation of atoms is relatively unimportant, and electrons are the main instigators of plasma phenomena. Therefore, the main dissociation processes in an electrical discharge through oxygen include[^5]:

\[
\begin{align*}
O_3 + e^- & \rightarrow O^+ + O + 2e^- & - (P_1) \\
O_3^{++} & \rightarrow 3e^- & - (P_2) \\
O^{++} + O + 3e^- & - (P_3) \\
O^+ + O & - (P_4) \\
O^+ + O^+ + e^- & - (P_5) \\
2O + e^- & - (P_6) \\
\end{align*}
\]

In the atomic source, fast electrons with magnetically-enhanced path lengths would produce a "cascade" of such ionisation and dissociation products: these would either accelerate to the electrodes (producing further collisions along the way), or remain in the plasma for a time, or move to the walls of the gun. Neutral species had the further option of passing through the front orifice of the gun to constitute part of the beam that impinged on the substrate. The neutral (and excited neutral) oxygen atoms originating from the discharge plasma were referred to generically in Ch. 4 as free atomic radicals[^6], or simply as the "atomic beam". A typical voltage threshold for the formation of atoms (for process \( P_1 \), say) is \( V = 19.2 \) eV.

A 4.2.5 THRESHOLD MECHANISM

For the atomic source, only \( p_o, I_d \) and \( V_d \) could be monitored: this was by no means an exhaustive set of parameters. Fortunately, it seemed that a qualitative explanation of the threshold effect was possible on the basis of this data. The first step was to isolate the factors that determined the probability of generating an oxygen atom in the discharge plasma. These were taken to be:

**T1:** The overlap integral between the collision cross-section curve for molecular oxygen (as a function of incident electron energy) and the energy spectrum of electrons in the discharge;

**T2:** The electronic number density in the plasma;

**T3:** The number density of molecules in the plasma.

Strictly speaking, T1 should be the sum of the various overlap integrals for all the
processes by which oxygen atoms are generated in the plasma. Fortunately, all the electron-induced dissociation processes (see above) have collision cross-section curves that are similar to the total collision cross-section curve. They all peak at similar energies\(^\text{A4.2.7, A4.2.9-A4.3.11}\), and they all depend in a similar manner on \(V\): the collision cross-section\(^\text{A4.2.7}\), \(\sigma\), is small at threshold, but increases rapidly to a broad maximum at \(V = 40 \rightarrow 150\) volts; it then falls off slowly\(^\text{A4.2.1}\). The peak of the collision cross-section curve for the generation of atoms should occur at about \(V = 100\) volts\(^\text{A4.2.11, A4.2.12}\). It follows that the total collision cross-section curve for molecular oxygen to electronic impact can be taken as representative of the factor \(T_1\) in atomic production.

As shown earlier, \(V\) for primary electrons can be identified with \(V_e\). The primaries undergo inelastic collisions with source gas molecules in the NG region (some of these collisions generate the desired atomic oxygen) until they are collected by the anode. Although energetic (fast) electrons have a relatively small cross-section for atom-generating collisions\(^\text{A4.2.13}\), the cross-section increases as \(V\) drops. The overlap integral will be small when the source is driven in a high voltage, low current regime; however, reducing \(V_e\) decreases the inelastic mean free path of the fast electrons, and a larger proportion of atoms will then appear in the beam. In principle, the maximum efficiency in atomic generation will occur when the operating conditions maximise the overlap integral described in \(T_1\) (this will probably occur for values of \(V_e\) in the vicinity of a few hundred volts).

The factors \(T_2\) and \(T_3\) can also influence the atomic flux rate. Below 30 mA, \(I_a\) was observed to be roughly proportional to gas flow (and hence to gas pressure in the gun): \(T_3\), therefore, was roughly proportional to \(I_a\). Also, \(I_a\) was the collected electron current at the anode, which we suppose was related to \(T_2\) in some way. Ignoring secondary processes (such as dissociation by multiple impact and recombination) we may postulate that, as a first approximation, the atomic production at a given \(V_e\) is proportional to \(T_2 \times T_3\), or \((I_a)^2\). A plot of atomic flux rate versus \((I_a)^3\) was made (Fig. A4.2.1) using the data in Table 4.1: it fitted a straight line within the error bars, until about 10 mA, whereupon the "surface saturation" effect came into play. A linear regression gave the standard deviation as \(1.6 \times 10^{13}\) O atoms/cm\(^2\)/s, and a negative y intercept of approx. \(7.3 \times 10^{12}\) O atoms/cm\(^2\)/s. The latter figure was very close to the expected atomic removal rate due to contaminants (as calculated from the "drift" in Section 4.5.3).

We are now in a position to explain how the factors \(T_1\) to \(T_3\) might bring about a threshold effect at low \(I_a\) as observed in Fig. 4.7. As an order of magnitude fit, the atomic flux should be proportional to \((I_a)^2 \times T_1\). The \((I_a)^2\) dependence would give a parabolic curve shape near the origin. In addition, below about 5 mA, \(V_e\) was constant and high, virtually 5 kV (see Fig. A4.2.2): the energy spectrum of the fast electrons entering the discharge would therefore peak at high energy, and \(T_1\) would be at a minimum. All three factors, then, would be unfavourable for atomic generation, and virtually no atoms would be produced: a threshold,
or "tail", would be expected in the plot of atomic flux versus $I_d$ below about 5 mA. Furthermore, $I_d$ was not quite linear with $p_0$: $I_d$ was a little sluggish to get under way as $p_0$ was increased from zero (but after about 5 mA it rose almost linearly until "breakdown"); this would also contribute to the threshold effect by reducing T2. The above assertions are entirely consistent with the data in Fig. 4.7, in which the measured atomic flux appears to tail off below about 5 mA.

### A 4.2.6 HIGHER DISCHARGE CURRENTS

Beyond 8 mA or so, $V_d$ began to fall quite rapidly, and we would therefore expect a rise in the efficiency of atomic generation. Eventually, a pressure is reached where electrical "breakdown" occurs in the gas: the ionisation processes avalanche catastrophically (i.e. the "magnification factor" is high), and the discharge becomes effectively a short-circuit plasma. This transition is marked by a large increase in $I_d$ for virtually no increase in gas pressure, and $V_d$ drops to a steady value of about 600 V (Thompson\[4^2\]) observed such an effect in oxygen discharges, in which there was a sudden drop in "cathode fall" when the pressure exceeded a certain value, approx. 20 mTorr in his system). In this regime the discharge current is limited by the output impedance of the power supply. At breakdown, a sudden increase in the % of atoms in the beam is expected: although the gas flow (i.e. factor T3) remains almost constant, T1 will have increased greatly; also, the jump in $I_d$ (more than x2) due to breakdown means that T2 will have increased accordingly. In addition, the secondary electron emission coefficient maximises in this $V_d$ regime\[4^2\], which further enhances atomic generation.

### A 4.2.7 ENERGETIC NEUTRALS*

Energetic neutrals are generated by charge-transfer processes in the CDS. An event which is quite likely is: $O + O^* \rightarrow O^+ + O$, in which an ion becomes an atom while retaining most of its kinetic energy. Also, bombardment of the walls and anode by energetic ions produces energetic neutrals. It may be that energetic neutrals are detrimental to epitaxial growth: the average crystal quality of layers grown in Run 15 was considered slightly poorer than that of Run 14. Also, films processed at high $I_d$ (as described in Section 4.8.3) acquired small quantities of surface impurities to a depth consistent with the implantation of neutrals having an energy $< eV_d$. Now, the proportion of energetic neutrals in the beam could rise dramatically as $V_d$ is reduced\[4^2\], since the charge-transfer/recombinative cross-sections increase with reduced ion energy. On the other hand, the neutrals formed will be (on average) less energetic. These are factors that should be borne in mind, particularly if larger discharge currents are pursued. Fortunately, there was no direct line of sight to the substrate from most of those regions in the gun where energetic neutrals are abundantly formed.
A 4.2.8 SUMMARY

An adequate model has been found to account for the "threshold effect" observed in the atomic flux measurements of Ch. 4. Several factors are involved. For $I_d < 8$ mA or so, the atomic flux appears to have a roughly parabolic dependence on current. Another factor contributing to the threshold effect can be put as follows: at high discharge voltages (which, in the source, corresponded to low values of collected electron current), a greater proportion of the discharge electrons were of high energy, so that atomic generation was inefficient; as the gas throughput was increased, the current rose, but the voltage dropped, and this was accompanied by a rise in atomic generation efficiency. Further work is needed to check the validity of the assumptions made in the discussions.

REFERENCES

A 4.2.2 L.I. Maissel and R. Glang, "Handbook of Thin Film Technology" (McGraw-Hill, New York, 1970) p. 4-2 et seq.
A 4.2.4 Ref. A4.2.2: pp. 4-4, 4-8, 2-125, 4-5; Chapman, p. 207.
A 4.2.5 Chapman: p. 211; p. 105; p. 26-28; p. 117.
A 4.2.6 Chapman: pp. 132, 365.
A 4.2.8 Dr. R. Clampitt: references 4.4 and 4.5.
A 4.2.9 Dr. R. Clampitt, PhD thesis: see reference 4.6.
A 4.2.10 Chapman: p. 29.
A 4.2.13 Chapman, p. 116; p. 362.

* Energetic Neutrals: postscript. At the time of going to press, two papers were brought to my attention: K. Tominaga et al, "Energetic Oxygen Atoms in RF Sputtering of ZnO", Jpn. J. Appl. Phys. 26 (1987) Supplement 26-2, pp. 22-25 (+ ref. 8 therein); and (by the same author) "Mean Free Path of Energetic Oxygen Atoms in the Sputtering of ZnO", Jpn. J. Appl. Phys. 23, 7 (1984) 936-937 (short notes). These showed that the energy distributions of ions and neutral atoms in oxygen plasmas tend to peak near $V_d$; also, the mean free path of oxygen species was shown to decrease with reduced $V_d$. For the interaction $O^+ \rightarrow O$, the mean free path was about 3 cm at 10 mTorr. Further points are raised which may be of interest to the reader.
FIGURE A4.2.1:

OXYGEN-ATOM FLUX RATE versus $I_d^2$
(Flux deduced from oxidation experiments)

Oxygen-atom flux rate
$(10^{13}/\text{cm}^2/\text{s})$

LINEAR REGRESSION:

Slope: $1.1 \times 10^{18}$ O atoms/cm$^2$/s/A$^2$

y intercept: $-0.73 \times 10^{13}$ O atoms/cm$^2$/s

Standard deviation: $1.6 \times 10^{13}$ O atoms/cm$^2$/s = "S"
FIGURE A4.2.2: CHARACTERISATION DATA FOR THE ATOMIC OXYGEN RADICAL SOURCE

(i) $V_d$ vs. $p_0$

(ii) $I_d$ vs. $p_0$

- $V_d$ limited by output impedance of power supply.
- $I_d$ determined by impedance of plasma.

(iii) $V_d$ vs. $I_d$

(iv) Graph showing relationship between chamber/beam pressures and $p_0$.

(Baratron, atomic source)
APPENDIX 4.3

DATA CHECKS; VALIDITY OF CHAPTER 4 OXIDATION DATA

A look at Table 4.1 shows that one silver layer had a similar thickness to a layer reported in the literature: the 29 nm Ag layer in the literature\cite{4.3.1} required the equivalent of \( \approx 1.1 \times 10^{14} \) O atoms/cm\(^2\)/s for 13.2 min. to reach full oxidation; compare this with the 29.5 nm Ag layer oxidised by the author, which required the equivalent of \( 8.8 \times 10^{13} \) O atoms/cm\(^2\)/s for 15 min. to fully oxidise. The total oxygen uptake for these two layers should have been almost the same (given that they attained the same final composition): the ratio of oxygen uptakes calculated from the above data is 0.90. The ratio for another pair of layers (one from the literature, and one by the author) is 1.02, when corrected for the difference in thickness. These are excellent agreements, from which one might infer that the thicknesses, oxygen flux rates, and other relevant data quoted in Ch. 4 are to be trusted; in particular, the data of Fig. 4.7 is given an extra measure of reliability.

A further check for the self-consistency of the data was performed. The total frequency change in Fig. 4.5 was measured from the graph (accounting for drift), giving 607 Hz. Now, the frequency change upon oxidation should be roughly proportional to initial layer thickness: the expected change in frequency for a 295Å layer upon oxidation is then:

\[
295\text{Å} + 810\text{Å} \times 607 \text{Hz} = 220 \text{Hz}.
\]

This is in remarkable agreement with the observed value (206 Hz) for this layer. For another (typical) layer, the corresponding figures were: 430 Hz (calculated, as above), and 460 Hz (observed).

It was also possible to estimate the final composition of the silver layer oxidised as shown in Fig. 4.5: the total oxygen atom flux was equivalent to about \( 1.4 \times 10^{14} \) O atoms/cm\(^2\)/s for 27 min., which gave a predicted final composition of Ag\(_{25}\)O, close to that of the common bulk oxide. Data for another (typical) layer predicted Ag\(_{49}\)O. Unfortunately, neither AES analysis nor RBS could be usefully performed on the silver oxide layers in order to confirm these predicted compositions. For AES, the argon ion beam reduced the material in an unquantifiable manner, and gave misleading results\cite{4.3.2}; RBS was attempted\cite{4.3.3}, but the unpolished and uneven nature of the layer, combined with the swamping of the layer's oxygen peak by the signal from the quartz substrate, made compositional analysis impossible.

It should be remembered that the above estimates of the silver oxide composition cannot be used to estimate \( C_{\text{m}} \) (which is assumed to be close to unity). This is because the quoted O flux rates are calculated from the observed rates of mass gain; these, in turn, depend
on C_{\text{r}}. So, although the product "time x observed rate of mass gain" should be constant for layers of a given thickness, the results above tell us nothing about C_{\text{r}} or the true beam flux; they do, however, give a genuine estimate of the final oxide composition, as well as a lower limit on the atomic flux rate.

Finally, the only independent quantitative data that could be found concerning atomic flux generation in D.C. oxygen discharges was by Thompson\textsuperscript{[4.3.4]}. Using his data, and an estimate of the pressures, etc. inside the atomic source, an O flux rate in excess of about 10^{15}/cm^2/s was predicted at the substrate for an internal gun pressure of about 1 mTorr. This predicted flux is within one order of magnitude of the appropriate fluxes estimated from the oxidation experiments of Ch. 4 (> 10^{14} O atoms/cm^2/s, see Table 4.1). This is a good agreement given that the prevailing conditions inside the gun were not accurately known, and that the measured fluxes were expected to be underestimates.

REFERENCES


A 4.3.3 RBS work performed at Dept. of Mathematical and Physical Sciences, University of Sussex, Falmer, Nr. Brighton, E. Sussex, England, BN1 9QH (Dr. Peter Chandler and Dr. Peter Townsend, Private Communication).

## APPENDIX 5.1: TABLES OF TYPICAL X-RAY DATA FOR CHAPTER 5

### TABLE A5.1 X-RAY POWDER DIFFRACTION AND RHEED DATA FOR A MIXED-PHASE NIQUEMUM OXIDE LAYER

<table>
<thead>
<tr>
<th>(d_{\text{pub}}/\text{Å}) (PUBLISHED DATA)</th>
<th>(d_{\text{obs}}/\text{Å}) (OBSERVED DATA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{NbO}_2^{[5,8]})</td>
<td>(\text{NbO-6C f.c.c.}^{[3,0]})</td>
</tr>
<tr>
<td>(110) 3.422</td>
<td></td>
</tr>
<tr>
<td>(101) 2.547</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.50 (med)</td>
</tr>
<tr>
<td></td>
<td>2.46 (111)</td>
</tr>
<tr>
<td>(200) 2.417</td>
<td></td>
</tr>
<tr>
<td>(111) 2.253</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.03 (str)</td>
</tr>
<tr>
<td></td>
<td>1.79 (v.wk)</td>
</tr>
<tr>
<td>(211) 1.753</td>
<td></td>
</tr>
<tr>
<td>(220) 1.710</td>
<td></td>
</tr>
<tr>
<td>(310) 1.528</td>
<td></td>
</tr>
<tr>
<td>(002) 1.498</td>
<td>1.50 (220)</td>
</tr>
<tr>
<td>(301) 1.419</td>
<td></td>
</tr>
<tr>
<td>(112) 1.369</td>
<td></td>
</tr>
<tr>
<td>(320) 1.347</td>
<td></td>
</tr>
<tr>
<td>(202) 1.271</td>
<td>1.281 (311)</td>
</tr>
<tr>
<td>(321) 1.222</td>
<td>1.224 (222)</td>
</tr>
<tr>
<td>(400) 1.209</td>
<td></td>
</tr>
<tr>
<td>(410) 1.173</td>
<td></td>
</tr>
<tr>
<td>Data ends.</td>
<td>1.060 (400)</td>
</tr>
<tr>
<td></td>
<td>0.972 (331)</td>
</tr>
<tr>
<td></td>
<td>0.949 (420)</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.865 (422)</td>
</tr>
<tr>
<td></td>
<td>0.817 (333, 511)</td>
</tr>
</tbody>
</table>

Footnotes: The above layer was 1.15μm of \(\text{NbO}_2\), grown at 650°C on z-cut sapphire. It was polycrystalline, and gave the RHEED ring patterns presented in Fig. 5.2 (c); typical RHEED error in \(d_{\text{pub}}\) was < 2%. The X-ray powder diffraction data was presented in Fig. 5.2 (b) (ii): typical error < 1 %.

"?" indicates that these lines were not observed either by RHEED or X-ray analysis: this was probably due to orientation effects or low intensity;

[a] Extra line, or the weak 2.491Å X-ray line in card 9-235 for \(\text{NbO}_2^{[5,9]}\);

[b] Extra line, or weak 2.014Å X-ray line for \(\text{NbO}_2^{[5,9]}\);

[c] Extra line, or weak 1.792Å line observed by electron diffraction for \(\text{NbO}_2^{[5,3]}\);

[d] Published X-ray data for \(\text{NbO}_2\) does not extend this far (hence a new \(\text{NbO}_2\) line?)

190
TABLE A5.2  X-RAY POWDER DIFFRACTION DATA
FOR AN OXIDISED NIOBium OXIDE LAYER

<table>
<thead>
<tr>
<th>$d_{\text{obs}}$ for $\gamma$ niobium pentoxide$^{\text{a,b}}$/Å (weakest lines omitted)</th>
<th>Observed $d_{\text{obs}}$/Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.932</td>
<td>3.95 (very strong, sharp)</td>
</tr>
<tr>
<td>3.150</td>
<td>3.12 (strong, fuzzy)</td>
</tr>
<tr>
<td>3.087</td>
<td></td>
</tr>
<tr>
<td>2.734</td>
<td>2.73 (weak)$^*$</td>
</tr>
<tr>
<td>2.455</td>
<td>2.44 (medium, sharp)</td>
</tr>
<tr>
<td>2.429</td>
<td></td>
</tr>
<tr>
<td>2.121</td>
<td>2.12 (very weak)</td>
</tr>
<tr>
<td>2.010</td>
<td>2.01 (very weak)</td>
</tr>
<tr>
<td>1.965</td>
<td>1.97 (medium, sharp)</td>
</tr>
<tr>
<td>1.829</td>
<td>1.84 (diffuse, weak)</td>
</tr>
<tr>
<td>1.797</td>
<td>1.79(6) (diffuse, weak)</td>
</tr>
<tr>
<td>1.790</td>
<td></td>
</tr>
<tr>
<td>1.666</td>
<td>1.66 (medium, sharp)</td>
</tr>
<tr>
<td>1.659</td>
<td></td>
</tr>
<tr>
<td>1.631</td>
<td>1.63(5) (weak)</td>
</tr>
<tr>
<td>1.576</td>
<td>1.56(4) (very weak, slightly fuzzy)</td>
</tr>
<tr>
<td>1.570</td>
<td></td>
</tr>
<tr>
<td>1.463</td>
<td>1.45(3) (very weak, slightly fuzzy)</td>
</tr>
<tr>
<td>1.458</td>
<td></td>
</tr>
<tr>
<td>1.338</td>
<td>1.32(6) (weak, fuzzy)</td>
</tr>
<tr>
<td>1.325</td>
<td></td>
</tr>
<tr>
<td>1.196</td>
<td>1.19(8) (very weak)</td>
</tr>
</tbody>
</table>

$^*$ (201) line of NbO$_2$ (see text of Ch. 5). Layer details: 1.1 µm of NbO$_{1.1}$ grown at 640°C on z-cut sapphire; oxidised at 420°C in pure, dry oxygen.