Surface machining lithium niobate using Ti diffusion technique

A thesis submitted in fulfillment of the requirements for the degree of Doctor of Philosophy

Vijay Prasad Sivan
B.Eng., M.Eng., M.S.

School of Electrical and Computer Engineering
Science, Engineering, and Technology Portfolio
RMIT University
Melbourne, Australia
August 2009
Declaration

I certify that except where due acknowledgement has been made, the work is that of the author alone; the work has not been submitted previously, in whole or in part, to qualify for any other academic award; the content of the thesis is the result of work which has been carried out since the official commencement date of the approved research program; any editorial work, paid or unpaid, carried out by a third party is acknowledged; and, ethics procedures and guidelines have been followed.

Vijay Prasad Sivan

August 2009
Acknowledgements

I wish to acknowledge and thank all the people who have supported me in my pursuit of this degree.

Firstly, I’d like to thank my senior supervisor, Prof. Arnan Mitchell for providing me with this research opportunity. His ideas, endless support, inspiration and encouragement were the most valuable over the course of this research. I’d also like to thank my second supervisor, Dr. Anthony Holland, particularly for teaching me the principles of micro-fabrication and the fruitful discussions. I’d also like to thank Prof. Mike Austin, Prof. Suresh Bhargava, Dr. Timothy Priest, Dr. Lam Bui and Dr. Anthony O’Mullane for the inspiring discussions and valuable suggestions.

Technical support was a very crucial factor for completing this degree and for this I want to express my wholehearted thanks to the technical staff, Mr. Yuxon Cao, Mr. Paul Jones and Ms. Chiping Wu.

I acknowledge the financial support provided by Defence Science Technology Organization, Adelaide, without which I would not have been able to carry out this research.

I’d also like to thank my colleagues for creating an exciting, motivating and always entertaining atmosphere. Thank you Gorgi, Madhu, Sharath, Tristan, Geeth, Eike, Uday, Mahyar, Ernest, Niusha, Hossien, Kushan, Sam and Sasi. Many thanks to Raaj, Shabeen, Bindu and Sumana for their great friendships. To all my friends, I would like to thank you.

I’d like to express my deepest gratitude to my parents, Prem and Surabi, who have always been supportive, especially during the low points, and to my wife, Nalini for her love and encouragement. Their endless, unconditional love and support has brought me this far. I thank them all for putting up with me, especially during my PhD.

Last but not least, I thank God for his grace.
Abstract

The thesis presents a novel technique for realizing smooth micro-scale etched features on lithium niobate. Etching of lithium niobate is observed when annealing two wafers in contact with an intermediate titanium strip. A variety of etching characteristics result when the two wafers are different combinations of X, +Z and -Z crystal orientations.

Material analysis provides evidence of a titanium free etched surface with the crystallinity of the bulk lithium niobate remaining intact. The optical properties of the etched surface of lithium niobate also remain unaffected. These results provide insight into the physical mechanism causing etching.

Evidence suggests that the etching is in fact hydrogen plasma etching that occurs in the proximity of the diffusing titanium strip. It is hypothesized that during titanium diffusion, charged ions originate at the interface of the lithium niobate/titanium interface, diffuse through the Ti film and emerge after some time at the surface. The charged ions react with water molecules and generate hydrogen which causes etching of the adjacent wafer. Control over etch depth was hence achievable through parameters that affect titanium diffusion such as annealing duration, titanium film thickness and patterned titanium strip widths.

Optical waveguiding was observed under the etched trenches of narrow widths. These impurity free waveguides support both the ordinary and the extra-ordinary polarizations with modest transmission losses. This optical waveguiding phenomenon has been attributed to residual stress and offers great potential for high power handling and compact waveguiding.
In summary, a novel and highly controllable etching technique has been discovered which creates smooth, precise features on the surface of lithium niobate without degrading material and optical properties. A physical and chemical model of the etching process is developed. This etching process is applied to the realization of impurity free stress waveguides and shows promise for the development of lithium niobate integrated optical systems with strong waveguides and compact grating reflectors.
Contents

Declaration i

Acknowledgements ii

Abstract iii

List of Figures xii

List of Tables xiii

Glossary xiv

1 Introduction 1

1.1 Introduction ......................................................... 1

1.2 Synopsis ................................................................. 3

1.3 Original Scientific Contributions ........................................ 5

2 Etching LiNbO$_3$ using Ti diffusion technique 6

2.1 Introduction ................................................................. 6

2.2 Literature review of Ti diffusion process in LiNbO$_3$ .................. 8

2.2.1 History of Ti diffusion ............................................... 8
2.2.2 Parameters affecting the Ti diffusion process .......................... 9
2.2.3 High temperature kinetics of Ti diffusing into LiNbO$_3$ .................. 10
2.3 Demonstration of surface modification through Ti diffusion in LiNbO$_3$ .......... 13
  2.3.1 Review of fabrication techniques ........................................ 13
  2.3.2 Fabrication procedure ..................................................... 13
2.4 Etching LiNbO$_3$ during Ti diffusion process ............................... 20
2.5 Conclusion .............................................................................. 26

3 Characterization of etching in LiNbO$_3$ using Ti diffusion technique 27
  3.1 Role of water vapor content in the annealing atmosphere .......... 28
    3.1.1 Etch depth with varying water vapor content in the annealing atmosphere 28
    3.1.2 How does water content influence the etching process? ............ 30
  3.2 Investigation of annealing duration and etch depth .................. 30
    3.2.1 Etch depth with varying annealing time for 100 nm thick Ti films . . . 31
    3.2.2 Etch depth with varying annealing time for 500 nm thick Ti films . . . 35
    3.2.3 Discussion of the physical mechanism causing etching ............... 36
  3.3 Etch depth with varying Ti thickness for 10 hour annealing duration .. 39
  3.4 Surface roughness characterization ......................................... 44
    3.4.1 Discussion of surface roughness in Ti diffused region and etched trenches 46
  3.5 Patterned Ti strip width and etch depth .................................. 49
  3.6 Summary and Conclusion ...................................................... 53

4 Material and optical characterization of etched LiNbO$_3$ 56
4.1 Introduction ......................................................... 56
4.2 Crystallinity characterization ...................................... 57
4.3 Material composition characterization ............................ 59
  4.3.1 Material composition characterization using EDS technique ...... 60
  4.3.2 Material composition characterization using XPS technique ...... 61
4.4 Optical characterization ........................................... 63
4.5 Summary .......................................................... 65

5 Etching characteristics for different crystal orientations of LiNbO$_3$ 66
  5.1 Introduction ......................................................... 66
  5.2 Survey of techniques for etching X and Z cut LiNbO$_3$ .............. 67
    5.2.1 Wet etching of Z cut LiNbO$_3$ .................................. 67
    5.2.2 Dry etching of Z cut of LiNbO$_3$ ................................ 70
    5.2.3 Summary ....................................................... 71
  5.3 Etching during Ti diffusion of X and Z-cut LiNbO$_3$ ................. 71
    5.3.1 Etching of X, +Z and -Z cut top wafer with X-cut bottom wafer ... 72
    5.3.2 Etching of X, +Z and -Z top wafer with +Z and -Z bottom wafer ... 77
    5.3.3 Normalization of etch depths with respect to that on X-cut ........ 81
  5.4 Summary and Conclusion .......................................... 82

6 Stressed Waveguides on LiNbO$_3$ 83
  6.1 Ridge waveguide .................................................. 83
    6.1.1 Geometry of the ridge waveguide .............................. 84
CONTENTS

6.1.2 Fabrication and testing procedure ........................................ 84
6.1.3 Results and Discussions .................................................. 88
6.1.4 Conclusion ........................................................................ 89

6.2 Impurity free Stressed Waveguide .......................................... 89
6.2.1 Waveguide sample preparation ........................................... 90
6.2.2 Optical Waveguide Measurements ....................................... 90
6.2.3 Summary of the stressed waveguide .................................... 95

6.3 Summary and Conclusion ........................................................ 96

7 Conclusions and Directions for future work ................................. 97

7.1 Outcomes of this work .......................................................... 97
7.2 Suggestion for future work .................................................... 99
7.2.1 Refinement of the etching model ......................................... 99
7.2.2 Optical characterization .................................................... 100
7.2.3 Engineer compact integrated optical waveguides and devices .... 100

7.3 Conclusion ............................................................................ 101

Bibliography .............................................................................. 102
List of Figures

2.1 Main steps involved in the fabrication of Ti diffused waveguides, (a) Ti film is deposited on the LiNbO$_3$ wafer, photo-resist is spun on the wafer, the photo-resist is exposed using contact lithography procedure, (b) the photo-resist is developed and the metal is etched to leave Ti patterned waveguide structure (c) the cross-section of the Ti patterned waveguides with the resist removed, (d) the cross-section of the Ti patterned waveguides diffused into LiNbO$_3$ .......................... 14

2.2 Main fabrication steps involved in diffusing Ti into LiNbO$_3$ ............................... 15

2.3 Photograph of the Ti patterned 3-inch wafer ......................................................... 16

2.4 Micrograph image of the Ti patterned wafer with the patterned widths (bottom to top) 3, 3.5, 4, 4.5, 5, 5.5, 6, 6.5 and 7 µm ......................................................... 18

2.5 Ti patterned 5 µm strip ............................................................................................. 19

2.6 Raised ridge formation on the Ti diffused region ..................................................... 19

2.7 Experimental procedure for etching LiNbO$_3$ during Ti diffusion process ............ 22

2.8 Micrograph image of the Ti diffused (bottom wafer) in wet oxygen atmosphere for 10 hours at 1050°C .......................................................... 24

2.9 Micrograph image of the top etched wafer .............................................................. 24

2.10 AFM images of the raised ridge on Ti diffused region of the bottom wafer ....... 25

2.11 AFM images of the etched trench on the top wafer ............................................. 25
3.1 Etch depths on the top LiNbO₃ wafer obtained for different concentrations of wet oxygen with 100nm thick Ti on bottom LiNbO₃ wafer ........................................... 29

3.2 Etch depth in nm as a function of annealing duration hour for the sample with original Ti thickness of 105 nm. The plot is divided into three distinctive zones. ZoneA - no etching observed. ZoneB - linear increase in etch depth and ZoneC - saturated etch depth ....................................................... 32

3.3 Profile characteristics of the bottom sample and the complementary region on the top sample with the original Ti thickness as 105 nm (a) 4 hour annealing period representing ZoneA, (b) 8 hour annealing period representing ZoneB and (c) 20 hour annealing period representing ZoneC ......................................................... 33

3.4 Etch depth in nm as a function of annealing duration hour for the sample with original Ti thickness of 480 nm. The plot is divided into three distinctive zones. ZoneA - no etching observed. ZoneB - linear increase in etch depth and ZoneC - saturated etch depth ......................................................... 37

3.5 Profile characteristics of the bottom sample and the complementary region on the top sample with the original Ti thickness as 480 nm (a) 7 hour annealing period, (b) 10 hour annealing period and (c) 30 hour annealing period .................... 38

3.6 Etch depth as a function of Ti thickness. The plot is distinguished by three regions, Region A - linear increase in etch depth, Region B - constant etch depth and Region C - reduced etch depth .............................................................. 42

3.7 Profile characteristics of the bottom Ti sample and the complementary region on the top sample after a 10 hour annealing period with the original Ti thickness as (a) 73 nm (RegionA), (b) 315 nm (RegionB) and (c) 483 nm (RegionC) ..... 43

3.8 RMS roughness as a function of initial Ti thickness for: Ti as deposited (triangle down); raised ridge formed after normal Ti diffusion (squares); raised ridge on Ti diffused wafer covered with bare LiNbO₃ wafer (triangles up); etched trench on top bare wafer after diffusion (circles) .............................................................. 45

3.9 Scanning Electron Microscope(SEM) image of the surface of a covered Ti diffused region before annealing. The pre-diffused Ti thickness was 483 nm. ............ 48
3.10 Scanning Electron Microscope(SEM) image of the surface of a covered Ti diffused region after annealing for 10 hours at 1050°C in wet oxygen atmosphere. The pre-diffused Ti thickness was 483 nm. 48

3.11 Etch depth obtained for different widths of patterned Ti (pre-diffused) 50

3.12 Profile characteristics of the patterned Ti strip, uncovered Ti diffused, covered Ti diffused and the complementary etched region on the top sample after a 12 hour annealing period with the original Ti thickness as 103 nm with widths (a) 3 µm, (b) 5 µm and (c) 7 µm 51

4.1 XRD diffractograms performed on bare and etched X-cut LiNbO₃ 58

4.2 Prism coupler refractive index (n₀ and nₑ) plot on the untreated and etched LiNbO₃ 64

5.1 Hexagonal unit cell of LiNbO₃ [1] 68

5.2 Atomic position of Li and Nb with respect to oxygen octahedra in the ferroelectric phase of LiNbO₃ [1] 69

5.3 AFM micrographs of Ti diffused regions and the etched regions for Ti strip width of 5 µm. Ti is diffused into X-cut LiNbO₃, etching X, +Z and -Z faces of LiNbO₃ 74

5.4 AFM micrographs of Ti diffused regions and the etched regions for Ti strip width of 5 µm. Ti is diffused into +Z, etching X, +Z and -Z faces of LiNbO₃ 79

5.5 AFM micrographs of Ti diffused regions and the etched regions for Ti strip width of 5 µm. Ti is diffused into -Z, etching X, +Z and -Z faces of LiNbO₃ 80

6.1 Schematic diagram of a ridge waveguide 84

6.2 Schematic diagram of the mask used for ridge waveguide fabrication 85

6.3 Fabrication steps employed for ridge waveguides 86

6.4 The resulting ridges and etched trenches 87
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.5</td>
<td>Optical testing setup with a CCD camera to observe the modal profile of the output</td>
</tr>
<tr>
<td>6.6</td>
<td>Schematic diagram of the fabricated wafer with the dicing line along which the sample was diced</td>
</tr>
<tr>
<td>6.7</td>
<td>Schematic diagram of the diced wafer</td>
</tr>
<tr>
<td>6.8</td>
<td>Fabricated device for testing</td>
</tr>
<tr>
<td>6.9</td>
<td>Mode profiles obtained in a 5 µm etched trench for TE and TM polarizations with its respective intensity plots</td>
</tr>
<tr>
<td>6.10</td>
<td>Optical testing setup with a power meter to measure the output power</td>
</tr>
<tr>
<td>6.11</td>
<td>Output power (dBm) vs length of the waveguide (cm) for a etched trench of width 5µm</td>
</tr>
</tbody>
</table>
List of Tables

4.1 Material composition in atomic percentage (A%) using Energy Dispersive Spectroscopy .................................................. 60

4.2 Material composition in atomic percentage (A%) using X ray Photoelectron Spectroscopy .................................................. 62

4.3 Refractive index measurements of etched and untreated LiNbO₃ using prism coupler .................................................. 63

5.1 Etch depth in nm on X, +Z and -Z faces using Ti diffusion in X-cut LiNbO₃ .......................................................... 73

5.2 Etch depth and ridge height in nm on X, +Z and -Z faces using Ti diffusion into X, +Z and -Z faces of LiNbO₃ .......................... 78

5.3 Normalized ratio of etch depth obtained on +Z and -Z surfaces when compared with that obtained on the X-cut LiNbO₃ .................................................. 81

6.1 Attenuation coefficients (dB/cm) of the waveguides formed under the etched trenches of different widths in TE and TM polarizations ........................................... 95
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFM</td>
<td>Atomic Force Microscope</td>
</tr>
<tr>
<td>CCD</td>
<td>Charge coupled device</td>
</tr>
<tr>
<td>DI</td>
<td>De-ionised</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>ESEM</td>
<td>Environmental Scanning Electron Microscope</td>
</tr>
<tr>
<td>GI-XRD</td>
<td>Grazing incidence angle X-ray diffraction</td>
</tr>
<tr>
<td>HMDS</td>
<td>hexamethyldisilazane</td>
</tr>
<tr>
<td>IBE</td>
<td>Ion Beam Etching</td>
</tr>
<tr>
<td>ICP</td>
<td>Inductively coupled plasma</td>
</tr>
<tr>
<td>IPA</td>
<td>Iso-propyl-alchohol</td>
</tr>
<tr>
<td>lpm</td>
<td>litre per minute</td>
</tr>
<tr>
<td>n_e</td>
<td>extra-ordinary refractive index</td>
</tr>
<tr>
<td>n_o</td>
<td>ordinary refractive index</td>
</tr>
<tr>
<td>PPLN</td>
<td>Periodically poled lithium niobate</td>
</tr>
<tr>
<td>RIE</td>
<td>Reactive Ion Etching</td>
</tr>
<tr>
<td>RMS</td>
<td>root mean square</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
</tr>
<tr>
<td>SNOM</td>
<td>Scanning near-field optical microscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>XRMD</td>
<td>X-ray Microdiffraction</td>
</tr>
</tbody>
</table>
Chapter 1

Introduction

1.1 Introduction

Photonic transport of high frequency information has become ubiquitous. The transfer of information signal from the electrical to the optical domain can incur a significant penalty in terms of conversion loss, but this is more than compensated for by the extraordinary bandwidth offered by optic fibres. Since there is significant cost associated with conversion of electrical signal for transport in a photonic medium, it would be desirable to take advantage of the capabilities of photonics for signal processing rather than just using it for transport. Photonic processing of high-speed signals is attractive because of its very high time-bandwidth product capabilities. Photonic processors can remove the bottlenecks caused by limited sampling speeds in conventional electrical systems.

The unique functional advantages of photonic signal processors include their inherent speed, the ability to perform parallel signal processing, and the ability to generate true time delays. This has led to a diverse range of operations [2, 3]. These include signal filtering with programmable capabilities [4], multi-Gbit/s A/D converters [5], frequency converters and mixers [6], signal correlators [7], and beam-formers for phased arrays [8]. The processing of wideband signals directly within the fibre optic transmission link is attractive in applications such as signal distribution in fibre-radio mobile access systems [9] and in radar phased array antennas [8]. Since in such fibre optic systems, the signal is already in the optical domain, it is desirable to incorporate photonic signal processing into the optical fibre network, as this can provide in-built signal conditioning that can be integrated with the fibre optic system. However, fibre optic signal processing systems formed from discrete components can become extremely complex, bulky and expensive.
On the other hand, planar integrated optical devices allow various functionalities to be realized on the wafer scale. Since the development of integrated optics, the structures for various processors have continuously evolved to the invention of new photonic devices for efficient operation and the integration of various photonic signal processors on a single chip. Such optical circuits are designed for a number of applications in optical communications, instrumentation and sensing. One material that is enabling integrated optics is the ferroelectric crystal lithium niobate (LiNbO$_3$).

LiNbO$_3$ is a man-made dielectric material possessing some inherent properties that make it attractive for various applications. Although first discovered in 1949 [1], it was not until 1964 that LiNbO$_3$ was synthesized in single crystal form [10]. LiNbO$_3$ single crystals possess a unique combination of physical properties which include ferroelectric, piezoelectric, and pyroelectric properties. In addition to this, it also has high nonlinear optical and electro-optical coefficients and a high degree of photorefractive sensitivity. The richness of large magnitude physical effects has caused LiNbO$_3$ to become widely used in optical and acoustic devices. Some of the applications include acoustic wave transducers, acoustic delay lines, acoustic filters, optical amplitude modulators, second harmonic generation, Q-switches, beam deflectors, phase conjugators, dielectric waveguides, memory elements and holographic data processing devices to name just a few.

Metal diffusion into LiNbO$_3$ was first achieved in 1974 [11]. The primary purpose of metal diffusion was to increase the refractive index in the near-surface layers of LiNbO$_3$ for optical waveguiding applications. Titanium (Ti) diffusion into LiNbO$_3$ gained much attention because of its strong light confinement and relatively strong increase in the ordinary and extra-ordinary indices. The physical mechanism of the Ti diffusion process has also been extensively studied. Understanding of the physical mechanism has enabled fine tuning of the diffusion process in order to improve the quality of the optical waveguides.

A variety of efficient integrated optical devices incorporating Ti diffused waveguides on LiNbO$_3$ for ultra-fast all-optical signal processing at 1.55$\mu$m wavelength have been developed. Some of the common applications of Ti diffused waveguides in LiNbO$_3$ include modulators, switches, couplers, interferometers and mode convertors. It would seem that with its wealth of desirable properties that LiNbO$_3$ would be an ideal material for realizing complex photonic information processing systems in integrated optic form. This would be true except for the
fact that the traditional Ti diffused waveguides are relatively weak and thus compact bends and circuits are impossible. Indeed some efforts have been made to realize integrated photonic signal processing systems on LiNbO$_3$ chips; but these demonstrations have been impractically large with systems often requiring all of the real estate of an entire wafer.

To make LiNbO$_3$ integrated optics more compact, either facet mirrors or gratings are required to deflect the beam sharply within a compact space; or tightly confined optical waveguides with small bending radii (such as etched ribs) must be realized. Gratings can be achieved on LiNbO$_3$ using photo-refraction, but these are rather weak and temporally unstable [12].

Surface machining of LiNbO$_3$ is a potential opportunity to realize tight waveguides, facet mirrors and strong permanent gratings. Much research has been performed on LiNbO$_3$ surface machining in the recent years. Some of the applications of surface machined LiNbO$_3$ include the realization of efficient optical modulators [13], photonic crystals [14] and surface relief gratings [15]. Since LiNbO$_3$ is robust and relatively inert, it is also known to be difficult to etch. Several machining techniques have been adopted to realize surface machining in the micro-/nano-scale. Some of the existing techniques for micro-machining LiNbO$_3$ include mechanical tooling, laser ablation, wet acid erosion, ion beam etching and argon based plasma etching. Significant research is currently underway to assess the adaptability of these micro-machining techniques in realizing integrated optical devices with an emphasis on the quality of surface machined LiNbO$_3$.

1.2 Synopsis

The work in this thesis aims to identify a suitable technique to surface machine LiNbO$_3$ as a precursor to realizing integrated optical systems on a LiNbO$_3$ platform with the possibility of strong waveguides and compact grating reflectors.

Chapter 2 presents a detailed overview of the surface morphological changes on LiNbO$_3$ that accompany the Ti diffusion process. A literature review of the Ti diffusion process into LiNbO$_3$ is presented to understand the cause for surface modification. A hypothesis is deduced from the literature review for a new technique to etch LiNbO$_3$. An experimental investigation to test the hypothesis leads to the discovery of etching, confirming the hypothesis. Micron scale patterns of extremely smooth quality, comparable to optical grade un-processed LiNbO$_3$ wafers was demonstrated distributed over the full wafer.
Chapter 3 presents a systematic study to investigate the parameters that can be used to control the etching process discovered in Chapter 2. With Ti diffusion driving the etching process, the investigation aims to determine the relationship between etch depth and the parameters that affect Ti diffusion such as annealing duration, thickness of original Ti film and the strip width of the patterned Ti film. An attempt is made to explain the etching mechanism.

Chapter 4 presents a detailed investigation of the material characteristic changes in the crystallinity, material composition and optical index of the surface which is etched during Ti diffusion. The characterization studies were performed by comparing the results obtained on the etched surface with that of a bare LiNbO$_3$ wafer. It is found that the etched LiNbO$_3$ material remains largely unaffected and still retains its desirable optical properties.

Chapter 5 presents the etch characteristics on different crystal orientations of LiNbO$_3$. A detailed characterization study on the etch depths for the different combinations of the etching wafer and the Ti diffusing wafer is reported. The results provide further insight into the nature of the etching process. The Chapter also presents a model for the etching mechanism, describing the observed etch characteristics on the different crystal combinations.

In Chapter 6, the etching technique presented in Chapter 2 is employed to realize impurity free optical waveguides. A review is conducted to investigate the cause for the waveguiding phenomenon to occur under the etched trenches realized using the technique presented in Chapter 2. The results from the loss measurements performed on these formed optical waveguides are reported.

Chapter 7 summarizes the work undertaken in this thesis and the conclusions that have been drawn. Steps to develop this technique further so that it can be applied to the realization of surface relief gratings and tightly confined waveguides are discussed.
1.3 Original Scientific Contributions

The original contributions made by this thesis are:

1. Etching of LiNbO$_3$ using standard Ti diffusion technique [16]

2. Etching characteristics on X, +Z and -Z crystal orientations using Ti diffusion in X, +Z and -Z [17].

3. Detailed etching characterization using parameters that control the Ti diffusion process such as original Ti thickness [16], annealing time [18] and patterned Ti strip widths.

4. The physical and chemical mechanism involved during the etching process [19, 20].

5. Demonstration of impurity free optical waveguides supporting ordinary and extra-ordinary polarizations [21].
Chapter 2

Etching LiNbO$_3$ using Ti diffusion technique

2.1 Introduction

LiNbO$_3$ is a well known, inert material used in the optical device industry for applications such as directional couplers [22], spectrum analyzers [23], optical switches [24], modulators [25–27], polarization converters and filters [28], among many other devices. In the past several decades, optical devices have been fabricated by diffusing titanium into LiNbO$_3$, forming graded-index optical waveguides [29]. This technique of fabricating optical waveguides remains the most popular technology for its relatively simple fabrication process and highly reproducible performance [30]. Ti diffused waveguides induce subtle changes in the refractive index enabling gradual waveguide devices, but for higher index contrast structures, surface modification of LiNbO$_3$ is necessary.

Surface morphology modification of LiNbO$_3$ is an equally well researched area. With LiNbO$_3$ being a hard and relatively inert material, the surface modification process usually involves micro-machining technologies such as mechanical tooling [31], laser ablation [32], wet acid erosion [33], ion beam etching [34], reactive ion etching [35] or argon plasma sputtering [36]. Surface modified LiNbO$_3$ is important in the optical device industry for realizing efficient modulators [13], photonic crystals [14] and especially gratings [15].

Gratings on LiNbO$_3$ are important in the development of various integrated optic devices [37]. In applications where optical devices use 1.55 $\mu$m wavelength, the period of gratings are in the sub-micron scale (periods of the order of 350 nm). These gratings can be volumetric gratings
Volumetric gratings on LiNbO$_3$ have been generated by inhomogeneous periodic illumination to excite the charge carriers of impurity ions (e.g. Fe$^{3+}$) [38], doped within the crystal, into the conduction or valence bands [39]. The movement of these charge carriers is due to the bulk photovoltaic effect [12]. The excitation rate in the darker regions is smaller than the brighter regions, inducing a space-charge field and thus modulating the refractive index via the electro-optic effect. A common problem associated with these gratings is that homogeneous illumination erases the stored light patterns. Thermal fixing overcomes this effect to some degree, but requires constant illumination to reveal the index modulation. Thus, although gratings can be of high quality, they are typically quite weak, requiring the length of the gratings to be of many millimeters; and are also impermanent requiring 'refreshing' via optical illumination prior to each use.

A permanent alternative is surface relief gratings. These are periodic surface corrugations on the waveguide inducing periodic index perturbation. Several techniques for the fabrication of surface relief gratings on LiNbO$_3$ have been reported. Some of them include dry-etching techniques [40], Si overlays of the waveguiding structure [7], index changed gratings using femtosecond laser [41] and proton exchange [42]. The existing surface modification techniques often cause surface roughness and may reveal unwanted crystal facets [16], and may also change the crystal properties to some degree. Thus, although these gratings are strong, irregularities may cause significant optical scattering loss.

This thesis aims to identify a technique that could enable smooth surface modification that is strong enough for compact gratings and also uniform enough to minimize losses, without affecting the crystal properties.

It has been observed that Ti diffusion into LiNbO$_3$ can be accompanied by modification in the surface morphology of the crystal [29]. After Ti diffusion, a ridge appears in place of the Ti strip and has been measured to be greater than the thickness of Ti initially deposited. The surface modification is significant and is very smooth [29]. It is possible that the phenomenon leading to the creation of these surface features may offer the right combination of smoothness and strength required for the grating applications that are an objective to this thesis.

This chapter is organized as follows. A literature review of the process of Ti diffusion into
Etching LiNbO$_3$ is presented in Section 2.2. An experimental verification of Ti diffusion into LiNbO$_3$ was conducted in Section 2.3 to ensure that the surface modification as observed in the literature could be repeated in the laboratory. Section 2.3 includes the fabrication procedure and the results. An hypothesis for a novel technique to etch LiNbO$_3$ during Ti diffusion is deduced from the literature survey and is presented in Section 2.4. An experimental method to test this hypothesis and the observed results are described in this Section. The unexpected observations achieved in Section 2.4 suggest avenues for further investigations and these are presented in Section 2.5.

2.2 Literature review of Ti diffusion process in LiNbO$_3$

This Section presents a review of the Ti diffusion process in LiNbO$_3$. The review begins with a brief history of Ti diffusion, then presents an overview of the parameters controlling the diffusion process. The physical mechanisms occurring during Ti diffusion is then reviewed in detail.

2.2.1 History of Ti diffusion

The earliest work on LiNbO$_3$ waveguiding used slab guides that covered the whole surface [43]. This work was derived from experimentations using glass waveguides conducted in the early 1970’s [44]. The slab waveguides were fabricated by the out diffusion of Li ions. However, Li out diffused waveguides support modes only in the extraordinary polarization. It is advantageous for some applications to guide both polarizations. This led to the development of metal diffusion into LiNbO$_3$.

Schmidt and Kaminow were the first to report metal diffusion into LiNbO$_3$ in 1974 [11]. The primary purpose of metal diffusion was to increase the refractive index in order to enable optical waveguides [25,45]. Optical waveguides in LiNbO$_3$ have been formed by diffusing several species of metal ions such as Mg, Ni, Zn, Fe, Co, Cr, V, and Ti. Diffusion of the metal ions causes modification of the optical properties, specifically the refractive index [11,46–48]. It was observed in [49] that the diffusion of divalent metallic ions such as Ni, Zn and Mg caused a reduction in the extraordinary index ($n_e$). The ordinary index ($n_o$) is also decreased when Mg is diffused, but increased when Ni or Zn were diffused. With trivalent or tetravalent ions such as Fe, Cr and Ti, an increase in both $n_e$ and $n_o$ was observed. It was understood that the
divalent ions substituted Li ions during the diffusion process while trivalent and tetravalent ions substituted Nb ions in the LiNbO$_3$ crystal lattice [49].

The study of Ti in-diffusion into LiNbO$_3$ gained much attention because Ti diffused waveguides exhibit fairly strong light confinement, with a relatively large increase in both ordinary and extra-ordinary refractive indices, supporting optical waveguiding in both TE and TM modes [49]. Since the introduction of Ti diffusion in 1974 [11], many low-loss, guided-wave optical devices have been demonstrated. Significant research has been conducted to study the Ti diffusion mechanism in LiNbO$_3$.

2.2.2 Parameters affecting the Ti diffusion process

A review presented in [49] provides an overview of the Ti diffusion process. Diffusion of Ti films into LiNbO$_3$ has been carried out in argon, oxygen, nitrogen or ambient air environments, at temperatures between 900 and 1150°C for time durations ranging from 0.5 to 30 hours [49]. The effect of temperature, annealing time and atmospheric conditions on the mode structure, refractive index profile, morphology and composition of planar Ti diffused waveguides has been characterized [29] and it was concluded, at the time, that the optimum conditions for reproducible results were diffusions carried out at temperatures above 1100°C in air or pure oxygen. Observation of a Gaussian Ti concentration profile was reported under the Ti diffused region with the diffusion time greater than the interval required for the metal film to diffuse into the crystal [50]. A graded refractive index change, directly proportional to the Ti concentration, was observed in the diffused region with $\delta n_o<0.02$ and $\delta n_e<0.04$ making this process suitable for optical device fabrication [29].

However, the waveguides were accompanied by an undesirable effect of surface guiding on the uncoated regions for extraordinary polarization only [46]. This led to strong lateral leakage of light polarized along the extraordinary axis. It was also observed that the quality of the crystal degraded during diffusion [51]. The surface of the Ti diffused region was observed to have a high degree of roughness when the Ti film was not completely depleted, but eventually became smooth with prolonged diffusion duration [29]. In order to better understand the cause of these effects, the physical and chemical reactions involved during the Ti diffusion process were studied.
2.2.3 High temperature kinetics of Ti diffusing into LiNbO₃

In Section 2.2.2, an overview of the parameters influencing the Ti diffusion process was presented. The undesirable effects of surface guiding, the degradation in the crystal quality and the rough surface exhibited on the diffused surface when Ti is not completely depleted were some of the observations found in the literature. In order to understand the cause of these phenomena, a review of the physical and chemical reactions occurring during the diffusion process was conducted. This Section presents a brief review of the physical crystal kinetics occurring during the diffusion process.

The initial step in the Ti diffusion process is the oxidation of the Ti thin film. A Ti film oxidizes to form TiO₂, (at a temperature around 300°C) and is predominantly in the rutile form [52]. The oxidation mechanism involves capturing of oxygen ions from the diffusion atmosphere and the LiNbO₃ substrate [53]. As the temperature increases, the Ti-oxide bond is broken and the Ti⁴⁺ ions diffuse into the LiNbO₃ substitutionally replacing Nb⁵⁺ ions from the LiNbO₃ wafer (at about 800°C) [52, 54]. The cation displacement during the diffusion process induces a charge variance in the diffusion region. It was shown that the Ti ions are of the Ti⁴⁺ oxidation state and with them replacing the Nb⁵⁺ ion during diffusion, there is an atomic rearrangement to balance the charge perturbation [54]. With the temperature at 1000°C, a ternary compound of mixed rutile oxide (Li₀.25Nb₀.75O₂)₁₋ₓ(TiO₂)ₓ with x=0.58 [52] or x=0.43 [54] is formed in the Ti diffused regions. The mixed rutile oxide has a greater molar volume than the Ti metal film. This causes a swelling in the Ti diffused region that leads to the formation of a ridge structure with a step height greater than the thickness of the Ti film [29]. The observation of this raised ridge is of particular interest to this investigation.

Lithium out-diffusion

The Li ions have high mobility during the diffusion process [49]. This causes Li to out-diffuse from the uncoated surface of the crystal while the Ti is in-diffusing. The out diffusion of Li from LiNbO₃ was first described in 1973 [43, 55]. The smaller size of Li compared to Nb suggests Li should be very mobile at high diffusion temperatures. In non-stoichiometric LiNbO₃ (which is used for optical waveguiding applications), Li is not as strongly bound to the oxygen lattice as Nb. The Li bonds are more ionic and weaker while the Nb bonds are more covalent and stronger [43]. The Li ions out-diffuse and evaporate leaving behind a Li deficient layer in the
Etching LiNbO$_3$ using Ti diffusion technique

uncoated region [55]. The Li deficiency causes the surface of the uncoated region to become rough, due to the formation of large epitaxial Li deficient crystallites of LiNb$_3$O$_8$ [49].

The LiNb$_3$O$_8$ has an isotropic index similar to the ordinary polarization of LiNbO$_3$. This index is higher than the extra-ordinary index of LiNbO$_3$ and thus, for the extraordinary polarization, the LiNb$_3$O$_8$ forms a surface waveguide, while no surface guide is formed in the ordinary polarization. The phenomenon of Li out-diffusion on the uncoated LiNbO$_3$ regions is responsible for the surface guiding effect observed for extraordinary polarization, affecting the performance of stripe waveguides [56]. Li out-diffusion also affects the quality on the crystal surface leading to scattering losses. Several methods are suggested in literature to suppress the Li out-diffusion. A review is presented on the different techniques used to avoid this unfavorable phenomenon in the following Section.

Suppression of Li out-diffusion

A review presented in [57] elaborates on the different techniques that are used to prevent the loss of Li and avoid the surface guiding effect. Some of the techniques presented include controlling of Li partial pressure [58], magnesium co-diffusion [59], diffusion in platinum box crucible [60] and diffusion in an atmosphere containing water vapor [46]. It was the Ti diffusion in atmosphere containing water vapor that yielded the most reproducible results [46, 57]. Water vapor was introduced into the diffusion atmosphere by bubbling pure oxygen through a column of water heated at 60-90°C before flowing into the furnace tube [57]. This technique produced high quality waveguides with a very smooth diffused surface [51] and very low propagation loss (<0.2dB/cm) exhibiting relatively strong optical confinement in both polarizations [61].

The physical mechanism leading to the suppression of Li out-diffusion in wet oxygen environment can be described as follows. Oxygen carrying water vapor introduced into the furnace as the diffusion gas, dissociates itself into H$^+$ and OH$^-$ ions. The OH$^-$ ions react with the out-diffused Li ions at the surface forming a thin film of LiOH compound. The LiOH compound is very stable and is impermeable to Li ions. Thus, once a complete monolayer of LiOH is formed at the surface, the out-diffusion of Li ions from the uncoated surface is terminated. The maintenance of Li pressure by this LiOH layer also suppresses the formation of LiNb$_3$O$_8$ crystallites and hence prevents the surface roughness associated with diffusion in a dry atmosphere. Ti diffusion in LiNbO$_3$ using a wet oxygen atmosphere has made the fabrication of reproducible low
loss optical waveguides possible, and has rendered the Ti:LiNbO$_3$ platform an industry standard procedure for optical device fabrication [49].

**Surface morphology of Ti diffused region**

As mentioned previously, after Ti diffusion into LiNbO$_3$, a ridge structure in the Ti diffused region can be observed with the height of the ridge being greater than the initial thickness of Ti film. A review of the mechanisms that lead to this change in surface morphology was conducted in [29]. This Section presents an overview of the changes that occur on the surface during the Ti diffusion process.

It was observed that during the initial diffusion phase of Ti into LiNbO$_3$, the surface develops significant roughness [62]. The surface of a freshly oxidized Ti film can be as smooth as the adjacent LiNbO$_3$ surface. Maximum surface roughness was observed on the Ti film only after 30 minutes of annealing [29]. A similar observation was made in [50]. The cause of the surface roughness was explained to be the effect due to dislocation and defect mechanism in the crystal lattice and these defects were annealed out with time. It was also observed, through material analysis, that the surface of the Ti film contained significant concentration of Nb. The Nb ions at the surface of the strip will be exposed to wet oxygen, and hydrolyzed to form niobic acid (Nb$_2$O$_5$.H$_2$O). Niobic acid is highly active and is generally a catalyst with chemical reactions in which water is present [63]. The formation of a solid solution (Li$_{0.25}$Nb$_{0.75}$O$_2$)$_{1-x}$(TiO$_2$)$_x$ with $x=0.43$ [54], neutralizes the niobic acid. This mixed oxide of Li-Ti-Nb-O is responsible for the swelling effect leading to the formation of the ridge structure in the area initially covered by Ti.

As mentioned previously, the surface swelling is of particular interest to this thesis investigation. A surface modification technique is required to shape the surface of LiNbO$_3$ for potential grating applications. Literature suggests that the Ti diffused region of LiNbO$_3$ can exhibit significant modification in the surface morphology. Importantly, these features are smooth and of significant thickness. If these features can be controlled, then they may be useful for grating applications. Before embarking in an explanation of controlling this phenomenon, it is important that such surface swelling can be observed in a repeated experiment conducted in the laboratory.
2.3 Demonstration of surface modification through Ti diffusion in LiNbO$_3$

Surface modification of the Ti diffused region has been observed in [29] in the form of a ridge structure with the step height greater than the thickness of Ti strip initially deposited. The review conducted in Section 2.2.3 suggested that the swelling is caused by the increase in the molar volume during the formation of the rutile-like phase of Li-Nb-Ti-oxide [29]. In this Section, the conditions leading to this ridge formation are recreated with the aim of observing similar features in our experiments.

2.3.1 Review of fabrication techniques

This Section presents an overview of a typical fabrication procedure to achieve Ti diffusion into LiNbO$_3$. Figure 2.1 presents a diagram of the main steps involved in the Ti diffusion process. Thin films of Ti metal have been deposited by RF sputtering [64] or evaporation [11] onto the LiNbO$_3$ wafer. The thickness of the Ti film range from 16.5 nm to 500 nm [29]. Conventional photolithography has been used to pattern the thin film with stripe features. The lift-off method, wet chemical etch method and Ti plasma etching in CF$_4$ atmosphere are procedures that have been employed to produce Ti:LiNbO$_3$ stripe waveguide patterns [49]. The patterned films have been diffused at a temperature just below the Curie temperature of LiNbO$_3$ (950 to 1142°C) [11]. The annealing time is long enough for all of the Ti to diffuse into the crystal (3 to 30 hours) [11]. A diffusion process has been developed empirically at RMIT based on previous investigations and has been shown to achieve low loss waveguides supporting both polarizations. This technique is outlined in the following Section.

2.3.2 Fabrication procedure

A fabrication procedure was employed to verify that the ridge structure formation observed in the literature could be reproduced. Figure 2.2 presents the fabrication procedure used for this verification study. In this experiment, a Ti film was deposited and Ti strips were defined photolithographically. The strips were then diffused into LiNbO$_3$. This Section presents an detailed description of the experimental procedure conducted in the study.
Etching LiNbO$_3$ using Ti diffusion technique

Figure 2.1: Main steps involved in the fabrication of Ti diffused waveguides, (a) Ti film is deposited on the LiNbO$_3$ wafer, photo-resist is spun on the wafer, the photo-resist is exposed using contact lithography procedure, (b) the photo-resist is developed and the metal is etched to leave Ti patterned waveguide structure (c) the cross-section of the Ti patterned waveguides with the resist removed, (d) the cross-section of the Ti patterned waveguides diffused into LiNbO$_3$

**Wafer preparation and Ti deposition**

A congruent X-cut LiNbO$_3$ (48.6 mol% Li$_2$O) single crystal 3-inch wafer was used in this investigation. The wafer was scrubbed clean with acetone to remove organic impurities. The acetone residue was rinsed from the wafer with IPA. The wafer was then rinsed with deionized (DI) water and blown dry with a stream of nitrogen gas. Dehydration of the wafer was carried out by baking the wafer at 110°C for 20 min. A Ti film with a nominal film thickness of 100 nm was evaporated onto LiNbO$_3$ wafer using the BALZERS / BAK 600 e-beam evaporation batch coating system.

**Photolithographic patterning**

Conventional photo-lithography was used to pattern the Ti film into strips. The Ti coated LiNbO$_3$ wafer was spin coated with the adhesion promoter hexamethyldisilazane (HMDS) and was baked in an oven at 90°C for 1 min. The wafer was spin coated with AZ1512 resist from Clariant to yield a 1.2 µm thick film. The spin coated wafer was then baked on a hotplate at 95°C for 120 seconds. A 4-inch quartz mask was used for the UV exposure of the photo-resist.
Etching LiNbO$_3$ using Ti diffusion technique

Figure 2.2: Main fabrication steps involved in diffusing Ti into LiNbO$_3$

1. Step 1: LiNbO$_3$ wafer cleaned and dehydrated
2. Step 2: Titanium evaporated on LiNbO$_3$
3. Step 3: Photolithography
4. Step 4: Etching of Titanium
5. Step 5: Ti diffused into LiNbO$_3$
Etching LiNbO$_3$ using Ti diffusion technique

Figure 2.3: Photograph of the Ti patterned 3-inch wafer
Etching LiNbO$_3$ using Ti diffusion technique

The mask contained strip patterns with widths ranging from 3 to 7 $\mu$m in 0.5 $\mu$m increments. The exposed wafer was then developed in a diluted solution of 25% AZ400K developer. This uncovered the Ti film in the exposed regions as shown in Figure 2.2. The Ti film on the developed wafer was etched in a dilute hydrofluoric acid solution (2%HF). Great care was taken to avoid over etching the pattern as this can cause undercutting (lateral etching) resulting in a narrower Ti strips than nominally defined on the mask. The photo-resist was then stripped using acetone. The Ti patterned wafer was then dehydrated by baking at 110°C for 20 min.

**Ti strip Inspection**

Figure 2.3 presents a photograph of the Ti patterned 3-inch wafer. A small section of the Ti patterned wafer can be seen in the optical micrograph image with the Ti strips of widths 3 to 7 $\mu$m in 0.5 $\mu$m increments (shown in Figure 2.4). An Atomic Force Microscope (AFM) micrograph of the 5 $\mu$m strip on Ti patterned wafer is shown in Figure 2.5. The AFM profiling indicated that the Ti patterned strip had a thickness of 103 nm.

**Ti diffusion into LiNbO$_3$**

The Ti patterned wafer was placed in a quartz tube furnace. The furnace was then heated to 1050°C±1°C at the rate of 17°C/min. The gaseous atmosphere within the furnace tube was a controlled flow of wet oxygen. This atmosphere was achieved by bubbling oxygen through a column of pure water maintained at 60°C flowing at the rate of 1 lpm. The annealing duration was 10 hours.

**In-diffused Ti:LiNbO$_3$ surface inspection**

To establish the surface morphology of the Ti in-diffused region of LiNbO$_3$, an AFM was used to profile the Ti diffused region. Figure 2.6 presents the AFM micrograph of the 5 $\mu$m Ti diffused strip. The Ti diffused region exhibits a raised ridge, which is observed to be very smooth. The height of the ridge formed was measured to be 197 nm, which, comparing to Figure 2.5, is larger than the thickness of the Ti film initially deposited (103 nm). The ridge formed, also exhibited a rounded structure, not retaining the sharp corners as on the patterned Ti strip. The neighboring uncoated LiNbO$_3$ surface is also very smooth with no defects evident.
Figure 2.4: Micrograph image of the Ti patterned wafer with the patterned widths (bottom to top) 3, 3.5, 4, 4.5, 5, 5.5, 6, 6.5 and 7 μm
Etching LiNbO₃ using Ti diffusion technique

Figure 2.5: Ti patterned 5 µm strip

Figure 2.6: Raised ridge formation on the Ti diffused region
Conclusion

An experiment was conducted to verify that the ridge structure formation that was observed in literature could be reproduced. The experimental method employed in this investigation was described in detail. A raised ridge was observed on the Ti diffused region. Its height was greater than (about twice) the thickness of Ti initially deposited. The uncoated surface was smooth with no surface defects evident. These observations correlate with the results reported in the literature suggesting that the experimental procedure and diffusion environment were similar to the ones reported and that raised ridge can be reproduced in the laboratory. Having established that smooth raised ridges can be formed in LiNbO$_3$, it is now possible to explore the control and application of these surface morphology features.

2.4 Etching LiNbO$_3$ during Ti diffusion process

Having succeeded in recreating the raised ridges observed in literature, it is now possible to investigate opportunities to control this phenomenon. To start with, a brief review of the key facts detailed from the literature in previous sections is presented. A detailed overview of the Ti diffusion process in LiNbO$_3$ was presented in Section 2.2. It was found from Section 2.2.2 that the effect of temperature, annealing time and oxidation conditions resulted in variations on the mode structure, refractive index profile, surface morphology and composition of planar Ti diffused region. The kinetics of Ti diffusion was reviewed in Section 2.2.3. An undesirable effect of surface guiding was observed when Ti was diffused in dry oxygen environment and this effect was due to the out-diffusion of Li ions from the uncoated surface. A wet oxygen environment was the preferred method to suppress this Li out-diffusion. It was found that the formation of stable LiOH compound, on the surface monolayer suppressed further Li out-diffusion.

It was also understood from Section 2.2.3 that the Ti diffusion process was not just a reaction that occurred at the interface between the Ti coated region and the surface of LiNbO$_3$, but reactions were evident on the surface of the Ti film. The transition of the surface morphology characterized by a very high degree of roughness on the partially diffused Ti film to the surface becoming smooth with increased diffusion time signifies the level of turbulence that the film encounters due to ionic migrations during the diffusion process.
Hypothesis

The swelling observed on the Ti diffused region suggests that a crystal phase transition may have occurred in the diffused region increasing its ridge height. The increase in ridge height indicates reactions with the oxygen environment. The water vapor content in the diffusing atmosphere provides OH\(^-\) ions to neutralize the Li\(^+\) out-diffusion, and the remaining H\(^+\) ions could be a source of some reactive species on the diffusing surface. Hence, with another LiNbO\(_3\) wafer placed on top of the Ti film of the diffusing wafer, it can be hypothesized that there would be a reactive effect on the surface of the top wafer. It may be that the top surface could bond with the diffusing wafer or that there could be significant etching. The following Section aims to explore this hypothesis.

Method

In this Section, an experimental investigation is conducted to observe the impact of the diffusing surface reactions on another LiNbO\(_3\) wafer. This was conducted by diffusing Ti into LiNbO\(_3\) with another LiNbO\(_3\) wafer placed in close proximity to the surface of the diffusing film. Figure 2.7 depicts the fabrication procedure used in this investigation to observe the effect of the Ti diffusing film on the bare LiNbO\(_3\) wafer.

The method for fabricating the Ti strips on LiNbO\(_3\) was the same as described in Section 2.3. However, in a departure from the traditional Ti diffusion procedure, another clean dehydrated bare congruent X-cut LiNbO\(_3\) wafer was placed on top of the Ti patterned wafer (as shown in Figure 2.7(d)) and then the two wafers were diffused as described in Section 2.3.

Results

After diffusion, the two wafers of LiNbO\(_3\) were easily separated. It was clear even with un-aided inspection that the top LiNbO\(_3\) wafer had been modified. Visual and surface inspection were performed on the top and bottom wafers after diffusion. An optical microscope was used for the visual inspection and an AFM was used for quantitative analysis of the surface.

Figure 2.8 presents the micrograph image of the Ti diffused wafer under the top bare sample. It can be observed that the surface of the Ti diffused region appears to be smooth. The uncoated
Etching LiNbO$_3$ using Ti diffusion technique

Step 1: LiNbO$_3$ wafer cleaned and dehydrated

Step 2: Titanium evaporated on LiNbO$_3$

Step 3: Photolithography

Step 4: Etching of Titanium

Step 5: Place another bare LiNbO$_3$ wafer on top of the patterned wafer and anneal them together at 1050°C in wet oxygen atmosphere

Figure 2.7: Experimental procedure for etching LiNbO$_3$ during Ti diffusion process
region is also smooth with no visible defects. Figure 2.9 presents a micrograph image of the top bare wafer. It can be seen that the top bare sample has undergone some topographical surface modification. These modifications can be observed only in the regions where Ti was present on the bottom wafer. The top wafer above the uncoated regions of the Ti diffusing wafer was smooth and no defects could be sighted in these regions.

Figure 2.10 shows the AFM images of the bottom wafer, in the region of diffusion of a 5 µm Ti strip. A ridge can be observed in the Ti diffused region and its height was measured to be 259 nm. The surface of the ridge and its sidewalls were observed to be very smooth. The surface profile exhibited here was similar to the raised ridge formed during normal Ti diffusion (Figure 2.6), with the ridge height measured to be greater than that of the normal Ti diffused sample.

The complementary region on the top wafer was also examined with the AFM and is shown in Figure 2.11. The top wafer does indeed exhibit significant etching and the depth was measured to be 181 nm. The etched surface was very smooth with a RMS roughness of 12 Å (similar to bare LiNbO₃ substrate).

**Discussion**

It was hypothesized that the reactive surface of the Ti diffusing region may have an impact on the bare wafer placed in close proximity. An experiment was conducted to investigate this hypothesis. The results observed in Section 2.4 provides qualitative and quantitative evidence of etching occurring in the region directly above the Ti diffusing region. A significant etch depth of 181 nm was obtained which is more than the thickness of Ti initially deposited (103 nm). The ridge formed on the Ti diffusing substrate was measured to be greater than the one obtained during conventional Ti diffusion process and about 2.5 times the thickness of the original Ti strip. It is suggested that the increased ridge height can be attributed to the re-deposition of the material removed from the top wafer onto the Ti diffusing strip. An AFM analysis of the roughness revealed that the quality of the etched surface and its sidewalls, to be very smooth.
Figure 2.8: Micrograph image of the Ti diffused (bottom wafer) in wet oxygen atmosphere for 10 hours at 1050°C

Figure 2.9: Micrograph image of the top etched wafer
Etching LiNbO₃ using Ti diffusion technique

Figure 2.10: AFM images of the raised ridge on Ti diffused region of the bottom wafer

Figure 2.11: AFM images of the etched trench on the top wafer
2.5 Conclusion

The aim of the Chapter is to identify a technique that could enable smooth surface modification while retaining the crystal properties of LiNbO$_3$. An extensive literature review revealed the physical processes that occur during the ridge formation. It was postulated that these physical reactions occur on the surface of the Ti diffusing film and that these reactive processes may be used to alter a second wafer of LiNbO$_3$ placed in close proximity.

An investigation was performed with another LiNbO$_3$ wafer placed on top of the Ti diffusing wafer to study the impact of the physical reactions on the top wafer. This led to the serendipitous discovery of a technique that could be used to etch LiNbO$_3$. AFM micrographs reveal the quality of the etched surface to be very smooth. These etched surface features could be deep enough and smooth enough to achieve grating-like features.

However, before attempting to utilize these etched features, they must be characterized to determine the parameters effecting their formation and their application to various forms of LiNbO$_3$ must be explored. An attempt must also be made to explain this observed phenomenon in terms of the known physics and chemistry of LiNbO$_3$. These investigations are conducted in the following Chapters.
Chapter 3

Characterization of etching in LiNbO$_3$ using Ti diffusion technique

Chapter 2 presented a novel technique that can be used for surface machining LiNbO$_3$. Significant etching was evident with a high quality etched surface. In this Chapter, a systematic study is performed to investigate the parameters that can be used to control the etching process. This characterization study aims to provide the insight into this etching technique that may be required for fabricating many application oriented optical devices including surface relief gratings.

It was found from the literature study presented in Section 2.2, that the Ti concentration profile in the diffused region fits the profile of a Gaussian function [50, 65]. The Gaussian function for the diffusion profile is related to the parameters such as annealing time, temperature, thickness of the Ti film and the width of the Ti strip [11].

In this Chapter, a characterization study is conducted to determine the behavior of the etching process with respect to the parameters that affect the Ti diffusion process. The experimental results for the characterization of etch depth by varying parameters such as water vapor content in the annealing atmosphere, the annealing duration, thickness of the original Ti film and the strip width of the patterned Ti on the bottom sample are related to the resulting etch depths observed on the top sample after co-annealing. The observed results are discussed and a conclusion is derived for the investigation.

This Chapter is organized as follows: Section 3.1 presents a quantitative study on etch depth by varying the water vapor content in the annealing atmosphere. Section 3.2 presents
a quantitative study on etch depth by varying the annealing time. Section 3.3 presents the etch depth characteristics for different Ti thicknesses annealed for an uniform time duration. Section 3.4 presents a qualitative comparison of the surface morphology of the annealed samples. Section 3.5 presents the etch depth characterization study for different pre-diffused Ti strip widths. Finally, conclusions are drawn from the characterization study and is presented in Section 3.6.

3.1 Role of water vapor content in the annealing atmosphere

In this Section, an investigation is performed to determine the role of water vapor content in the etching process. It is hypothesized that the etching process is an electrochemical process [16] in which the H\(^+\) ions from the water vapor play a role. To test this hypothesis, several identical Ti strip samples were prepared and diffused in the presence of a bare top wafer for different quantities of water vapor content in the annealing atmosphere. The resulting etch depths were measured and tabulated.

3.1.1 Etch depth with varying water vapor content in the annealing atmosphere

The samples were prepared using a similar procedure as described in Section 2.3.2. The fabrication procedure is reviewed again here for the reader’s convenience. A thin film of Ti was deposited on a clean congruent X-cut LiNbO\(_3\) wafer. The Ti coated wafer was wafer photolithographically patterned to form strips of width 5 \(\mu m\) and separation 150 \(\mu m\). The wafer was then diced into 6 small samples (5 \(mm\) x 10 \(mm\)). Another bare congruent X-cut LiNbO\(_3\) wafer was diced into the same dimensions. The Ti patterned sample was annealed at 1050\(^\circ\)C for 12 hours with a bare LiNbO\(_3\) sample placed on top of the patterned sample. Wet oxygen was produced by passing dry oxygen through a column of deionized water heated at 60\(^\circ\)C. The wet oxygen was then mixed with dry oxygen using a gas flow controller and then passed through the annealing furnace at a rate of 1 liter per minute. For each of the 6 pairs of samples a different mixture of wet and dry oxygen was used. The ratios of wet to dry oxygen used were 0\%, 20\%, 40\%, 60\%, 80\% and 100\%. After annealing, the etch depth achieved on the top sample was measured using an atomic force microscope (AFM).

Figure 3.1 presents the collated etch depths for different ratios of wet and dry oxygen,
Figure 3.1: Etch depths on the top LiNbO$_3$ wafer obtained for different concentrations of wet oxygen with 100nm thick Ti on bottom LiNbO$_3$ wafer.
with the X-axis representing the ratio of wet and dry oxygen and the Y-axis representing the corresponding etch depths. A low precision gas flow controlled was used to control the wet and dry oxygen levels flowing through the annealing furnace and this is represented through a horizontal error bar. The etch depths were measured at four different regions of the sample. The maximum and minimum points of the error bars are determined from the four measurements and the mean value is represented by the data point.

From Figure 3.1, a decrease in etch depth is observed with decreasing water vapor content in the annealing atmosphere with the etch depth approaching zero with 0% wet oxygen (100% dry oxygen). This result thus provide conclusive evidence that water vapor plays an important role in the etching process and warrant further discussion.

3.1.2 How does water content influence the etching process?

It was observed from Figure 3.1 that water vapor plays an important role in the etching process. An investigation has reported observations of the interaction of water vapor at the defective surface of TiO$_2$ [66]. It was reported that the defects cause the water vapor to dissociate into H$^+$ and OH$^-$ ions. The OH$^-$ ions are absorbed and immobilized on the defective surface of TiO$_2$ while the H$^+$ ions are released [67,68]. It can thus be concluded that the defects diffusing to the surface of the Ti strip in the samples react with the available water vapor to create free H$^+$ ions and these ions are responsible for etching the top sample. Maximum number of H$^+$ ions is available for 100% wet oxygen and hence maximum etch depth is observed. Hence, it is likely that the etching process is electrochemical in nature with water vapor serving as the electrolyte [20].

3.2 Investigation of annealing duration and etch depth

Having established the fact that water vapor plays an important role in the etching process, it is now necessary to investigate the role of the parameters that influences Ti diffusion process. One such parameter is the the annealing time duration. It is hypothesized that the degree to which the etching occurs maybe closely correlated to the Ti diffusion process and variations in the annealing duration can affect the resulting etch depths. To test this hypothesis, a number of identical Ti strip samples were prepared and diffused in the presence of a bare top wafer for
different annealing durations. The resulting etch depths were measured and tabulated.

3.2.1 Etch depth with varying annealing time for 100 nm thick Ti films

The samples were prepared using a similar procedure as described in Section 2.3.2. A thin film of Ti was deposited on a clean LiNbO$_3$ wafer. The Ti coated wafer was diced into smaller samples of size 15 mm x 15 mm. The samples were then photolithographically processed to retain Ti on one-third of the sample. Another bare congruent X-cut LiNbO$_3$ wafer was diced into the same dimensions. The Ti patterned sample was annealed with a bare LiNbO$_3$ sample placed on top of the patterned sample. Different annealing time durations ranging from 2 hours to 30 hours were set for each experiment. After annealing, the etched depths on the bare LiNbO$_3$ sample were measured using a contact profilometer.

The thickness of the Ti film prior to diffusion was measured to be 105 nm. Figure 3.2 presents the collated etch depths for different annealing durations, with the X-axis representing annealing time durations and the Y-axis representing the corresponding etch depths. Note that the Y-axis range is deliberately enlarged for easy comparison with the other plots in this Chapter. Error bars were determined by repeating the experiment in analogous conditions and measuring the etch depths. Maximum and minimum points of the error bars are determined from the two measurements and the mean value is represented by the data point. Three distinctive etching zones can be observed in Figure 3.2. For annealing durations of less than 4 hours, no etching was observed. This region was labelled as ZoneA. For annealing durations between 5 hours and 10 hours, a linear increase in etch depths can be observed with increasing annealing duration. This region was labelled as ZoneB. For prolonged annealing durations $> 10$ hours, the etch depths are observed to saturate with annealing period and remains constant. This region is labelled as ZoneC.

The topographical profiles of the Ti film before annealing, the etched region and its corresponding Ti diffused region is shown from a set of samples from each regime. Figure 3.3(a),(b) and (c) present the profile characteristics of ZoneA (samples annealed for 4 hour duration), ZoneB (samples annealed for 8 hours) and ZoneC (samples annealed for 20 hours) respectively.

From the results presented in Figure 3.2, it is interesting to note that no etching is observed on samples that are annealed for less than 5 hour duration (ZoneA). The profile characteristics
Figure 3.2: Etch depth in nm as a function of annealing duration hour for the sample with original Ti thickness of 105 nm. The plot is divided into three distinctive zones. Zone A - no etching observed. Zone B - linear increase in etch depth and Zone C - saturated etch depth.
Figure 3.3: Profile characteristics of the bottom sample and the complementary region on the top sample with the original Ti thickness as 105 nm (a) 4 hour annealing period representing Zone A, (b) 8 hour annealing period representing Zone B and (c) 20 hour annealing period representing Zone C.
in Figure 3.3(a) show an increase in the ridge height in the Ti diffused region (about three times the original thickness of Ti) and irregular surface undulations can be observed in the Ti diffused region. A profile on the surface of the top bare sample shows that the top surface remains unaffected for this annealing period.

The profile characteristics of the sample from Zone B (annealing time 8 hours) is presented in Figure 3.3(b). A slight increase in the ridge height can be observed on the Ti diffused region when compared to Figure 3.3(a) with surface undulations still evident in the Ti diffused region. Etching is observed on the bare wafer in the regions where Ti was present with the etched surface remaining as smooth as the unetched surface.

For prolonged annealing durations (Zone C), the profile characteristics presented in Figure 3.3(c) show that the undulations on the surface of the Ti diffused region have been smoothed out and the ridge height is observed to have increased to about 5 times the original thickness of the Ti strip. An increased etch depth with a smooth profile can be observed on the etched surface.

Etching was observed to vary with annealing duration while holding all other annealing conditions constant. The etch depth was found to increase linearly for annealing periods between 5 hours and 10 hours. For longer annealing durations, the etch depth remains constant. These results are in good agreement with the hypothesis that the annealing duration influences the etching mechanism. However, an interesting and unexpected observation in this investigation was that no etching was evident for annealing durations less than 5 hours.

From these observations, it is possible to conclude that whatever causes the etching, observed in Figures 3.3(b) and (c) is not present for the first 4 hours of annealing. This indicates that the annealing environment and the Ti film are not the causes. On this basis, it is possible to hypothesize that something which originates at the interface between the Ti film and the LiNbO₃, diffuses through the Ti film over a period of 4 hours, could be responsible for the etching. To test this hypothesis, the experiment was repeated with a thicker Ti film. If the commencement of etching takes longer, then it can be concluded that the etching is caused by something that diffuses through the Ti film from the interface of the Ti and the LiNbO₃.
3.2.2 Etch depth with varying annealing time for 500 nm thick Ti films

It was observed that the Ti film with an original thickness of about 100 nm requires over 4 hours of annealing for etching to commence on the top wafer. It can be hypothesized that if etching is due to some defect or ion which originates at the interface between the Ti strip and LiNbO$_3$, a longer duration may be necessary for a thicker Ti film when all the other conditions for the etching process remain unaltered. A film of a nominal thickness of 500 nm was used for this investigation.

Another set of samples were prepared for this investigation with a thicker Ti film and adopting the same procedure as in Section 3.2.1. The etch depth characterization was performed for different annealing durations of 4 hours to 30 hours.

The etch depths for different annealing durations of the 500 nm thick Ti films are presented in Figure 3.4. Here again, as in Figure 3.2, the resulting etch depths exhibit three distinct zones, with no etching (Zone A), linear etch rate (Zone B) and finally, etch depth saturation (Zone C). As presented in Section 3.2.1, the profile of a set of samples from each regime is also presented here. Figures 3.5 (a), (b) and (c) are the profile characteristics of 7 hour, 10 hour and 30 hour annealed samples representing Zone A, Zone B and Zone C respectively.

The profile characteristics of the sample from Zone A (annealing time 7 hours) is presented in Figures 3.5 (a). An increased ridge height in the Ti diffused region can be observed (about three times the original Ti thickness) with irregular surface undulations. A profile on the surface of the top bare sample shows that the top surface remains unaffected during this annealing period.

The profile characteristics of the sample from Zone B (annealing time 10 hours) is presented in Figures 3.5 (b). The ridge height is observed to be slightly increased when compared to Figures 3.5 (a) with the irregular undulations more prominent. Etching is observed on the top bare sample in the regions that were adjacent to the Ti strip and the etched surface remain smooth.

The profile characteristics for prolonged annealing duration (Zone C) with an annealing duration of 30 hours is presented in Figures 3.5 (c). The surface undulations on the Ti diffused region have been smoothed out completely. The ridge height is observed to have increased by 5 times the original thickness of Ti. An etch depth of 1.1 µm is observed on the top bare sample.
with the etched profile remaining smooth.

It can be observed from Figure 3.4, that the etching characteristics are similar to that of the 100 nm Ti film observed in Figure 3.2. The etch depths observed in Figures 3.2 and 3.4 are however different for the same annealing time period. The profile characteristics of Figure 3.5 are similar to the characteristics of Figure 3.3, with the ridge height increasing as the annealing time is increased and the undulations disappearing with prolonged annealing time durations. Note that short annealing durations reveal an extremely rough surface on the Ti strip region (Figure 3.5 (b)), however, the etched surface is extremely smooth. This observation is consistent in both thin and thicker Ti films as presented in Figures 3.3 (b) and 3.5 (b).

The commencement of the etching process for the thicker film is after 7 hours of annealing. This observation supports the hypothesis that the etching process commencing after a longer annealing time duration for a thicker Ti film (7 hours for 500 nm) than with thinner Ti film (4 hours for 100 nm). Therefore, it is possible to hypothesize that some defect or ion which is generated at the interface of Ti strip and LiNbO$_3$ during annealing is required at the surface of the Ti strip to act as a catalyst and to provide sites for water dissociation for the etching process to occur. This constituent is required to diffuse through the oxidized Ti strip to reach its surface before etching can commence. This observation leads to the question - what can be the possible constituent that is available at the surface from the interface of LiNbO$_3$ and Ti film?

### 3.2.3 Discussion of the physical mechanism causing etching

At this point it will be useful to discuss some possible mechanisms that could be responsible for the observed etching. In the literature review presented in Section 2.2, a detailed overview of the Ti diffusion process into LiNbO$_3$ was presented. From this review, it was found that Ti diffusion into LiNbO$_3$ occurs via cation migration [69]. It is known that Nb ions diffuse from the LiNbO$_3$ surface into the oxidized Ti film (TiO$_2$) simultaneous to the diffusion of Ti ions into the LiNbO$_3$ bulk [50, 69]. The migration of Nb ions from the bottom of the TiO$_2$ film to its surface, via diffusion alone, would occur after a considerable period of time during annealing.

It is proposed that the etching process commences only after the Nb ions reach the surface of the TiO$_2$ film [20]. The Ti ions exhibit a +4 oxidation state while the Nb ions exhibit +5 oxidation state [54]. Hence, there exists a charge imbalance at the site of a Nb ion defect in the
Characterization of etching in LiNbO$_3$ using Ti diffusion technique

Figure 3.4: Etch depth in $nm$ as a function of annealing duration $hour$ for the sample with original Ti thickness of 480 nm. The plot is divided into three distinctive zones. 

- **Zone A** - no etching observed.
- **Zone B** - linear increase in etch depth
- **Zone C** - saturated etch depth
Figure 3.5: Profile characteristics of the bottom sample and the complementary region on the top sample with the original Ti thickness as 480 nm (a) 7 hour annealing period, (b) 10 hour annealing period and (c) 30 hour annealing period
TiO$_2$ film. This may be compensated with an OH$^-$ ion from a dissociated water molecule, but only at the TiO$_2$ film surface. If every Nb ion that reaches the surface is compensated with an OH$^-$ ion, then there is a H$^+$ ion generated as well. The production of the reactive H$^+$ ions could be considered as the active species causing the etching on the top wafer. The model agrees with the observations presented in Section 3.1 that no etching occurs in the absence of water vapor in the annealing atmosphere.

Thus, ZoneA in Figures 3.2 and 3.4 are where the Nb$^{5+}$ ions have not yet reached the surface. In the intermediate annealing stages (ZoneB in Figures 3.2 and 3.4), the etch rate is observed to be linear with annealing durations. This can be attributed to the continuous surfacing of the Nb ions simultaneous to the Ti diffusion into the LiNbO$_3$ bulk. If every Nb ion reaching the surface, captures an OH$^-$ ion and thus generating an excess H$^+$ ion, then the increased etch rate can be attributed to the rate at which the Nb ions are exposed at the surface.

For prolonged annealing durations (ZoneC in Figures 3.2 and 3.4), it is known that the Ti is completely ‘depleted’ [18]. It can be expected that the relative concentrations of Ti and Nb within the strip and in the LiNbO$_3$ below the strip become equal, meaning that any further inter-diffusion does not result in a charge imbalance being generated and hence no unbalanced charge migrates to the surface. This would result in the termination of the production of H$^+$ ions at the surface. The etching thus ceases, resulting in saturation of etch depth for prolonged annealing duration.

Etch depth characterization was performed for two different thickness of Ti films and this resulted in identifying a plausible physical mechanism causing etching. This observation suggests that the thickness of Ti, a parameter that affects Ti diffusion process, causes variations in etch depth for the same annealing periods. A systematic characterization study of etch depth for different Ti thicknesses is thus required to relate etch depth as a function of Ti thickness.

### 3.3 Etch depth with varying Ti thickness for 10 hour annealing duration

From the characterization study performed in Sections 3.2, it has been observed that annealing time influences the etch depth. A second experiment, conducted with a thicker Ti film yielded a deeper etch. This showed that the Ti film thickness also has an influence on the etch
characteristics. In this Section, a more detailed experimental study is conducted to establish
the relationship between thickness of the Ti film and etch depth with all the other parameters
maintained constant.

An annealing period of 10 hours was selected so that complete Ti depletion at the surface
of LiNbO₃ can be expected for the thin Ti films, while for thicker Ti films, the etching process
is expected to have just initiated. The sample preparation for this investigation was performed
in a manner similar to that described in Section 2.3.2. The procedure is reviewed again here for
the reader’s convenience. A 3-inch X-cut congruent LiNbO₃ wafer was diced into small samples
(7 mm x 5 mm). The samples were cleaned and dehydrated. Ti films of different thickness were
deposited on each sample. Nominal Ti film thicknesses of 20, 60, 100, 150, 230, 320 and 480 nm
were selected for this study. The samples were then photolithographically processed to retain Ti
on one-third of the sample. Each of these samples were then covered with a small bare uncoated
LiNbO₃ sample (7 mm x 5 mm) such that a portion of the Ti was covered on the lower sample.
The samples were annealed in a wet oxygen atmosphere for 10 hours.

A contact profilometer was used to measure the Ti film thicknesses of the samples before heat
treatment. They were measured to be 29, 74, 108, 160, 234, 315, and 483 nm. After diffusion,
the etch depth on the top samples were measured. Figure 3.6 presents the etch depths obtained
after annealing for 10 hours. The original Ti film thickness of the samples is represented in
the X-axis and the resulting etch depths are represented in the Y-axis. Note that the Y-axis
range has been scaled for easy comparison with the other plots in this Chapter. Error bars were
determined by repeating the experiment in analogous conditions and measuring the etch depths.
Maximum and minimum points of the error bars are determined from the two measurements
and the mean value is represented by the data point.

From Figure 3.6, the etch characteristics can be divided into three distinct regions. The
etch depth is observed to increase linearly with increasing Ti film thickness. This characteristic
etching behavior is observed for samples having less than 110 nm thick Ti films and is named
Region A. With increasing Ti film thicknesses beyond 110 nm, the etch depths is observed to
be constant and is named Region B. A decreased etch depth can be observed for the thickest
Ti film in this experiment and is named Region C.

The topographical profiles of the pre-diffused Ti film, the etched region and its corresponding
Ti diffused region is shown from a set of samples from each regime. Figure 3.7(a), (b) and (c)
present the profile characteristics of RegionA (Ti film thickness of 73 nm), RegionB (Ti film thickness of 315 nm) and RegionC (Ti film thickness of 483 nm) respectively.

The profile characteristics of a sample from RegionA with a thin Ti film is presented in Figure 3.7(a) and shows that the Ti diffused surface and the etched surface are very smooth. The ridge formed on the Ti diffused region is about twice the thickness of the original Ti thickness. The profile characteristics of a sample from RegionB with Ti film of an intermediate thickness is presented in Figure 3.7(b). It can be observed that the Ti diffused region possess undulations on its surface, while the etched surface is very smooth. The profile characteristics of a sample from RegionC presents significant undulations on the surface of the Ti diffused region. But again, on the etch surface, it is observed to be very smooth.

The Ti films of thicknesses less than 110 nm (RegionA) are expected to be completely depleted for annealing durations of less than 10 hours. As the annealing continues the etch depth does not increase. This could be due to the depletion of Ti on its surface. This can be related to the observations made in Section 3.2. In Figures 3.2 and 3.4, it was observed that for prolonged annealing durations (ZoneC) the etch depth obtained on the top sample tends to saturate. Thus, RegionA in Figure 3.6 exhibits similar characteristics to ZoneC in Figures 3.2 and 3.4. These are in-fact the same cross-section through the same region in two different dimensions (annealing time and Ti thickness).

In RegionB with thicker Ti films, all of the Ti has not completely diffused into the LiNbO₃ substrate within the 10 hour annealing period. The etching process terminates at the end of the annealing period (which is 10 hours) and the Ti is not fully depleted. Comparing RegionB of Figure 3.6 to Figures 3.2 and 3.4, it is evident that RegionB of Figure 3.6 shares the property of ZoneB in Figures 3.2 and 3.4.

For a very thick Ti films (> 315 nm), the Ti is not depleted and in fact only a small amount of Nb will have reached the surface. An explanation of this effect was presented in Section 3.2. It was shown that the Nb ions take longer to surface through thick Ti films and hence the initiation of the etching process is delayed considerably. The delay in the commencement of the etching process results in a reduced etch depth when the annealing time duration is 10 hours. Comparing RegionC of Figure 3.6 to Figures 3.2 and 3.4, it is evident that RegionC in Figure 3.6 lies between ZoneA and ZoneB of Figures 3.2 and 3.4.
Figure 3.6: Etch depth as a function of Ti thickness. The plot is distinguished by three regions, *Region A* - linear increase in etch depth, *Region B* - constant etch depth and *Region C* - reduced etch depth
Figure 3.7: Profile characteristics of the bottom Ti sample and the complementary region on the top sample after a 10 hour annealing period with the original Ti thickness as (a) 73 nm (Region A), (b) 315 nm (Region B) and (c) 483 nm (Region C)
The relationship between the original Ti film thickness and its effect on etch depth was established. The observed results agree with the model presented in Section 3.2.3. It can be inferred that the arrival of Nb ions at the surface initiates the etching process. The depletion in the Ti concentration ceases the etching process in completely diffused LiNbO$_3$ samples.

It was observed in Figure 3.7 that the undulations of the raised ridge increased significantly with increasing Ti film thickness. Figures 3.3, 3.5 and 3.7 also show that the undulations formed on the Ti diffused region does not affect the etched surface, which remains smooth. It will be valuable to quantitatively investigate the relationship between the surface roughness on the Ti diffused region with respect to the Ti film thickness prior to diffusion and its effect on the etched surface.

### 3.4 Surface roughness characterization

The roughness of the etched surface and the Ti ridge covered with the top LiNbO$_3$ are shown in the profile characterizations presented in Figures 3.2, 3.4 and 3.7. It was observed quantitatively that the surface roughness of the Ti diffused strip for a completely diffused sample was very smooth, while a significant increase in surface roughness was observed on the sample where the Ti was not completely diffused. Interestingly, the etched profile was apparently unaffected by the surface roughness on the Ti diffused strip. In this Section, a quantitative study is performed to investigate the relationship between surface roughness and the original Ti strip thickness. This analysis aims to provide a better understanding of the various roughness features observed in Section 3.3 and perhaps provide further insight into the physical basis of the etching mechanism.

The samples prepared for the Ti thickness characterization study in Section 3.3 were used in this study. Additionally, another set of normal Ti diffused samples without the top wafer, having the same thickness of Ti film were diffused for the same time period under the same diffusion conditions as in Section 3.3. The RMS surface roughness of the raised ridge for both covered and uncovered diffusions, the etched trench and the original Ti strip prior to diffusion were measured using a contact profilometer and the results were tabulated.

Figure 3.8 presents the RMS surface roughness of each of the samples. The X axis represents the thickness of the Ti film and the Y axis represents the RMS roughness on the surface. Note that the Y-axis is in the logarithmic scale. Error bars were determined by repeating
Figure 3.8: RMS roughness as a function of initial Ti thickness for: Ti as deposited (triangle down); raised ridge formed after normal Ti diffusion (squares); raised ridge on Ti diffused wafer covered with bare LiNbO$_3$ wafer (triangles up); etched trench on top bare wafer after diffusion (circles)
the experiment in analogous conditions. Maximum and minimum points of the error bars are
determined from the two measurements and the mean value is represented by the data point.
From Figure 3.8, it can be observed that the surface roughness of the original Ti film is smooth
in each case. From the same Figure, it is also evident that for Ti thickness less than 100 nm
the roughness of the raised ridge, formed in the Ti diffused region, in both covered (with the
presence of a bare LiNbO₃) and uncovered (normal Ti diffused) conditions, does not depend on
Ti thickness and is essentially the same as the optically polished wafer whose RMS roughness
is about 1.2 nm. For Ti thicknesses greater than 100 nm, the roughness of the raised ridge
increases exponentially with Ti thickness for both the covered and uncovered samples. However,
the roughness of the etched surface remains unchanged for all Ti thicknesses and is very close
to the roughness of the polished wafer, independent of the roughness of the raised ridge.

The surface roughness of the diffused covered and uncovered samples, observed for thicker
Ti films (< 100 nm) can be attributed to the fact that the Ti film is not depleted. For the
samples where Ti is depleted at the surface of LiNbO₃ (< 100 nm Ti films), it can be observed
that the surface roughness of the Ti diffused region on the covered and uncovered sample is very
smooth.

3.4.1 Discussion of surface roughness in Ti diffused region and etched trenches

An important question is, what is causing the roughness on the raised ridges? It is known
that when Ti is annealed in an oxygen atmosphere, Ti absorbs oxygen and forms TiO₂ in the
rutile phase [54]. Over time at high temperature, the rutile forms crystallites [51]. Evidence
of the formation of crystallites can be seen in Figure 3.7 (c). To further illustrate the presence
of the crystallites, Scanning Electron Microscope (SEM) image of the sample of Figure 3.7 (c)
was taken and this is presented in Figure 3.10 (Figure 3.9 is a SEM image of a Ti deposited
sample before annealing). Here it is clear that the surface of the sample has a flaky structure,
presumably TiO₂ in the rutile phase.

Now, as annealing continues, Nb from the TiO₂/LiNbO₃ interface diffuses through the TiO₂
film. As it progresses, it reacts with the TiO₂ and forms a mixed oxide solid solution [52].
This mixed oxide solid solution dissolves the rutile crystals. Thus as annealing continues, the
roughness of the rutile crystal reduces until the Nb concentration in the TiO₂ film saturates and
all of the flaky structure is dissolved. This model is consistent with the observations presented
in Section 3.2 and 3.3.

On the top samples, the etched surface exhibited no change in surface roughness. The etched surfaces remain smooth and the measured surface roughness values were the same as that for the unprocessed LiNbO$_3$ wafer, suggesting that the roughness does not affect the mechanism of the etching process.

The surface roughness characterization study revealed that the surface roughness on the Ti diffused region does not affect the surface morphology of the etched region which retains its degree of smoothness, the same as an unprocessed LiNbO$_3$ wafer. This surprising result could be explained if etching occurs layer-by-layer. With the H$^+$ ions as the etching species, the crystal structure of LiNbO$_3$ is destroyed on the near surface layers ($< 10nm$) [70] and this may contribute to the smoothness on the etched surface with the bulk of the crystal remaining intact.
Characterization of etching in LiNbO$_3$ using Ti diffusion technique

Figure 3.9: Scanning Electron Microscope(SEM) image of the surface of a covered Ti diffused region before annealing. The pre-diffused Ti thickness was 483 nm.

Figure 3.10: Scanning Electron Microscope(SEM) image of the surface of a covered Ti diffused region after annealing for 10 hours at 1050°C in wet oxygen atmosphere. The pre-diffused Ti thickness was 483 nm.
3.5 Patterned Ti strip width and etch depth

It was observed in Sections 3.2 and 3.3 that the annealing time and the Ti thickness, which are the parameters that influence the Ti diffusion process, significantly influence the etch depths. The delayed commencement of the etching process led to the hypothesis that the etching process commences with the Nb ions reaching the surface of the oxidized Ti film. In the study reported in this Section, the volume of Ti deposited is varied by varying the widths of the Ti strips and maintaining a constant thickness. The hypothesis for this study is explained as follows. It is well established that the Ti ions diffuse into LiNbO$_3$ by swapping with Nb ions [69]. With a uniform Ti film thickness, the time taken for the Nb ions to reach the surface (as suggested in Section 3.2.3), will be constant. But with the lateral dimensions varying, the volumetric quantity of the Nb ions swapping with the Ti ions can be expected to vary. The etch depth can thus be expected to depend on the volumetric quantity of Ti ions swapping with the Nb ions and thereby reducing the etch depth for narrow Ti strips. Thus, it can be expected that a broad Ti strip may etch deeper than a narrow Ti strip.

To investigate this hypothesis, a sample with different Ti strip widths was fabricated. The sample preparation for this investigation was performed in the same manner as described in Section 2.3.2. Ti strips of widths 3, 3.5, 4, 4.5, 5, 5.5, 6, 6.5, 7, and 10 $\mu$m, 100, 200, 300, 400 and 500 $\mu$m and 1, 2 and 5 mm were formed on a LiNbO$_3$ wafer. Another LiNbO$_3$ wafer was placed on top of the patterned wafer and etched using the Ti diffusion process. The annealing duration was for a period of 12 hours in wet oxygen atmosphere at 1050°C. The etched wafer was surface profiled using a contact profilometer.

The patterned Ti film thickness and its width was measured using a contact profilometer. The Ti strips were measured to be 103 nm thick with patterned widths of 3 to 7 $\mu$m in 0.5 $\mu$m increments, 10 $\mu$m and larger strips measuring 100, 200, 300, 400 and 500 $\mu$m and 1, 2 and 5 mm.

After diffusion, the bare top samples were profiled to measure the etch depths. Figure 3.11 presents the resulting etch depths after annealing, represented in the Y-axis, plotted against their respective patterned Ti strip widths represented in the X-axis. The Y-axis range of Figure 3.11 is set to enable comparison with the other Figures in this Chapter. Error bars were determined by repeating the experiment in analogous conditions and measuring the etch depths. Maximum
Figure 3.11: Etch depth obtained for different widths of patterned Ti (pre-diffused)
Characterization of etching in LiNbO$_3$ using Ti diffusion technique

Figure 3.12: Profile characteristics of the patterned Ti strip, uncovered Ti diffused, covered Ti diffused and the complementary etched region on the top sample after a 12 hour annealing period with the original Ti thickness as 103 nm with widths (a) 3 µm, (b) 5 µm and (c) 7 µm.
and minimum points of the error bars are determined from the two measurements and the mean value is represented by the data point.

It can be observed in Figure 3.11 that the etch depth increases linearly with the Ti patterned width until 10 \( \mu m \). With Ti widths greater than 100 \( \mu m \), a constant etch depth is observed.

Figures 3.12 (a), (b) and (c) presents profiles of the Ti diffused region of the covered and uncovered sample and the corresponding region on the top covered wafer for Ti patterned strips of 3 \( \mu m \), 5 \( \mu m \) and 7 \( \mu m \) respectively. From the Figures 3.12 (a), (b) and (c), it can be observed that the sidewalls of the etched trench are smooth. These sidewalls are more gradual than the original Ti strip. The width of the sidewalls from the etched surface can be measured to be about 7\( \mu m \). It is evident that the etched surface is flat and smooth. A flat top is observed on the covered Ti diffused sample while a rounded top is observed on the uncovered Ti diffused sample.

The volume of the Ti film decreases with decreasing Ti patterned widths. From Figure 3.11, a linear increase in etch depth can be observed between 3 \( \mu m \) and 10 \( \mu m \) Ti patterned strips. This agrees with the hypothesis that the etching process is influenced by the amount of Ti available to diffuse.

It can be expected that the broader strips should have a linearly increasing etch depth. However, it can be observed in Figure 3.11 that the etch depth is constant for broader Ti strips with widths (\( > 100 \mu m \)). This observation can be explained as follows. The diffusion of Ti into LiNbO\(_3\) with broader Ti strips can be considered to be a one dimensional diffusion process. The measure of the lateral distance of the etched sidewalls is approximately the same as the diffusion length (about 4 \( \mu m \)) that can be expected for the annealing conditions used in this experiment. This can be observed in profiles of the etched surface shown in Figures 3.12 (a), (b) and (c). It can also be observed that the sidewalls are gradual and extend a long distance from the edge of the patterned Ti strip (about 7\( \mu m \)), suggesting that the production of the reactive H\( ^+ \) ions that may cause the etching process is not limited to the top surface of the Ti diffusing strip but is also produced on the sidewalls of the Ti diffusing strip. For narrow strips, the diffusion process can be considered to be two dimensional where the Ti can be considered a point source. As the strip gets wider, the Ti diffuses both outward from the strip edges, as well as, inward from the strip edges into the interior. The interior of the strip thus gets an increased dose of Ti. Once the strip approaches two diffusion lengths wide, the Ti diffusing from the strip edges no longer
reaches the middle of the strip and thus the Ti dose of this center point is not further increased for the strips wider than two diffusion lengths. If there is a correlation between Ti concentration and etch depth, then the etch depth will increase with increasing Ti strip width only until the strip width is two diffusion lengths wide. This model is supported by the fact that the etch depth stops increasing once the Ti strip width exceeds 10 \( \mu m \). The nominal diffusion length in X-cut LiNbO\(_3\), for the annealing conditions of this experiment, can be calculated and is about 4 \( \mu m \).

Comparing the diffused profiles in of an uncovered Ti diffused sample and a covered Ti diffused sample in Figure 3.12 (a), (b) and (c), it can be observed that the covered Ti diffused region has a greater ridge height than the uncovered Ti diffused region. These observations suggests that the material from the etched surface is re-deposited on the Ti diffusion region.

In summary, the relationship between the Ti patterned widths and etch depths was deduced. The plot presented in Figure 3.11 is in agreement with the hypothesis that the etching process terminates with the depletion of the Ti concentration, which thereby reduces the charge imbalance caused by the Nb ions at the surface of the Ti film. It was also suggested the surfacing of the Nb ions occurs on the top surface as well as the sidewalls of the Ti strip, and also on the surface of LiNbO\(_3\) where Ti is laterally diffused.

### 3.6 Summary and Conclusion

The etching of LiNbO\(_3\) using the Ti diffusion process was characterized with water vapor content in the annealing atmosphere, annealing time, the thickness of the Ti film and the patterned width of Ti strips. It was observed that variation of these parameters resulted in etch depth variations. The maximum etch depth that was obtained in this study was 1.1 \( \mu m \) for a 500 nm thick Ti film diffused for 30 hours.

It was also observed that for a short annealing duration, no etching was observed on the top wafer. An etching model was presented in Section 3.2.3 that the etching process commences when the Nb ions reach the surface of the oxidized Ti film. This process can be considered to occur simultaneously with the Ti diffusion process into the bulk LiNbO\(_3\). The etching model was tested by characterizing the etch depth with annealing time for a thicker Ti film. It was observed that the commencement of the etching process was longer than that observed for
thinner Ti films. The etch rate was found to increase with annealing time. This was attributed to the continuous arrival of Nb ions on the surface of Ti diffusing strip. The etch rate tends to diminish with prolonged annealing durations and this condition was related to the depletion of Ti from the surface into LiNbO$_3$.

Experiments were performed to characterize etch depth by varying the thickness of Ti for a fixed annealing time duration. The intermediate thickness of Ti film exhibited the maximum etch depth, while the thickest Ti film in the experiment exhibited very low etch depth. This condition was related to the delayed commencement of the etching process in the thickest Ti film. The result of a reduced etch depth at the end of 10 hours of annealing for the thickest Ti film is expected as the commencement of the etching process occurs after 7 hours of annealing and this result commends the etching model presented in Section 3.2.3.

The etched surfaces were very smooth even when the Ti diffusing surface of the bottom wafer exhibited a high degree of roughness. This suggests that the Nb ions evolved on the surface of the Ti diffusing strip produce H$^+$ ions that are responsible for etching. It can be proposed from the results observed through the etch depth characterization study that the etching process is a layer-by-layer process.

Varying the volume of Ti by varying the lateral dimension of the Ti strips with uniform thickness yielded varying etch depths, with shallow etch depths obtained for narrow Ti strips, with all other parameters maintained constant. A linear increase in etch depths was observed with increasing Ti strip widths. Increasing the Ti strip width beyond 10 $\mu$m did not increase etch depth. This result was attributed to the diffusion length of Ti in LiNbO$_3$.

It can be observed from the investigations to determine the etch characteristics that the Ti diffusion characteristics primarily influence the etching process. However, in order to derive a mathematical expression for the etching, it may be required to consider the diffusion of H$^+$ ions as it is observed that these ions play an important role in the etching process as well.

In conclusion, the investigations carried out in this Chapter provided evidence that the etch depth can be controlled with the same parameters (annealing time, Ti thickness and patterned Ti widths) that the diffusion of Ti into LiNbO$_3$. A plausible model for the etching mechanism was derived. It was suggested that the etching process was caused by the reactive H$^+$ ions generated by the charge imbalance at the surface of the Ti film due to the surfacing of the Nb
ions. A smooth quality etched surface was observed suggesting that this technique could be used for optical device applications.
Chapter 4

Material and optical characterization of etched LiNbO$_3$

4.1 Introduction

A novel technique to etch LiNbO$_3$ using Ti diffusion was demonstrated in Chapter 2. From the results presented in Section 2.4, significant etching can be observed on the bare LiNbO$_3$ wafer that is placed in close proximity to the Ti diffusing region with the quality of the etched surface very smooth. A characterization study performed in Chapter 3 revealed that the etching process can be controlled using the same parameters that control Ti diffusion process. Some of the parameters that were used to control the etch depth include the annealing time, the thickness of the Ti film and the patterned Ti strip widths. Having examined the morphology of the surfaces in detail, it will now be in structure to investigate the material properties of the ridges and etched trenches. This may add further insight into the physical processes leading to the observed etching.

In this Chapter, a detailed investigation is presented on the study of the material characteristic changes in the crystallinity, material composition and optical index of the etched surface. The characterization study was performed by comparing the results obtained on the etched surface with that of the bare LiNbO$_3$ wafer. Section 4.2 presents the crystallinity of the etched surface determined using X-Ray Diffraction (XRD) technique. Section 4.3 presents the material composition study performed using Energy Dispersive X-ray Spectroscopy (EDS) and X-ray Photoelectron Spectroscopy (XPS). Section 4.4 presents the optical index characterization performed using the Prism coupling technique. Section 4.5 presents a summary and concluding
4.2 Crystallinity characterization

In Section 3.4, the surface roughness characterization study performed on the etched surface revealed that the quality of the etched surface was not compromised by the high surface roughness of the corresponding raised ridge of the bottom sample. In the discussions in Chapter 3, it was considered that the H\textsuperscript{+} ions produced at the surface of the Ti strip causes etching of the top sample. This was claimed to be evidence of layer-by-layer etching. The act of etching is essentially destroying the crystal. If the etching process is not layer-by-layer, then it would be expected that the crystal at the surface of the etched trench may exhibit some damage. In this Section, the hypothesis was investigated by studying the crystallinity of the etched surface using wide angled X-Ray Diffraction (XRD).

The sample preparation for this investigation follows the same procedure as described in Section 2.3.2. A brief description of the procedure is presented here for readers convenience. A clean X-cut LiNbO\textsubscript{3} sample of 1 cm\textsuperscript{2} was prepared with 100 nm of Ti film deposited using e-beam evaporation. Another clean bare X-cut LiNbO\textsubscript{3} sample of similar dimension was placed on top of the Ti deposited wafer and diffused simultaneously for 10 hours in wet oxygen atmosphere at 1050°C. The top etched sample was then used for this characterization study. An untreated X-cut LiNbO\textsubscript{3} sample was also analyzed as a reference.

The XRD pattern was obtained from a Bruker D8 Advanced X-ray diffractometer fitted with a Cu tube (Cu K\textalpha radiation), a monochromator and a divergent slit of 1 mm. A standard theta-2 theta scan (Bragg-Brentano geometry) was performed with a position sensitive detector.

Figure 4.1 presents the diffractograms of the etched wafer and the bare LiNbO\textsubscript{3} wafer. The X-axis presents the 2-theta angle and the Y-axis presents the intensity. An off-set on the Y-axis was included to compare the diffractograms. It can be observed from the Figure 4.1 that the diffractograms of the etched sample and the bare LiNbO\textsubscript{3} presented appear identical. The diffractograms provided by the wide angled XRD is an average over a depth of 10 \(\mu\text{m}\) from the surface to within the bulk of the crystal. Hence, a single crystal orientation is observed over 10 \(\mu\text{m}\) depth of the etched sample. No additional peaks were observed on the etched sample.

The diffractograms obtained from the etched sample was compared with that of the bare
Material and optical characterization of etched LiNbO$_3$

Figure 4.1: XRD diffractograms performed on bare and etched X-cut LiNbO$_3$
LiNbO$_3$ sample. The comparison of the diffractograms reveal no additional peaks, hence ruling out the possibility of any additional crystalline phase formation. These results support the hypothesis that the etching is layer-by-layer, meaning that if the LiNbO$_3$ material is modified by the $\text{H}^+$ ions, then the modified material is immediately removed.

### 4.3 Material composition characterization

It was established in Section 4.2 that the crystallinity within the bulk of the etch LiNbO$_3$ crystal had no evidence of additional crystalline phase formation. This suggests that the material composition on the etched surface may be the same as untreated LiNbO$_3$. Furthermore, it was observed in Section 2.4 that the raised ridge resulting on the bottom wafer was larger than the raised ridge that results from uncovered Ti diffusion. It was suggested that this extra material could be redeposited material from the top etched sample.

It is hypothesized that if the etched trench is pure LiNbO$_3$, then its composition should match untreated LiNbO$_3$. Similarly, if the raised ridge is coated with redeposited LiNbO$_3$, its composition should be different from an uncovered raised ridge.

In this Section, a material composition analysis was performed on the etched sample and compared with that of the bare LiNbO$_3$ wafer. A comparative study was also performed on the covered Ti diffused region and uncovered Ti diffused sample.

Two techniques were used to study the material composition of the etched sample, Energy Dispersive X-ray Spectroscopy (EDS) and X-ray Photoelectron Spectroscopy (XPS). Both of these techniques were used to measure the atomic concentrations of different species on the surface of etched LiNbO$_3$ and untreated LiNbO$_3$. A comparison of the material composition was also performed on the raised ridge formed on the bottom wafer when etching and on the raised ridge formed by normal uncovered Ti diffusion. Unfortunately, neither of these techniques can measure the Li concentration as the element is too light. Therefore, the atomic concentration of Li must be ignored.

The same samples prepared for XRD analysis in Section 4.2 were used for these studies.
4.3.1 Material composition characterization using EDS technique

The material composition of the samples was analyzed using Energy Dispersive X-ray Spectroscopy (EDS), function of a FEIe Quanta 200 Environmental Scanning Electron Microscope (ESEM), at 30 kV, low vacuum and in the back scattering light condition. ZAF matrix correction method was implemented during quantification. The acquisition time was maintained constant at 10 seconds for all the samples analyzed. The nominal depth of analysis is about 1 μm and hence the atomic percentage presented is an average over this depth. Error bars were obtained by repeating the measurement at four different regions of the same sample.

Table 4.1 gives the Atomic percentage (A%) of Nb, O and Ti, for the bare un-processed LiNbO₃ substrate, bare LiNbO₃ substrate processed by annealing for 10 hours in wet oxygen atmosphere, raised ridge from an uncovered Ti diffusion, the raised ridge resulting from Ti diffused region covered with a top bare LiNbO₃ wafer and the etched surface of the top wafer.

It can be observed from the material composition analysis performed on the etched sample that there was no Ti observed on the etched surface. From the comparative study of the material composition between the bare LiNbO₃, the bare wafer annealed in wet oxygen and the etched sample, it can be observed that there is no significant difference in their composition. This shows that the etching process does not induce any composition changes, which further supports the hypothesis that etching is layer-by-layer.
The study performed on the Ti diffused region of the uncovered and covered Ti diffused samples reveals a slight change in composition of Nb and Ti. The increased atomic percentage of Nb and decreased atomic percentage of Ti on the covered Ti diffused sample suggests that material from the top wafer (which has no Ti content) is deposited onto and mixed with the Ti rich raised ridge of the bottom wafer, reducing its Ti concentration. This supports the hypothesis that the increased ridge height is due to re-deposition from the top wafer.

### 4.3.2 Material composition characterization using XPS technique

A material composition analysis using EDS was performed on the unprocessed and processed samples and presented in Section 4.3.1. The nominal depth of analysis using EDS technique was about 1 $\mu m$ and hence the atomic percentage composition was an average over the depth of analysis. With this process considered to be a layer-by-layer process, it is necessary to examine the atomic concentration on the near-surface of the unprocessed and processed samples. The X-ray photoelectron spectroscopy (XPS) was used for this analysis.

Measurements of the atomic concentrations of each sample were conducted using the X-ray photoelectron spectroscopy (XPS) function of the VG Instruments Model 310 Auger/XPS spectrometer. The surface composition analysis was performed on an area of 5 mm x 1 mm using an aluminium $K_\alpha$($Al K_\alpha$) X-ray source with an energy of 1485 eV. Carbon peaks (due to adventitious carbon) were used to calibrate the resulting spectra to account for any surface charging effects. Error bars were determined by repeating the measurement at four different regions of the same sample. The analysis using this technique performed on the surfaces of each of the same samples used in Section 4.3.1. Again, the samples were an un-treated bare LiNbO$_3$, a bare LiNbO$_3$ processed by annealing for 10 hours in wet oxygen atmosphere, a raised ridge from an uncovered Ti diffusion, the raised ridge resulting from Ti diffusion covered with a top bare LiNbO$_3$ wafer and the etched surface of the top wafer were used. Table 4.2 gives the Atomic percentage (A%) of Nb, O and Ti for all these samples measured using XPS.

It can be observed from Table 4.2, that the material composition at the surface of an annealed bare LiNbO$_3$ wafer and etched wafer are very similar. No evidence of Ti was observed on the etched surface. A decrease in the Ti and O atomic percentage while an increase in the Nb atomic percentage was observed on the Ti diffused sample with the presence of the top bare LiNbO$_3$ wafer.
Table 4.2: Material composition in atomic percentage (A%) using X ray Photoelectron Spectroscopy

<table>
<thead>
<tr>
<th>Atoms</th>
<th>Bare LiNbO$_3$ annealed for 10 hours in wet oxygen</th>
<th>Etched surface</th>
<th>Normal Ti diffused region</th>
<th>Ti diffused region with bare LiNbO$_3$ placed on top</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td>84.7±0.2</td>
<td>75.1±0.3</td>
<td>75.5±0.4</td>
<td>77.8±0.3</td>
</tr>
<tr>
<td>Niobium</td>
<td>15.2±0.7</td>
<td>24.8±0.4</td>
<td>24.4±0.3</td>
<td>21.5±0.5</td>
</tr>
<tr>
<td>Titanium</td>
<td>Nil</td>
<td>Nil</td>
<td>Nil</td>
<td>0.6±0.2</td>
</tr>
</tbody>
</table>

The material composition investigation was performed using two different techniques. The analysis performed using EDS provided an average atomic concentration over a depth of approximately 1 $\mu$m while the analysis performed using XPS provided the atomic concentration only at the surface. It can be observed from both the analysis techniques that there is no evidence of Ti on the surface of the etched sample. This result in good agreement with the hypothesis that the etching process is a resultant effect of the Ti diffusion process into LiNbO$_3$. The etched surface exhibited a very similar material composition to that of the annealed bare LiNbO$_3$ sample. The material composition study performed on the normal Ti diffused and Ti diffused in the presence of a top bare wafer revealed changes in the material composition. An increase in the Nb atomic percentage can be attributed to the re-deposition of material etched from the top wafer, thereby decreasing the atomic percentage of the Ti ions.

In conclusion, the material composition of the etched surface and Ti diffused region were studied. It is observed that the results obtained are in agreement with the hypotheses that the Ti diffusion into LiNbO$_3$ causes the etching process, the etching process can be suggested as a layer-by-layer process and the material from the etched top wafer may be re-deposited on the bottom Ti diffused region.
Table 4.3: Refractive index measurements of etched and untreated LiNbO$_3$ using prism coupler

<table>
<thead>
<tr>
<th></th>
<th>Etched LiNbO$_3$</th>
<th>Untreated LiNbO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n_o$</td>
<td>2.2862</td>
<td>2.2859</td>
</tr>
<tr>
<td>$n_e$</td>
<td>2.2025</td>
<td>2.2028</td>
</tr>
</tbody>
</table>

4.4 Optical characterization

It was observed in Section 4.2 and Section 4.3 that the crystallinity and the material composition of the etched surface remained unaltered after the etching process. It must be noted that the study does not account for the composition of the Li or H ions. A Li deficit [43] or protonated surface [71] has been reported to increase the extra-ordinary index and thus exhibiting isotropic refractive indices in both ordinary and extra-ordinary polarizations. It may be possible that the etched surface has become Li deficient or protonated. Hence, by measuring the refractive index of both horizontal and vertical axes of the etched LiNbO$_3$ surface, we would be able to observe any Li deficit or protonation.

A prism coupling technique was employed to measure the refractive index of an etched sample. The same etched sample that was prepared for material characterization investigations as reported in Section 4.2 was used in this investigation. A Metricon 2010 Prism Coupler was used to measure the refractive index on the etched surface. The refractive index measurements were performed at 632.8 nm wavelength along the ordinary and extra-ordinary polarizations.

Table 4.3 presents the ordinary index ($n_o$) and the extra-ordinary index ($n_e$) measured on the etched surface and the untreated LiNbO$_3$ sample. Note the error in orienting a sample for measurement would result in averaging of the refractive indices values along the X and Z crystal axes (the differences of the refractive indices on the etched surface and un-treated LiNbO$_3$ sample could be attributed to such error). Figure 4.2 presents the plots of the prism coupler measurements performed on the etched and untreated LiNbO$_3$. 
Material and optical characterization of etched LiNbO₃

Figure 4.2: Prism coupler refractive index (nₒ and nₑ) plot on the untreated and etched LiNbO₃
4.5 Summary

Material characterization study was performed on the etched surface of LiNbO$_3$. The crystallinity beneath the etched surface was investigated using X-Ray Diffraction. The diffractogram was compared to that obtained from the bare LiNbO$_3$ sample. It was observed that the etched sample retained its crystal structure after the etching process by exhibiting no difference compared with the diffractogram obtained from the bare LiNbO$_3$ sample. The material composition of the etched sample was found to be similar to that of the bare LiNbO$_3$ sample. A material composition investigation was also performed on the Ti diffused region under the bare (top) LiNbO$_3$ sample. The results were compared with a normal Ti diffused sample. A composition difference was observed in these sample and was attributed to the material re-deposition from the etched sample onto the Ti diffused sample.

From the optical characterization study, it can be observed that the measured indices were similar to those of the bare congruent LiNbO$_3$ [72], indicating that the etching process does not cause index modification. With the ordinary and extra-ordinary index similar to the bare LiNbO$_3$, it can be suggested that the Li out-diffusion is suppressed and the etched surface is not protonated and thus retains the optical birefringence as exhibited by the bare congruent LiNbO$_3$ sample. This supports the material investigation that the crystal properties of the etched surface remains unaltered.

In conclusion, the material characterization study was performed on the etched LiNbO$_3$ to investigate its potential application in optical device fabrication. From this study, it can be suggested that the crystallinity of the bulk LiNbO$_3$ retained the structure of the bare LiNbO$_3$ single crystal. The optical properties of the etched surface of LiNbO$_3$ remains unaltered retaining its birefringence. This again suggests that the etching process does not induce any discernable damage to the crystallinity and material composition of the etched surface.
Chapter 5

Etching characteristics for different crystal orientations of LiNbO$_3$

5.1 Introduction

Chapter 2 presented a novel technique to etch LiNbO$_3$ using a standard Ti diffusion process. Evidence of significant etching using this process was observed. Chapter 3 thoroughly describes the dependence of the etching process on the parameters of the Ti diffusion. Significant control over etch depth was achieved while maintaining very smooth etched surfaces. A physical model was developed to explain the observations. Chapter 4 describes the material and optical characterization of the etched surface. It was revealed that the etched surface had no significant variance in crystallography or material composition compared to a bare LiNbO$_3$ wafer. The optical properties of the etched surface were also retained after the etching process. The conservation of the material and optical properties on the etched surface together with the smooth quality observed suggests that this technique could find its applications in optical device fabrication.

The etching characteristic studies described in Chapter 3 were performed on X-cut LiNbO$_3$ crystal orientation. It is known that LiNbO$_3$, being an anisotropic and ferroelectric material, has different properties with respect to its crystal orientation [73]. Hence, the characterization of etching during Ti diffusion for different crystal orientations is required to identify any limitations or opportunities for the application of this etching technique to various crystal faces of LiNbO$_3$.

In this Chapter, an investigation of the effect of LiNbO$_3$ orientation on etching during Ti diffusion is performed. Section 5.2 presents a brief literature survey of the etching of different crystal orientations of LiNbO$_3$. Section 5.3 presents an experiment conducted to investigate the
Etching characteristics for different crystal orientations of LiNbO₃

etching process with various combinations of the top and bottom wafer crystal orientations. A plausible model is also presented to explain the observed results. Section 5.4 summarizes the investigations of the chapter.

5.2 Survey of techniques for etching X and Z cut LiNbO₃

Reported etching characteristics of LiNbO₃ depend on the crystal orientation and the etching process. With LiNbO₃ being an anisotropic material, the etch rates vary with crystal orientation [73]. Figure 5.1 presents the hexagonal unit cell of LiNbO₃ and Figure 5.2 presents the atomic arrangement of LiNbO₃ parallel to Z axis [1]. The +X and -X faces of X-cut LiNbO₃ have similar ionic properties [1] and hence exhibit similar etching characteristics [73]. However, the +Z and -Z faces of LiNbO₃ present opposite ionic properties. The etching characteristics of the +Z and -Z faces of LiNbO₃ have been observed using wet etching processes [73,74], reactive ion etching and inductively coupled plasma etching [36]. Strong contrast in etching characteristics have been observed on the ±Z face of Z-cut LiNbO₃ especially in wet chemical etching [73–75]. Wet chemical etching is often used to identify the +Z and -Z faces, particularly in periodically poled lithium niobate (PPLN) [76]. Dry etching processes on the other hand often yield similar etch rates for both +Z and -Z faces [36].

It is necessary to understand the chemistry of the etching process in order to explain why the two surfaces of the Z-cut LiNbO₃ react differently in wet and dry etching processes. A literature review was conducted to understand the etching mechanisms of these two techniques.

5.2.1 Wet etching of Z cut LiNbO₃

Wet etching of LiNbO₃ is a chemical process. The common formulation of the wet chemical etchants used for etching LiNbO₃ include concentrated and dilute HF, HF with HNO₃, and orthophosphoric acid [73,77]. It has been observed that the ±Z faces of LiNbO₃ react differently to these etchants. The -Z face often exhibits a significant etch rate while the +Z face remains largely irresponsible to the chemical etchant [77]. An excellent review can be found in [74,78].

In the wet etching process, at its initial state, the -Z face of LiNbO₃ is terminated with negatively charged oxygen ions. In the presence of water, the surface is rapidly neutralized with H⁺ ions forming hydroxyl groups. Exposure of this surface to strong acids such as HF results in
Figure 5.1: Hexagonal unit cell of LiNbO$_3$ [1]
Etching characteristics for different crystal orientations of LiNbO$_3$

Figure 5.2: Atomic position of Li and Nb with respect to oxygen octahedra in the ferroelectric phase of LiNbO$_3$ [1]
Etching characteristics for different crystal orientations of LiNbO₃

the H⁺ component reacting with the hydroxyl termination and releasing oxygen from the crystal lattice as H₂O. This reveals the Nb ions. The exposed Nb ions react strongly with the F⁻ ions and are removed from the surface, revealing the oxygen ions. The oxygen ions are removed by the formation of hydroxyl group, which is released as H₂O by the reaction with HF. This reveals the Li ions. The Li ion is distant from the next oxygen layer and hence its bond strength is weak. It can thus be successfully attacked with F⁻ from the HF and removed [74]. This reveals another oxygen plane and thus the process continues.

To explain why the +Z face is irresponsive to wet chemical etchant, it is useful to review the chemical bonding behavior in Z-cut LiNbO₃. It can be reviewed from [74] that the +Z face has a short metal-oxygen bond length, thus increasing its bond strength. The OH⁻ and F⁻ ions cannot bond strongly to the already bound Li⁺ ions. The H⁺ ions cannot bond to the oxygen due to the repulsion of the Li⁺ ions at the surface. The HF acid thus cannot attack the underlying Nb and hence the +Z surface remains largely irresponsive.

So, the ability for H⁺ to infiltrate and react with the oxygen of the -Z face is responsible for the observed wet chemical etching of that face. H⁺ cannot infiltrate and react with the oxygen due to the repulsion by the positive Li⁺ ions and hence making the +Z face resistant to wet chemical acids.

5.2.2 Dry etching of Z cut of LiNbO₃

Having established the chemical mechanism for wet etching of Z-cut LiNbO₃ in Section 5.2.1, a similar literature review was conducted on the +Z and -Z surfaces of LiNbO₃ using reactive ion etching (RIE) and inductively coupled plasma (ICP) etching processes [35, 36]. These dry etching processes use SF₆, CF₄ and CHF₃ gases as the reactive species that causes etching. Several experimental accounts can be found here [35, 36]. It was observed in these investigations that the etch rate remained constant on the +Z and -Z faces of LiNbO₃.

The chemistry involved in order to explain this observation of similar etch depth on +Z and -Z faces is as follows. The reactive ion etching of LiNbO₃ is usually carried out in a F⁻ based chemical environment. This is because F⁻ is highly reactive with the metal ions of Li and Nb. The halogenated compounds of Nb are volatile [35] and thus responsible for the removal of the exposed Nb ions. The halogenated compound of Li, though non-volatile, can be easily sputtered off the crystal surface [35]. Hence, it was suggested that the repetitive process of the removal of
the halogenated Nb compound (volatile) and Li compound (sputtered) may explain the similar etching on the +Z and -Z faces. This non-chemical sputtering process is the essential difference between dry etching and wet etching of LiNbO$_3$.

Similar to the wet etching process, the -Z surface is more susceptible to chemical attack than the +Z surface. However the sputtering component of the etching can dominate the desired etch rate and thus essentially equal etch rates can be observed on both the +Z and -Z surfaces with a dry etching process that includes both sputtering and chemical effects.

### 5.2.3 Summary

It can be summarized that the etching observed in the wet chemical etching model is caused due to protonation (infiltration of H$^+$ ions) on the -Z face which allows removal of oxygen and gives the F$^-$ ions access to the Nb ions and weakly bonded Li ions. On the +Z face, protonation does not occur (H$^+$ is not absorbed from the environment) and the F$^-$ ions cannot remove the strongly bound Li ions. Whereas in a dry etching process, the strongly bound Li ions are removed by non-chemical sputtering and the Nb ions are removed by reactive etching of the volatile halogenated Nb compounds, together is responsible for etching to occur on both the +Z and -Z faces.

Now, considering the discussions in Chapter 3, it was proposed that H$^+$ plays an important role in the observed etching of LiNbO$_3$ during Ti diffusion. So, the question becomes, is the observed etching during Ti diffusion chemical in nature (relying on protonation) or more like dry etching (with a significant sputtering component)?

### 5.3 Etching during Ti diffusion of X and Z-cut LiNbO$_3$

Etching has been observed on X-cut samples during Ti diffusion in LiNbO$_3$. Chapter 3 also presented the characteristics of the etching process on X-cut LiNbO$_3$. It was proposed from the characterization study that H$^+$ is responsible for etching. Section 5.2 presents a review that found wet etching to result in differential etching, with the -Z face responding far more strongly than the +Z face. Conversely, it was found that the +Z and -Z faces etched equally when dry etched using RIE or ICP process.
An experiment was designed to verify whether the $+Z$ and $-Z$ faces can be etched using the Ti diffusion technique as already observed on the X-cut wafer and whether there are any characteristic differences to the observed etching.

### 5.3.1 Etching of X, $+Z$ and $-Z$ cut top wafer with X-cut bottom wafer

In a quest to observe the etch characteristics of the $+Z$ and $-Z$ faces using the Ti diffusion technique, the first experiment was performed so that the orientation of the bottom wafer was maintained similar to that used in the investigation of Chapter 2 and only the orientation of the top wafer to be etched was varied.

The etching characteristics of X, $+Z$ and $-Z$ faces of LiNbO$_3$ crystal were investigated by annealing them in contact with a Ti coated X-cut wafer. Samples of 10 mm x 15 mm of X, $+Z$ and $-Z$ crystal orientations were used in the characterization study. The fabrication procedure employed to generate Ti strip patterns for these samples was the same as described in Section 2.3.2. A Ti film with a nominal thickness of 100 nm was deposited on the clean, dehydrated X-cut samples. The Ti film was photolithographically patterned to realize 5 $\mu$m wide strips.

Un-processed LiNbO$_3$ samples with X, $+Z$ and $-Z$ faces were used as the top samples. The sample combinations were labelled X/X, $+Z$/X and $-Z$/X for each of X, $+Z$ and $-Z$ top wafers being etched by Ti diffusing into a X-cut bottom wafer. The three sets of samples were placed in the furnace and annealed together in the same conditions as reported in Section 2.3.2 for 12 hours. An atomic force microscope (AFM) was used to measure the topography of the top bare sample and the bottom Ti diffused region obtained in each combination.

The height of the patterned Ti was measured to be 103 nm with Ti strip width of 5 $\mu$m on all the samples. The resultant etch depths and ridge heights obtained for each combination are presented in Table 5.1. Error bars are obtain by measuring etch depths obtained by repeating the experiment in analogous conditions. The AFM micrographs of a Ti diffused region on the bottom samples with the corresponding region on the top sample are shown in Figure 5.3. Etching can be observed in all the upper samples. The etch depth is similar for $+Z$/X and $-Z$/X and is deeper for X/X. Figure 5.3 shows the etched surface is very smooth in all the three samples.
Table 5.1: Etch depth in nm on X, +Z and -Z faces using Ti diffusion in X-cut LiNbO$_3$

<table>
<thead>
<tr>
<th>Measurement</th>
<th>Wafer Combination</th>
<th>X/X</th>
<th>+Z/X</th>
<th>-Z/X</th>
</tr>
</thead>
<tbody>
<tr>
<td>Etched depth</td>
<td></td>
<td>191±12</td>
<td>152±8</td>
<td>151±11</td>
</tr>
<tr>
<td>Ridge height</td>
<td></td>
<td>271±15</td>
<td>234±13</td>
<td>300±7</td>
</tr>
</tbody>
</table>

It is thus possible to conclude that both the +Z and -Z faces of LiNbO$_3$ can be etched using the Ti in-diffusion technique. However, this raises two questions which warrant further discussion: (i) Why is it possible to etch the +Z face effectively? and (ii) Why is the observed etching efficiency the same for both the +Z and -Z faces?

**Discussion: Why are H$^+$ ions able to etch the +Z face?**

It was established in Chapter 3 that H$^+$ ions are generated from the Ti diffusing strip and are responsible for the etching process. With the bottom wafer as X-cut, it can be assumed that the influence of the H$^+$ ions on the top wafer (X, +Z and -Z surfaces) will be the same.

Section 5.2.1 described that wet chemical etching is effective on the -Z face, whereas the +Z face is irresponsible. This characteristic behavior was attributed to the strongly bound Li ions. Section 5.2.2 described that in reactive ion etching, a combination of sputtering (to remove Li ions) together with a chemical reaction (to remove Nb ions) was responsible for etching the +Z face. In both, wet and dry etch processes, a fluorine based environment was necessary.

An attempt is made to explain the etching process in a fluorine free environment. This is done by explaining the removal of Li and Nb ions individually.

Consider first the removal of Li ions; the Li ions may be sputtered off by the H$^+$ ions that are generated from the surface of the Ti strip. This can be considered unlikely because of the following reasons. The H$^+$ ions are lighter than the Li$^+$ ions. Moreover, at the diffusion temperature (1050°C), which is close to the Curie temperature, the Li ions are able to move very close to the oxygen plane to approach electrostatic equilibrium and hence the Coulomb force between the Li$^+$ and O$^-$ will be high and the energy required to sputter off the Li may similarly be high.
Etching characteristics for different crystal orientations of LiNbO$_3$

Figure 5.3: AFM micrographs of Ti diffused regions and the etched regions for Ti strip width of 5 $\mu$m. Ti is diffused into X-cut LiNbO$_3$, etching X, +Z and -Z faces of LiNbO$_3$. 
The other possible mechanism is the removal of Li in the form of Li$_2$O. It has been established in Chapter 3 that OH$^-$ ions from water molecules are consumed by the diffusing Ti strip. This results in a H$^+$ ions saturated region in air-gap between the Ti strip of the bottom wafer and the top wafer. The absence of OH$^-$ ions in the region above the Ti strip may allow the formation of Li$_2$O and out-diffuse from the top wafer. This can be considered to be a more plausible mechanism to remove Li ions.

Considering the removal of Nb ions, the surplus of H$^+$ ions present in the air-gap between the top and the bottom wafer can react with the NbO$_3^-$ to form HNbO$_3$. The formed HNbO$_3$ may precipitate and redeposit on the bottom Ti diffused region. This may explain the increase in ridge height in the Ti diffused region on the bottom wafer when compared to the ridge height of a normal Ti diffused wafer as observed in Chapter 2.

Having established a plausible physical and chemical mechanism for the removal of Li and Nb ions, it is now possible to suggest how this process may proceed on both the +Z and -Z surfaces.

On the +Z face, with Li ions on the outer most surface, Li$_2$O formation initiates the etching process and the subsequent layer of Nb is removed in the form of precipitation of HNbO$_3$. It can also be suggested that the rate of etching in this case depends on the concentration of the H$^+$ ions. A higher concentration of H$^+$ ions decreases the concentration of the OH$^-$ ions. The less OH$^-$ available in the atmosphere, the more Li$_2$O will out-diffuse providing access for the H$^+$ ions to the NbO$_3^-$ ions.

On the other hand, on the -Z face, the H$^+$ ions can easily infiltrate through the oxygen terminated face, and react to form HNbO$_3$ which precipitates. This reveals the Li$^+$ ions which are only loosely bound to the surface and readily dissociate. The rate of etching does not depend on the presence or absence of OH$^-$ ions, but depends strongly on the concentration of the H$^+$ ions.

If we assume this explanation to be true, then the -Z face should be more susceptible to etching than the +Z face because the Li ions must out diffuse from the +Z face before etching can proceed. However our observations show that the etch depth in both +Z and -Z faces are similar. Further development of the etching model is required to resolve this contradiction.

Having explained that the -Z face is more susceptible to etching, it is now necessary to
understand why the observed etch depth on the +Z and -Z faces are the same.

**Discussion: Why is the observed etching on the +Z and -Z face the same?**

To explain the observation of similar etch depths on the +Z and -Z face, the following factors may be considered to determine the etch rate:

i) The rate of generation of positive (H\(^+\)) ions at the surface of the Ti strip.

ii) The susceptibility of the upper wafer to etching by H\(^+\) ions.

iii) The amount of H\(_2\)O available to generate H\(^+\) ions.

The rate of generation of H\(^+\) ions at the Ti strip surface will be determined by the rate of diffusion of Ti into the lower wafer. In both cases, X-cut LiNbO\(_3\) was used and hence the rate at which H\(^+\) ions are generated should be identical. It has been reasoned above that although +Z may become somewhat susceptible to etching, it should be slower to etch than the -Z face due to the need for Li ions to out-diffuse before etching can proceed. Hence, the susceptibility of the +Z and -Z faces to H\(^+\) should be different.

So the fact that equivalent etching is observed on both +Z and -Z faces must be related to the amount of H\(_2\)O that is available at the diffusing Ti strip to generate H\(^+\) ions. To explain this observations, significantly more H\(_2\)O should be present when etching +Z, than when etching -Z face.

This can be explained by recalling from the review presented in Section 5.2.1 that in the wet etching process, the -Z face responds strongly to H\(^+\) ions from the water molecule. This is a key reaction that leads to strong etching of the -Z face in buffered HF. The whole of the -Z face will react with any water present and trap the H\(^+\) component leaving OH\(^-\) ions at the surface. At elevated temperature, this process is continuous and the environment must be continually refreshed with flowing wet oxygen. Conversely, it was found from the review in Section 5.2.1 that the +Z face does not respond to the H\(^+\) ions in the water molecule and this is why it remains unetched in buffered HF. The water in the environment will not be altered by exposure to the +Z face of LiNbO\(_3\). At the diffusion temperature, note that for X-cut, the Li\(^+\) ions are mobile along the XY planes and thus OH\(^-\) from water is required to prevent the out-diffusion of Li\(_2\)O. So in summary, water is consumed by the whole surface of -Z (leaving OH\(^-\) ions) and by
the whole surface of X (leaving H\(^+\) ions), but is unaffected by the +Z face. Hence, in the -Z/X combination, the entire surface of both top and bottom wafer are consuming the water from the environment. However, in the +Z/X combination, only the bottom surface is consuming water. This means that there is more water available at the Ti strip when etching +Z than -Z and thus there is a higher concentration of H\(^+\) ions created.

If this explanation were true, then it would be expected that the +Z/+Z should yield the largest number of H\(^+\) ions, resulting in a larger etch depth, while etching -Z/-Z should produce the least number of H\(^+\) ions, hence resulting in a smaller etch depth. This hypothesis is tested in the next Section.

### 5.3.2 Etching of X, +Z and -Z top wafer with +Z and -Z bottom wafer

In Section 5.3.1, it was suggested that the -Z face consumes H\(_2\)O while the +Z face does not. Hence the etching of +Z with the +Z/+Z combination would yield a large number of H\(^+\) ions resulting in a greater etch depth when compared with the -Z/-Z combination.

To investigate this proposal, this Section explores the characteristics of etching X, +Z and -Z driven by Ti in-diffusion into +Z and -Z faces.

Samples of 10 \(mm\) x 15 \(mm\) of +Z and -Z crystal orientations were used. The fabrication procedure employed to generate Ti strip patterns for these samples was the same as described in Section 2.3.2. A Ti film with a nominal thickness of 100 \(nm\) was deposited on the clean, dehydrated +Z and -Z samples. The Ti film was photolithographically patterned to realize 5 \(\mu m\) wide strips.

Un-processed LiNbO\(_3\) 10 \(mm\) x 15 \(mm\) samples with X, +Z and -Z faces were used as the top samples. The sample combinations were labelled X/+Z, +Z/+Z and -Z/+Z for each of X,+Z and -Z top wafers being etched by Ti diffusing into +Z bottom wafers and X/-Z, +Z/-Z and -Z/-Z for each of X,+Z and -Z top wafers being etched by Ti diffusing into -Z bottom wafers. The six sets of samples were placed in the furnace and annealed together in the same conditions as reported in Section 2.3.2 for 12 \(hours\). An atomic force microscope (AFM) was used to measure the topography of the top bare sample and the bottom Ti diffused region obtained in each combination.

The height of the patterned Ti was measured to be 103 \(nm\) with Ti strip width of 5 \(\mu m\) on
Table 5.2: Etch depth and ridge height in nm on X, +Z and -Z faces using Ti diffusion into X, +Z and -Z faces of LiNbO\textsubscript{3}.

<table>
<thead>
<tr>
<th>Combination</th>
<th>X/X</th>
<th>+Z/X</th>
<th>-Z/X</th>
<th>X/+Z</th>
<th>+Z/+Z</th>
<th>-Z/+Z</th>
<th>X/-Z</th>
<th>+Z/-Z</th>
<th>-Z/-Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Etched depth</td>
<td>191 ±12</td>
<td>152 ±8</td>
<td>151 ±11</td>
<td>49 ±6</td>
<td>141 ±11</td>
<td>65 ±8</td>
<td>129 ±14</td>
<td>183 ±6</td>
<td>101 ±17</td>
</tr>
<tr>
<td>Ridge height</td>
<td>271 ±15</td>
<td>234 ±13</td>
<td>300 ±7</td>
<td>263 ±21</td>
<td>301 ±15</td>
<td>269 ±22</td>
<td>274 ±10</td>
<td>236 ±14</td>
<td>242 ±9</td>
</tr>
</tbody>
</table>

Each of the samples. The resultant etch depths and ridge height obtained in each combination is presented in Table 5.2. The data from Table 5.1 is also included for convenience. Error bars are obtained by measuring etch depths obtained by repeating the experiment in analogous conditions. The AFM micrographs of the Ti diffused region on the bottom samples with the corresponding region on the top sample are shown in Figure 5.4 and Figure 5.5.

From the results presented in 5.2, it can be observed that the highest etch depth is on the X/X and the lowest etch depth is on the X/+Z. It was hypothesized that the +Z/+Z combination would yield a larger etch depth while the -Z/-Z would yield a reduced etch depth. From Table 5.2, it can be seen that the +Z/+Z has indeed produced deeper etching than the -Z/-Z, however it is also evident that other combinations produces deeper etching than +Z/+Z. The results obtained are not quite as expected and this warrants further discussion.

It has been established in Section 3.1 that the etch rate is proportional to the water vapor content in the annealing atmosphere. The number of H\textsuperscript{+} ions is proportional to the amount of H\textsubscript{2}O present and also the number of Nb\textsuperscript{5+} ions surfacing the Ti strip. It has been reasoned that some surfaces of LiNbO\textsubscript{3} may consume water and this reduces the amount of H\textsubscript{2}O that is present at the active region and thereby reducing the amount of H\textsuperscript{+} ions produced. It is also possible that the rate of arrival of Nb\textsuperscript{5+} ions at the top of the Ti strip will be different for Ti diffusion into the different crystal faces. This will also impact the observed etch rate. Hence, a normalization method is required to conduct a proper comparison.
Figure 5.4: AFM micrographs of Ti diffused regions and the etched regions for Ti strip width of 5 µm. Ti is diffused into +Z, etching X, +Z and -Z faces of LiNbO$_3$. 
Figure 5.5: AFM micrographs of Ti diffused regions and the etched regions for Ti strip width of 5 µm. Ti is diffused into -Z, etching X, +Z and -Z faces of LiNbO₃.
Table 5.3: Normalized ratio of etch depth obtained on +Z and -Z surfaces when compared with that obtained on the X-cut LiNbO$_3$

<table>
<thead>
<tr>
<th>Ti diffused Bottom</th>
<th>Etched Top</th>
<th>X-cut</th>
<th>+Z face</th>
<th>-Z face</th>
</tr>
</thead>
<tbody>
<tr>
<td>X-cut</td>
<td>A</td>
<td>0.7 A</td>
<td>0.7 A</td>
<td></td>
</tr>
<tr>
<td>+Z face</td>
<td>B</td>
<td>2.8 B</td>
<td>1.3 B</td>
<td></td>
</tr>
<tr>
<td>-Z face</td>
<td>C</td>
<td>1.4 C</td>
<td>0.7 C</td>
<td></td>
</tr>
</tbody>
</table>

5.3.3 Normalization of etch depths with respect to that on X-cut

It has been suggested that the Ti diffusion co-efficient of the bottom wafer may depend on its crystal orientation. This may result in the rate of generation of H$^+$ ions from the Ti strip, also being crystal orientation dependent. Hence, it was suggested that a normalization method would be suitable to investigate the hypothesis.

Normalization of the etch depth was performed by maintaining the orientation of the bottom sample as constant and deriving a ratio between the etch depth obtained in each combination to that obtained on a X-cut sample. Table 5.3 presents the normalized etch rate for the different combinations.

The first row of Table 5.3 presents the etch depth achieved when diffusing Ti into X and etching X, +Z and -Z respectively. To aid comparison, the depth achieved by the X/X combination has been labelled ‘A’ and the other depths written as a proportion of this value. As found in Section 5.3.1, the etch depth achieved for +Z/X and -Z/X are similar and less than the X/X combination. It was anticipated that the etching of the +Z face would be more difficult than -Z face, but it has further been reasoned that the presence of the -Z face may deplete the concentration of H$_2$O in the active region.

The second row of Table 5.3 presents the etch depth achieved when diffusing Ti into +Z face and etching X, +Z and -Z respectively. To aid comparison, the depth achieved by the X/+Z combination has been labelled ‘B’ and other etch depths written in terms of this value. It can be seen here that indeed the most effective etching is achieved with +Z/+Z, which is more than twice as deep as X/+Z. It can also be seen that the -Z/+Z face etches slightly faster than the X/+Z case. This may be due to the -Z face being easier to etch in general than X as could be
expected from the discussion of chemical etching in Section 5.2.1.

The third row of Table 5.3 presents the etch depth achieved when diffusing Ti into -Z and etching X, +Z and -Z respectively. Again to aid comparison, the depth achieved for X/-Z has been labelled ‘C’ and the other etch depths have been written in terms of this value. Here we see that the +Z/-Z combination is the most effective and the -Z/-Z is the least effective. This again supports the hypothesis that the presence of the -Z face consumes H$_2$O that is required for the etching process.

5.4 Summary and Conclusion

A detailed investigation was performed on the etching characteristics of different orientations of LiNbO$_3$ using Ti diffusion technique. Different combinations of the top and bottom samples were used in this characterization study. Etching was evident in all the combinations and the measured etch depth for each combination was different. An etching model was presented for this novel etching technique based on the mechanisms of dry and wet etching of LiNbO$_3$.

It was considered that the rate of H$^+$ ions generated from the surface region undergoing Ti diffusion varied with the orientation of the LiNbO$_3$ crystal. This can be considered as a factor leading to the observation of different etch depths on the top wafers for different sample combinations. A normalization method was suggested to quantify and explain the observed etch rates in each of the combinations.

It can be concluded that the etching process is a result of complex mechanisms. A physical process was suggested to explain the etching in the different crystal combinations. Further experiments are required to understand the role of domain inversion that may occur during the annealing process of the Z-cut LiNbO$_3$. 
Chapter 6

Stressed Waveguides on LiNbO$_3$

Chapter 2 presented an etching technique using standard Ti diffusion to surface machine LiNbO$_3$. Very smooth high quality etched trenches were observed. An etch depth characterization study was performed in Chapter 3 to determine the parameters that control the etching process. The material and optical characterization study performed in Chapter 4 revealed no significant variance in the material and optical properties of the etched surface when compared to an unprocessed LiNbO$_3$ wafer. These properties suggest that this etching method could be used to realize optical devices which require surface modification.

In this Chapter, the fabrication of an optical waveguide device is attempted. Section 6.1 presents the fabrication process and the test results of an etched optical ridge waveguide device. This experiment produced unexpected results. Rather than observing waveguiding between the etched trenches, guiding was observed directly beneath the etched trenches. These results innovate the discovery of an impurity free waveguide that can be attributed to residual stress. Section 6.2 presents an experiment to explore the fabrication procedure and the optical characterization of the impurity free stressed waveguide device. Section 6.3 presents the summary and the concluding remarks for the Chapter.

6.1 Ridge waveguide

Figure 6.1 presents a schematic diagram of a ridge waveguide. The refractive index within the ridge ($n_c$) is greater than that of the substrate ($n_s$). Ridge waveguides are used to enhance the optical confinement in waveguides [79], for efficient high frequency operation [80] and to control the size of the optical mode for increasing its efficiency in non-linear effects [81].
In this Section, an attempt is made to enhance the confinement of a Ti indiffused waveguide by forming a ridge waveguide using the etching process described in Chapter 2.

6.1.1 Geometry of the ridge waveguide

An example of the geometry for a ridge waveguide structure is reported in Reference [82]. In this report [82], a ridge waveguide on LiNbO₃ was achieved by surface machining a ridge structure of width 9 to 12 µm and depth 0.8 to 2.7 µm. Ti was then patterned on the ridge and diffused.

A similar geometry was chosen to fabricate ridge waveguide using the etching technique during Ti diffusion. A ridge with a nominal width of 3 to 7 µm and a depth of 0.8 µm was attempted. To achieve this geometry, it can be found from the characterization study performed on the etching parameters presented in Chapter 3, that a 15 hour annealing duration with a Ti film thickness of 500 nm is required on the bottom sample.

6.1.2 Fabrication and testing procedure

An un-processed X-cut LiNbO₃ wafer was cleaned and dehydrated. Ti film of thickness 500 nm was evaporated onto the wafer. The Ti film was photolithographically patterned using the mask which contained patterns of widths 3 to 7 µm in increments of 0.5 µm in both the clear field and dark field. A schematic of the mask is shown in Figure 6.2. Both positive Ti strips and
negative gaps on the Ti film were realized using the mask. The patterned wafer was annealed in a wet oxygen atmosphere for 15 hours with an un-processed LiNbO$_3$ wafer placed on top. Care was taken to place the crystallographic Y-axis of the un-processed wafer aligned parallel to the Ti patterns. Figure 6.3 presents a step by step diagram of the fabrication process.

Etching in the regions where Ti was present resulted in both ridge features and etched trenches on the top sample. Figure 6.4 presents a diagram of the ridge structures and the etched trenches. The ridge height and the etch depths were measured using a contact profilometer.

The resulting ridge height formed by etching the negative 5 $\mu$m gap was 785 nm and the etch trench in the region where the 5 $\mu$m Ti strip was present was measured to be 425 nm.

Ti was then diffused into the formed ridge structure. This was performed by depositing a thin film of Ti (100 nm) on the processed top wafer and photolithographically patterned so that Ti is retained only on the ridge features. The Ti patterned wafer was then diffused in a wet
Figure 6.3: Fabrication steps employed for ridge waveguides
The Ti diffused samples were then prepared for optical testing. After diffusion, the Ti diffused samples were diced using a Disco DAD321 Automatic Dicing SAW. To couple optical power into the waveguides, it is important to ensure that the sample’s end-face is optically flat and chip free. The dicing process causes the diced edges to be scratched. The scratches are required to be removed on the end faces through which the optical power is coupled. The scratches are removed by a lapping and polishing process. The lapping and polishing was performed on the end faces using a Logitech PM5 Precision Lapping and Polishing machine.

The prepared sample was then subjected to optical testing. A schematic of the optical test setup is shown in Figure 6.5. A 632.8 nm wavelength source was employed to perform the test and verify whether light was guided through the fabricated ridge waveguide.

The light was first passed through a single mode fibre and fibre collimator and focused onto a rotating polarizer. This rotating polarizer was used to set the input in the vertical (TM) and horizontal (TE) polarizations. The prepared sample was placed on a precision XYZ micro-positioner stage. The polarized light was focused through a 20x microscope objective lens to the region under the etched trench with the aid of the micro-positioning stage. A visible spectrum CCD camera was used to observe the optical power output using a 20x microscope objective lens to focus the output beam onto the camera.
6.1.3 Results and Discussions

It was observed that the light was not guiding through the fabricated ridges in either TE or TM polarizations. But unexpectedly, it was discovered that optical guiding was observed ‘under’ the etched trenches in both TE and TM polarizations.

Optical waveguiding was not observed in the Ti diffused ridge structure, but was observed under the etched trenches. This observation is unexpected because the optical characterization study in Chapter 3, was performed on the larger etched surface area of LiNbO$_3$ and it revealed no significant difference in the refractive index when compared to that of the un-processed LiNbO$_3$. Hence, this observation warrants further discussions as to what causes an increase in the refractive index under these etched trenches.

What causes an increase in the refractive index?

Some of the methods used to increase the refractive index of LiNbO$_3$ include metal diffusion [11], Li out-diffusion [43], proton-exchange [71], ion implantation [83], formation of domain boundaries [84] and strain [85]. Comparing each of the techniques, it may be possible to deduce the
cause for the increased refractive index observed under the etched trench.

It was concluded from the material investigations presented in Chapter 4 that there was no evidence of Ti on the etched surface. This rules out the possibility of metal diffusion and ion implantation. Proton exchange and Li out-diffusion induces an increased refractive index only in the extra-ordinary polarization. The observation of light guiding in both ordinary and extra-ordinary polarizations rules out the possibility that the waveguiding property is a resultant of proton exchange or Li out-diffusion.

The increase in refractive index under the etched trench may be attributed to stress. In order to relate the effect of stress to the observed waveguiding phenomenon, it will be valuable to understand the effect of temperature on the LiNbO$_3$ crystal. LiNbO$_3$ has anisotropic thermal co-efficients with the X and Y axis exhibiting uniform and relatively low values when compared to the Z-axis [86]. In the process of etching LiNbO$_3$ using Ti diffusion, etching occurs at 1050°C. It can be suggested that at the annealing temperature, the etched trench and its surroundings are at electrostatic equilibrium. Once the cooling process is initiated, the anisotropic thermal coefficients may induce a residual stress at the corners of the etched trench. This effect can induce an increase in the refractive index under the etched trench.

It is reported that the strain induced in the Ti diffused region is in the range between $10^{-5}$ to $10^{-3}$ [65]. The reason that no waveguiding was observed in the Ti diffused ridge could be that the strain induced under the etched trench is greater than that induced in the Ti diffused region.

6.1.4 Conclusion

It can thus be concluded that a residual stress is generated under the etched trench resulting in an increased refractive index and this explains the optical waveguiding under the etched trench.

6.2 Impurity free Stressed Waveguide

Waveguides are normally fabricated by diffusing dopants or impurity ions into LiNbO$_3$ to induce a localized change in the refractive index. A detailed overview on the different dopants that can be used to fabricate waveguides was presented in Section 2.2. However, these dopants
can enhance photorefractive damage limiting their application to infrared and low-power operation [87]. Proton exchange waveguides are often used when guiding at visible wavelengths with sufficient power to obtain nonlinear behavior. These waveguides are less susceptible to photorefractive damage, but generally only guide one polarization [71] and can degrade the electro-optic and second harmonic properties of LiNbO$_3$ [88].

It is also possible to fabricate optical waveguides in LiNbO$_3$ without chemically altering the material properties through the use of residual stress. Stress-induced waveguides have been fabricated on LiNbO$_3$ [85]. This was achieved by depositing patterned SiO$_2$ on LiNbO$_3$ at an elevated temperature. With a mismatch in the thermal expansion coefficients for SiO$_2$ and LiNbO$_3$, when the device is retrieved to room temperature, residual stress resulted in optical waveguiding.

In this Section, an investigation is conducted where a range of trenches of different widths (and depths) are formed on LiNbO$_3$ using standard Ti diffusion and the optical properties of any resulting waveguides are characterized.

### 6.2.1 Waveguide sample preparation

The sample preparation for this investigation was performed in the same manner as described in Section 2.3.2. Ti strips of widths 3 to 7 µm with 0.5 µm increment were fabricated on a LiNbO$_3$ wafer. Another LiNbO$_3$ wafer was placed on top of the patterned wafer. Care was taken to place the top bare wafer with its crystallographic Y-axis parallel to the Ti strips. The wafers were annealed together in a diffusion tube furnace for a period of 12 hours in a wet oxygen atmosphere.

After diffusion, the wafer was diced. A schematic diagram of the etched trenches and the dicing lines along which the wafer was diced is presented in Figure 6.6. The diced sample (Figure 6.7) was then lapped and polished. Figure 6.8 presents a photograph of the diced and end-face polished sample.

### 6.2.2 Optical Waveguide Measurements

The prepared sample was then subjected to optical testing. A 632.8 nm wavelength source was used to determine the quality of the waveguides formed under the etched trenches.
Figure 6.6: Schematic diagram of the fabricated wafer with the dicing line along which the sample was diced

Figure 6.7: Schematic diagram of the diced wafer
Modal profiles

In order to observe the modal profiles of the guided light, a similar procedure as in Section 6.1 was employed. The same setup as shown in Figure 6.5 was used. Figure 6.9 presents a mode profile and intensity profile in both polarizations of the waveguide formed by 5 \( \mu m \) etched trench. The modal profiles observed from the waveguides formed under the etched trenches of widths 3 to 7 \( \mu m \) were single mode. This was verified by translating the sample stage in the X and Y direction separately. The disappearance of the mode with no additional appearance confirms that the waveguide formed under the etched trench is single mode in both the TE and TM polarizations.

Waveguide Loss

The quality of the waveguide was determined by conducting optical loss measurements. This was performed by using the same setup as shown in Figure 6.5, with the CCD camera replaced by a visible wavelength power meter (Figure 6.10). The cut-back technique was adopted to measure the attenuation. The attenuation was measured separately for the TE and TM polarizations.
Figure 6.9: Mode profiles obtained in a 5 \( \mu m \) etched trench for TE and TM polarizations with its respective intensity plots.

Figure 6.10: Optical testing setup with a power meter to measure the output power.
Figure 6.11: Output power (dBm) vs length of the waveguide (cm) for an etched trench of width 5µm
The output power was measured in the TE and TM polarizations for three different lengths of the same waveguide (55 mm, 45 mm and 35 mm). The different lengths were achieved by dicing followed by lapping and polishing. Figure 6.11 presents the plot of the output power with respect to the length of the waveguide formed under the 5 µm etched trench. Similar graphs were also plotted on the other waveguides with different widths. The attenuation coefficients were then derived from the linear fits of the data points in the TE and TM polarization for different waveguide widths and is presented in Table 6.1.

It is apparent from the excellent linear fit to the data observed in Figure 6.11 that the error in this measurement is quite low and that the waveguide itself has very uniform losses. It can be seen from Table 6.1 that the waveguide formed under the etched trench of width 7 µm exhibited the lowest loss in the set of waveguides measured, having an attenuation coefficient of 1 dB/cm in the TE polarization and 1.6 dB/cm in the TM polarization.

### 6.2.3 Summary of the stressed waveguide

It was observed that an optical waveguide was formed under the etched trench. The waveguide supported single mode transmission for a 632.8 nm source and exhibited modest attenuation coefficients of 1 dB/cm and 1.6 dB/cm in TE and TM polarizations. This loss is surprisingly good considering the stress nature of the waveguide. It should also be noted that no attempt has been made to optimize this loss and so it may be possible to develop this technique such that it
can produce waveguides which are competitive with Ti in-diffused waveguides. An investigation into the nature of these losses should be conducted in order to guide the development of low loss waveguiding using this technique.

The absence of any impurities can make it is possible for the stress induced waveguides to find applications in high power transmission and nonlinear optical processing (such as PPLN) with a reduced effect due to photorefractive damage.

6.3 Summary and Conclusion

The optical characterization study conducted in Section 4.4 revealed no changes in the refractive indices in the ordinary and extraordinary polarizations on the etched surface. It was suggested that the absence of any chemical or physical induced behavior causes the etched surface to retain its optical properties. However, the increased refractive index under the narrow etched trenches results in optical waveguiding. This can be attributed to the residual stress induced due to the geometry of the etched trenches.

The optical modal profile of the stress induced waveguides resulted in single mode profile for 632.8 nm wavelength. A low loss waveguide was demonstrated suggesting that this technique could be used in realizing efficient optical waveguides. A detailed characterization study is suggested as a requirement to further understand the optical waveguiding behavior.
Chapter 7

Conclusions and Directions for future work

The objective of the thesis was to explore for a suitable technique to enable smooth quality surface machining of LiNbO$_3$ for realizing integrated optical systems on LiNbO$_3$ with the possibility of strong waveguides and compact grating reflectors as components. This objective was satisfied by the demonstration of a technique using the standard Ti diffusion process to realize surface relief features. The serendipitous discovery of this technique required a thorough characterization study to achieve control, investigation of the material and optical properties and its application on different crystal orientations of LiNbO$_3$. Finally, the application of this technique was demonstrated for optical device fabrication. A summary of each of these achievements is given below.

7.1 Outcomes of this work

Chapter 2 presented the first demonstration of a newly discovered technique to etch LiNbO$_3$ using Ti diffusion. A detailed experimental procedure was presented. Surface morphology characterization was conducted using an AFM to reveal extremely smooth etched profiles.

Chapter 3 presented results which provide evidence that the etch depth was controllable with the same parameters that affect Ti diffusion such as annealing duration, Ti thickness and Ti strip widths. A maximum etch depth of 1.1 $\mu m$ was achieved in this study. The etch surface quality in each experiment was observed to reveal extremely smooth etched surfaces with an RMS roughness of less than 1.2$nm$. 


97
A plausible etching model was derived from the observation of etching characteristics. The model suggested that the etching process was caused by reactive H$^+$ ions during the Ti diffusion process. These H$^+$ ions were generated due to the ionization of the water molecules in the diffusion atmosphere by the Nb ions that reach the surface of the Ti film from the interface of Ti:LiNbO$_3$.

Chapter 4 presented the material analysis results and optical characterization of the etched surface. The material analysis investigations included the determination of the crystallinity and material composition on the etched surface. It was observed through XRD analysis that the etched LiNbO$_3$ retained its crystallinity, exhibiting no significant difference when compared with that of an un-processed LiNbO$_3$ wafer. EDS and XPS analysis on the etched surface of LiNbO$_3$ revealed no significant variations in the material composition when compared with the bare LiNbO$_3$ wafer. From the optical characterization study, it was observed that the etched LiNbO$_3$ exhibited no variations in the optical indices in either the ordinary or extra-ordinary polarizations and thus retained its optical birefringence, suggesting that it also retained its desirable ferroelectric properties.

Chapter 5 presented the etch characteristics on different crystal orientations of LiNbO$_3$. Different combinations of the top and bottom wafers were used in the investigation. It was observed that etching was evident in all combinations with a wide variety of etch depths observed for each of the different combinations. It was proposed that the rate of etching was proportional to the concentration of H$^+$ ions present, which was dependent on the orientation combination of the top and bottom wafers. A normalization method was adopted to relatively quantify the etch depths for the different combinations. The normalized observations supported the proposed model for the etching mechanism.

Chapter 6 presented observations of optical waveguiding under the etched trenches. The formation of impurity-free optical waveguides was attributed to residual stress. Optical characterization was performed on the formed waveguides for different widths of the etched trenches. It was found that the formed waveguides supported single mode operation at 632.8nm in both ordinary and extra-ordinary polarizations. The cut-back technique was used to measure the optical loss for the different waveguides. An attenuation of 1 dB/cm in the TE polarization and 1.6 dB/cm in the TM polarization was measured under an etched trench of width 7µm. The attenuation values are similar to the ones first reported on Ti diffused waveguides. These values
are close to what might be acceptable for integrated optic applications. There is likely to be a significant opportunity for improvement of these losses through engineering of the uniformity of the waveguides.

7.2 Suggestion for future work

The thesis aimed to develop a technique to surface machine LiNbO$_3$ that could be used to improve the prospects of LiNbO$_3$ as a platform for compact, complex photonic information processing system. The proposed future work can be categorized into three areas - material characterization to refine the physical/chemical etching models that have been proposed, optical characterization to investigate the optical properties of etched trenches with narrow widths, and engineering of compact integrated optical waveguides and devices using the etching technique. These are discussed as follows.

7.2.1 Refinement of the etching model

A simple model has been proposed in Chapter 3 to explain the etching process. This model suggested that the etching process was a result of reactive H$^+$ ions generated during Ti diffusion into LiNbO$_3$. A more detailed material investigation is required for the refinement of the model.

Firstly, the crystal structure analysis is required within nanometers of the surface of the etched LiNbO$_3$. This can be observed using Transmission Electron Microscopy (TEM). Any defects on the near-surface can also be observed using TEM. However, with LiNbO$_3$ sensitive to the electron beam, necessary error compensations may be a requisite.

The Grazing Incidence Angle X-Ray Diffraction (GI-XRD) using high energy synchrotron radiation may be a suitable method to acquire the near-surface strain, lattice relaxations, phase transitions and diffraction characteristics of etched LiNbO$_3$. This analysis will complement the results of the TEM analysis.

The material analysis performed in Chapter 4 does not account for the role of the Li ions as they were too light to detect in any material analysis undertaken. However, it can be expected that the Li ions play a significant role in the etching process. Material analysis with analytical instruments that can detect Li ions is required. Secondary Ion Mass Spectroscopy (SIMS) is an
analysis tool that can detect the Li ions together with the other ions (Nb, Ti, O) involved in the etching process.

An important factor which has not been considered in this thesis is the role of domain inversion, especially on Z-cut crystals. Ferroelectric domain mapping may be a requirement to explore the possibility of domain inversion occurring during the etching process.

An analytical expression will be obtained from the characterization of the etch depths presented in Chapter 3. This would enable the optimization of fabrication recipes for etching LiNbO$_3$ using Ti diffusion technique.

### 7.2.2 Optical characterization

Optical index characterization on large etched areas of LiNbO$_3$ presented in Chapter 4 showed no difference in the refractive indices, either in ordinary or extraordinary polarizations. However, a localized increase in refractive index was observed under etched trenches of narrow widths (Chapter 6). With no impurities found through material analysis (Chapter 4) and the observation of light guiding in both ordinary and extraordinary polarizations, the waveguiding phenomenon was attributed to stress.

A quantitative analysis is required to map the residual stress on the cross-section under an etched trench. This can be achieved through Micro-Raman analysis or the X-ray Microdiffraction (XRMD) using high energy synchrotron radiation. The stress analysis data can be used in developing Finite Element Analysis (FEA) models of residual stress waveguides.

A quantitative analysis is required to determine the refractive index change to support waveguiding. A cross-sectional mapping of the change in refractive index is necessary for modelling of optical devices using this etching technique. Scanning near-field optical microscopy (SNOM) in reflection mode can be employed for the high-resolution mapping of refractive index distributions on the cross-section of an etched trench.

### 7.2.3 Engineer compact integrated optical waveguides and devices

The research reported in this thesis was aimed at developing a suitable etching technique to enable fabrication of tight waveguides and compact reflectors on LiNbO$_3$. A suitable technique
has been demonstrated in this thesis to achieve smooth quality surface relief features. Additionally, the presence of a higher refractive index region under the etched trenches was discovered. By quantifying the change in refractive index, it may be possible to model surface relief features for various applications.

The engineering of optical waveguides using the etching technique can enable the characterization of these waveguides for bending loss, temperature dependent birefringence, photorefractive effect and electro-optic effect, to name a few.

7.3 Conclusion

In conclusion, an additional technique has been discovered to surface machine LiNbO$_3$. This technique provides optical grade quality smoothness. It has been proposed as a part of future work that a refinement in the etching model is required for more efficient applications. Impurity free optical devices have been demonstrated and this has been attributed to the effect of stress under etched trenches of narrow widths. A quantitative analysis of the refractive index change has been proposed as a part of future investigations to enable efficient modelling of optical devices using this etching technique. With a refined model and better understanding of optical characteristics, it may be possible to explore the use of this etching technique in various applications.
Bibliography


