TRIMMING OF SURFACE ACOUSTIC WAVE DEVICES;
OXYGEN BOMBARDMENT OF ALUMINIUM FILMS AND QUARTZ SUBSTRATES

BY

S.CHERECKDJIAN

A thesis submitted for the Degree of
Doctor of Philosophy
at the University of Surrey

Oct. 1984
Abstract.

The aim of this project is to investigate the many effects an oxygen ion beam has on a S.A.W resonator, realized by aluminium thin film deposition onto a ST-cut quartz substrate.

This then establishes a greater understanding of the processes involved in trimming a S.A.W device using an ion beam.

The effect of molecular oxygen implanted into aluminium films evaporated onto ST-quartz substrates at various energies and doses, have been investigated and the results summarised.

Amorphisation of the crystalline quartz for O$_2^+$ doses $<10^{16}$ atoms cm$^{-2}$ has been observed, with the vertical swelling, 'e', described by the linear expression,

$$e = 0.114 (R_p + 2\Delta R_p)$$

At higher doses, $>10^{16}$ oxygen atoms cm$^{-2}$, the sputtering yield of fused quartz was measured to be 0.05-0.13 molecules ion$^{-1}$ in the molecular oxygen ion energy range of 50-150keV.

At high oxygen doses, oxide formation was achieved in the evaporated aluminium films. The oxide formed was observed to consist of metal/metal oxide islands with the oxide bond state being Al$^{3+}$. Unlike amorphous anodic oxide films, the oxide formed was polycrystalline in nature.

Oxygen implant profiles in the aluminium film appear to agree with theory at low doses. The oxygen content of the layer is directly proportional to dose until the peak value of the oxygen/aluminium ratio reaches 1.5. At higher doses this maximum ratio was unaffected but the profile was observed to broaden. The peak oxygen/aluminium ratio for implanted samples compared well with anodized aluminium bulk specimens.
having oxide layers up to 250nm. A good correlation was also obtained between vertical surface expansion of the aluminium film and theoretical oxide growth.

Stress effects associated with this oxide formation was investigated using a 'triple bulk quartz resonator technique'.

Preliminary experiments with this 'triple resonator technique' gave simultaneous sputter and stress results for 50keV and 100keV Ar$^+$ ions implanted into gold and germanium films. A stress associated with the growing aluminium oxide with incident O$_2^+$ ions implanted into aluminium films at oxygen ion energies of 50, 100, and 150keV was observed. The stress was found to be compressive being dependent upon the number of oxygen ions implanted and the total depth of the oxygen implant.

Blistering of aluminium on quartz films was observed when the peak implant profile was close to the aluminium-quartz interface for oxygen doses $>10^{17}$ atoms cm$^{-2}$. This blistering was due to accumulation of oxygen at the aluminium-quartz interface.

With these results it is then possible to explain the change in the resonant frequency of a S.A.W resonator after implanting with 50keV O$_2^+$ ions.

Additional work (presented in Appendix 1) deals with the investigation of the mass loading and lateral stress caused by argon implantation of aluminium, and the angular variation of the sputtering yield (S$\delta$) of gold and germanium, with the same ion species. Both results were obtained using the 'triple resonator technique'.
This thesis is dedicated to my parents,

Bedros and Astrig Chorekdjian,

and my brothers and sisters.
Acknowledgements.

I would like to thank Dr.I.H.Wilson for his patience, and advice throughout the course of this work, and Mr.J.Mynard and the staff of the accelerator laboratory for providing the ions.

I am also indebted to Dr.J.Watt for the X.P.S data and the U.K. Science Research Council for financial support.
INTRODUCTION................................................................................................... 1

CHAPTER 1. The Triple Resonator Technique.............................................. 6
  1.1 Theory of the multi-resonator technique................................. 7
  1.2 Effect of Temperature............................................................... 7
  1.3 Static stress in the plate arising from external forces........... 8
  1.4 Areal density of material on the resonator plate surface..... 9
  1.5 Combination of the three effects.......................................... 9
  1.6 Experimental details.............................................................. 14

CHAPTER 2. Rutherford Backscattering Spectrometry............................ 18
  2.1 R.B.S The technique............................................................. 18
  2.2 Mass analysis........................................................................ 18
  2.3 Depth analysis....................................................................... 19
  2.4 Concentration analysis.......................................................... 19
  2.5 Theoretical R.B.S spectra...................................................... 21
  2.6 Experimental details............................................................. 21
  2.7 R.B.S sample preparation..................................................... 25

CHAPTER 3. Blistering................................................................................. 27
  3.1 Model for mechanism of blister formation........................... 28
CHAPTER 4. Anodizing of bulk aluminium.........................33
  4.1 The technique......................................................33
  4.2 The Process..........................................................33
  4.3 Preparation of samples...........................................33
  4.4 Dissolving the Anodic film......................................34
  4.5 Experimental details.............................................34

CHAPTER 5. The Talystep, T.E.M and S.A.W measurements............37
  5.1 The Talystep technique............................................37
  5.2 Experimental considerations for the Talystep...............37
  5.3 Talystep-sample preparation....................................38
  5.4 Preparation of T.E.M samples...................................38
  5.5 S.A.W measurements.............................................41

CHAPTER 6. Results......................................................43
  6.1 Implantation........................................................44
    6.1.1 Oxygen profiles.............................................44
    6.1.2 Oxygen concentration in the aluminium layer.........47
    6.1.3 Calculated Oxygen concentration and range data.....50
    6.1.4 Comparison of anodized and implanted films..........58
    6.1.5 Talystep measurements....................................62
  6.2 Chemical and Structural analysis...............................65
    6.2.1 T.E.M Investigation of crystal structure.............65
    6.2.2 X.P.S Investigation.........................................67
  6.3 Sputtering and Stress............................................69
    6.3.1 Gold results................................................70
    6.3.2 Germanium results.........................................78
  6.4 Trapped ions and Stress.........................................90
6.5 Surface Effects ................................................................. 97
6.6 S.A.W measurements .......................................................... 105

CHAPTER 7. Discussions and Conclusions ............................... 109
7.1 Physical and Chemical Effects ........................................... 109
7.2 Nature of implanted oxygen atoms .................................. 112
7.3 Sputtering and Stress ...................................................... 114
  7.3.1 Gold results ............................................................... 114
  7.3.2 Germanium results ................................................... 117
7.4 Stress and mass loading .................................................. 119
7.5 Interface Blistering .......................................................... 121
7.6 S.A.W Performance ....................................................... 122
7.7 Conclusions ................................................................. 125

APPENDIX 1.
APPENDIX 2.

REFERENCES.
LIST OF FIGURES

1 Application range of bulk and S.A.W resonators..........................5
1.1 Typical frequency-temperature curves for the AT-cut crystal...10
1.2 Calculated values of the constant K for the popular YXL, $\phi$ family of quartz crystallographic cuts...............................11
1.3 Sample holder set-up for quartz crystal resonators.................16
1.4 Typical quartz crystal oscillator circuit.............................16
1.5 Experimental set-up for taking quartz crystal frequency data. Measurements are taken in situ...............................17
1.6 Simple comparator circuit for easier measurement of a reference temperature.........................................................17
2.1 Theoretical R.B.S spectra of 10nm Al$_2$O$_3$, 100nm Al, 50nm Al$_2$O$_3$, 100nm Al, and 10nm Al$_2$O$_3$ sandwiched together on a carbon substrate........................................22
2.2 Theoretical R.B.S spectra of 100nm of Al$_2$O$_3$ on a aluminium substrate.............................................................23
3.1 Sketch of a bubble of radius $b$ at a distance $R_b$ below the material surface. Maximum stresses are exerted on points A and B.................................................................31
3.2 Bubble fracture propagating along the z axis from point A towards the cavity surface.......................................................32
3.3 Bubble fracture propagating along the solid through the side walls.................................................................32
4.1 The experimental set-up used for the anodization of aluminium samples.................................................................36
5.1 Talystep samples for the investigation of the swelling of the crystalline quartz.........................................................40
5.2 Talystep samples for the investigation of the absolute sputtering yield of quartz.........................................................40
5.3 Cleaning procedure for all quartz slices................................40
5.4 Basic S.A.W layout on the ST quartz substrate............................42
5.5 S.A.W device-holder and 50$\Omega$ circuit board..........................42
5.6 Basic system required for the measurement of a S.A.W device ................................................. 42

6.1.1 R.B.S oxygen profile from 50keV O$_2^+$ implanted aluminium .......................................... 45

6.1.2 R.B.S oxygen profile from 100keV O$_2^+$ implanted aluminium .......................................... 45

6.1.3 R.B.S oxygen profiles from 50keV O$_2^+$ implanted aluminium (with no backgrounds) .... 46

6.1.4 R.B.S oxygen profiles from 100keV O$_2^+$ implanted aluminium (with no backgrounds) .... 46

6.1.5 R.B.S aluminium profiles from 50keV Cl$^+$ implanted aluminium ..................................... 48

6.1.6 R.B.S aluminium profiles from 100keV O$_2^+$ implanted aluminium ..................................... 48

6.1.7 Oxygen/aluminium ratio from backscattered spectrum versus implanted oxygen dose .... 49

6.1.8 R.B.S spectra of a 240nm aluminium layer implanted with 100keV O$_2^+$ ions to a dose of 5×10$^{16}$ atoms cm$^{-2}$ on a carbon substrate ...................................................... 51

6.1.9 Oxygen concentration from backscattered spectrum versus implanted oxygen dose .... 54

6.1.10 R.B.S profiles of anodized bulk aluminium samples with various oxide thicknesses .......... 59

6.1.11 Height 'e', of the swelling of the quartz implanted region shown as a function of the incident ion mass and energy .......................................................... 63

6.1.12 Height 'e', of the quartz implanted surface versus incident ion dose .................................. 63

6.1.13 Absolute sputter yield of quartz for various molecular oxygen implant energies ............... 64

6.1.14 Expansion of the aluminium layer versus incident oxygen dose for 50, 100 and 150keV molecular oxygen ions ................................................................. 64

6.2.2 X.P.S results from a aluminium film before and after oxygen implantation .................. 68

6.3.1 Argon bombardment of gold; Frequency shift versus argon dose ...................................... 72

6.3.2 Argon bombardment of gold; Areal mass change versus argon dose ............................... 73
6.3.3 Argon bombardment of gold; Sputter yield versus argon dose.................................74
6.3.4 Argon bombardment of gold; Accumulated lateral stress versus argon dose................75
6.3.5 Argon bombardment of germanium; Frequency shift versus argon dose.........................80
6.3.6 Argon bombardment of germanium; Areal mass change versus argon dose....................81
6.3.7 Argon bombardment of germanium; Sputter yield versus argon dose............................82
6.3.8 Argon bombardment of germanium; Accumulated lateral stress versus argon dose.............83
6.3.9 Argon bombardment of germanium; Electron microprobe analysis before and after implantation...86
6.3.10 Argon bombardment of germanium; Electron microprobe analysis of argon retention versus ion dose..........................................................87
6.3.11 Argon bombardment of germanium; X.P.S spectrum of germanium (3d), after an argon dose of $3 \times 10^{17}$ atoms cm$^{-2}$..................................................88
6.4.1 Oxygen bombardment of aluminium; Frequency shift versus oxygen dose....................92
6.4.2 Oxygen bombardment of aluminium; Frequency shift versus oxygen dose....................93
6.4.3 Oxygen bombardment of aluminium; Areal mass change versus oxygen dose..................94
6.4.4 Oxygen bombardment of aluminium; Accumulated lateral stress versus oxygen dose...........95
6.6.1 Oxygen bombardment of a S.A.W device; Frequency shift versus oxygen dose................108
LIST OF TABLES

6.1.1 Data extracted from figure 6.1.8 with backscattering parameters based on the Surface Energy Approximation........52

6.1.2 Experimental and theoretical range data...............................57

6.1.3 Approximations used in the analyses of figure 6.1.8.................57

6.1.4 Comparison between a R.B.S sample implanted at 100keV with a oxygen dose of $2.325 \times 10^{18}$ atoms cm$^{-2}$ and three anodized aluminium specimens...........................................60

6.1.5 Comparison of anodized samples with an implanted sample........61

6.2.1 Diffraction data from implanted aluminium films....................66

6.2.2 Diffraction data from a lifted anodized aluminium film............66

6.3.1 Measurement of sputtering yield and integrated lateral stress for 50keV argon bombardment of gold using the triple resonator technique.................................71

6.3.2 Measurement of sputtering yield and integrated lateral stress for 100keV argon bombardment of germanium using the triple resonator technique.................................79

6.5.1 Material composition investigation of edge blistering............101

6.5.2 Blister distribution with aluminium thickness.........................102

6.6.1 Results obtained from a S.A.W resonator implanted with 50keV molecular oxygen ions.................................106
LIST OF PLATES

6.3.1 Gold layer; as deposited.................................................76
6.3.2 Gold layer; after argon bombardment..............................76
6.3.3 Crystal defining aperture; showing a backspattered gold deposit.......................................................77
6.3.4 Diffraction pattern for a implanted Ge film
(unimplanted films are identical).............................................85
6.3.5 T.E.M micrograph of an unimplanted Ge film....................85
6.3.6 T.E.M micrograph of a argon implanted Ge film................85
6.3.7 Germanium layer; as deposited.........................................89
6.3.8 Germanium layer; after argon bombardment......................89
6.4.1 Aluminium layer; as deposited.........................................96
6.4.2 Aluminium layer; after oxygen bombardment....................96
6.5.1 Aluminium step on fused quartz.......................................99
6.5.2 Continuation of the above step......................................99
6.5.3 A aluminium-quartz edge, before and after stripping........100
6.5.4 Aluminium layer(141nm) after implanting with 150keV,\textsuperscript{+}ions.............................103
6.5.5 Aluminium layer(61nm) after implanting with 150keV,\textsuperscript{+}ions.............................103
6.5.6 S.E.M micrograph showing a ruptured blister made up of
a coalescence of smaller bubbles..........................................104
6.6.1 Typical frequency response from an unimplanted S.A.W resonator.........................................................107
SURFACE ACOUSTIC WAVE RESONATOR FILTERS

High Frequency Filters — 50 MHz–800 MHz
Low Loss — A few dB, depends on bandwidth (see Fig. 3).
Good stop-band performance — Typically −50 dB for a two-coupled resonator filter. May be improved by cascading further devices.
Narrow-bandwidth filters — 0.01%–0.10%
Temperature coefficient — Parabolic $|\alpha| = 31.25 \times 10^{-9} (T - T_o)^2$ where $T_o$ is determined by the cut of the crystal.

Until very recently V.H.F. and U.H.F. filters have had very broad bandwidths. However, recent advances in surface acoustic wave (SAW) technology have made it possible, for the first time, to produce compact, low-loss, narrow band V.H.F. and U.H.F. filters. These are made using SAW resonators coupled together to form different types of filters.

Plate 1: Three resonators lines are shown above, although only two are coupled together to form a narrow band filter. The dotted lines indicate the size of a filter at 160MHz.
Introduction.

Surface Acoustic Wave (S.A.W)[1] devices (see plate 1) are playing an increasingly important role in the fields of radar and telecommunications.

Electrical signals can be converted into acoustic waves that propagate along the surface of a solid substrate and these waves may be trapped and controlled along the path of propagation. Such properties are useful for the realisation of delay lines, resonators, filters etc.

The table below summarises the principal advantages and disadvantages of S.A.W devices.

<table>
<thead>
<tr>
<th>Advantages.</th>
<th>Disadvantages.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)High fundamental operating frequency and wide range(30-3000MHz).</td>
<td>(1)Excitation of bulk waves and conversion of surface waves into bulk waves limits Q to 2,000-20,000.</td>
</tr>
<tr>
<td>(2)Potentially inexpensive.</td>
<td>(2)Expensive E-beam lithography necessary at f&gt;1000MHzs.</td>
</tr>
<tr>
<td>(3)Small size, robust and post-tuning.</td>
<td>(3)Weak third harmonic response.</td>
</tr>
<tr>
<td>(4)Compatible with I.C.technology.</td>
<td></td>
</tr>
</tbody>
</table>

The S.A.W resonator[2] is a high Q device and is susceptible to manufacturing variations, though the ability to operate at frequencies far higher than is practicable with bulk wave resonators outweighs this disadvantage.

Unlike S.A.W resonators, volume wave devices achieve efficient reflection between the surfaces of quartz plates $\lambda/2$ thick, where $\lambda$ is the acoustic wavelength. A practical upper limit for fundamental
operation of a bulk wave device is 50 MHz, where a plate thickness of 0.5 mm makes the device fragile and difficult to mount.

Surface wave resonators are not burdened with this disadvantage where an upper fundamental frequency, set by photolithography limitations, of 2 GHz is possible. Figure 1 shows the typical operational range for volume and surface wave resonators.

As mentioned earlier, one of the advantages of a S.A.W device is its potential cheapness. An important criterion governing the manufacturing cost of any device is the percentage that meet the required specification at the end of the production process. Ideally the fabrication process would be precise enough to ensure an acceptably high pass rate, unfortunately this may not always be easily achieved.

The majority of S.A.W devices are constructed on a piezoelectric substrate (crystalline ST-quartz in our case) using thin film deposition to realise the transducers and distributed reflector banks. Substrate inhomogeneities and uncertainties in the thin film structures may result in a low yield of devices within specification. Selective deposition or etching is a widely used technique capable of trimming the performance of a device but suffers from uncertainties inherent during the initial device fabrication.

High energy incident ions may be used to advantage in the trimming of S.A.W device performance [3]. Ion implantation could offer a viable alternative technique.

The ion interactions can cause,

(1) Swelling of the quartz [4] or aluminium [5]

(2) Sputtering of the quartz [6] or aluminium [6]

(3) Stress effects [7,8]

(4) Compound formation [5,9,10]
and (5) Surface topography[11,12,13]

The contributions of each depend upon ion dose and energy.

Previous work in this field was done by S. James[14] and W. Ashby[15]. S. James investigated the parameter trimming of conventional S.A.W resonators by varying the energy of argon ion bombardment. While W. Ashby monitored the effects of sputter etching on the response of a S.A.W device by varying the argon ion dose. Both projects examined the feasibility of producing a method of trimming the responses of individual S.A.W devices.

Workers that have also contributed to this field include; P. Hartemann and M. Morizot (amorphisation of quartz substrates by ion implantation[16], and the variation of the surface acoustic wave velocity by ion implantation[17]), W. H. Haydl and P. S. Cross (parameter trimming by selective chemical etching[18], and fine tuning using metallisation thickness[19]), G. Volluet (tuning by magnetoelastic effect[20]), H. L. Garvin and R. D. Weglein (effect of ion beam sputtering on acoustic surface wave propagation[21]), and H. I. Smith et al (ion beam etching of reflective array filters[22]).

The aim of this project is to investigate the many effects a reactive ion beam has on a S.A.W device by analysing each ion effect mentioned previously. This then establishes a greater understanding of the processes involved in trimming a S.A.W device.

Molecular oxygen was implanted at energies between 50-200keV and doses from $3 \times 10^{14}$ to $2.3 \times 10^{18}$ oxygen atoms cm$^{-2}$ into thin (250nm) aluminium films evaporated onto ST quartz substrates.

Bombardment by oxygen ions gave essentially a clean system[10] in quartz, while being reactive in the aluminium film.
The implanted surfaces were examined by,

(1) Talystep measurements.

(2) Rutherford Backscattering Spectrometry. (R.B.S)

(3) Electron Probe Spectroscopy. (E.P.S)

(4) Secondary electron microscopy. (S.E.M)

(5) Transmission electron microscopy. (T.E.M)

(6) X-ray Photo-electron Spectroscopy. (X.P.S)

and (7) The Triple Resonator Technique. (T.R.T)

A triple quartz (bulk) resonator technique was developed in order to measure sputtering yields and lateral stress in ion bombarded thin films.
Figure 1: Application range of bulk and SAW resonators.
CHAPTER 1. The Triple Resonator Technique

Theory and experimental details.

Introduction.

Quartz resonators have been used for years as film-thickness monitors in the research, development and manufacture of thin films and thin-film devices[23]. These resonators act as microbalances and detect changes in the mass per unit area of thin films. Initial ion implantation workers[24-26] utilising this technique, measured sputtering yields for various deposited films. A single quartz crystal resonator was used in these cases.

A double resonator technique,[27] was introduced recently for simultaneous measurement of thin-film mass and stress measurements[28]. The technique utilises the fact that the thickness shear resonant frequency of a quartz resonator plate can be measurably shifted by strain effects through a static stress bias set up in the quartz plate by stress in a thin film on the plate surface. This stress-induced frequency shift is separated from the more commonly used mass loading frequency shift (used by standard vacuum deposition thin-film thickness monitors) by exposing two resonator plates of different crystallographic cuts to the same thin film effects. One then has two equations and two unknowns. The choice of crystallographic cut was the AT and BT for minimal thermal frequency shift effects.
1.1 Theory of the multi-resonator technique.

The basic idea, developed in this work, is to expose three resonators to the same environment, one being a dummy with a Cr-Al thermocouple and the other two resonators of different crystallographic cuts.

With the help of the resonator theory, one can separate out the desired information on more than one variable and be assured of unambiguous results. There are three major independent variables that affect the resonant frequency of the quartz resonator plate;

1.2 Effect of Temperature.

This has been treated the most extensively because of its importance in frequency control applications.

The most general expression for the effects of temperature, T, on the resonant frequency, \( f_0 \), of a quartz resonator is given by the series expansion,

\[
\frac{\Delta f}{f_0} = b_1 \Delta T + b_2 \Delta T^2 + b_3 \Delta T^3 + \ldots (1.1)
\]

Where \( \Delta f \) is the frequency shift in hertz, \( f_0 \) is the resonant frequency in hertz at temperature \( T_0 \), \( \Delta T \) is \( T-T_0 \) in °C, and \( b_n \) is the temperature coefficient for the \( \Delta T^n \) term in °C\(^{-n}\).

Figure 1.1 shows plots of the \( \Delta f/f_0 \) for the widely used AT-cut quartz resonator for slight rotations of the crystallographic cut about the ideal orientation[28]. One can see from figure 1.1 that the series expansion of equation 1.1 can vary considerably depending on which orientation or \( T_0 \) is actually used. An orientation for \( T_0 \) can be chosen to emphasize primarily the \( b_1 \) or \( b_3 \) terms of equation 1.1. By using the crystal blank at a turning point temperature (indicated by
the dashed line in figure 1.1), one can emphasize the $b_2$ term over small temperature excursions.

Another widely used crystallographic cut is the BT-cut which has a parabolic $\Delta f/f_0$ vs $T$ characteristic with the peak in the characteristic occurring at a zero temperature depending on the exact orientation of the cut.

### 1.3 Static stress in the plate arising from external forces.

The effects of static stress in the quartz plate set up by external mechanical forces arise from higher order elastic constant effects, i.e., from the fact that all solids including quartz do not obey exactly Hooke's Law of elasticity. Of primary interest here is the effect of the static bias set up in the quartz plate by internal stresses in the thin films on the surface of the plate.

The frequency shifts caused by such a stress bias have been treated elsewhere in detail[29].

The effect is described by

$$\frac{\Delta f}{f_0} = \frac{K \Delta S}{\tau_q} \quad ...(1.2)$$

where $f_0$ is the frequency at some reference stress (usually zero stress) in the thin film on the surface, $\Delta S$ is the integral through the film thickness of the net change in the film stress in dyne cm$^{-1}$, $\tau_q$ is the thickness of the quartz plate, and $K$ is a constant calculated from third-order elastic theory. The calculated value for $K$ for the $YXL$, $\phi$ family[28] is shown in figure 1.2 (this family contains the AT- and BT-cuts). Here, it is assumed that $\Delta S$ is positive for an increase in tension in the internal stress in the thin film. Note that the value
for $K$ seen in figure 1.2 does not change drastically for small changes in the crystallographic angle $\phi$. Thus, it is possible to make marked changes in the temperature coefficients such as seen in figure 1.1 and maintain $K$ relatively constant.

### 1.4 Areal density of material on the resonator plate surface

The third variable is the commonly used mass loading effect described by\cite{30},

\[
\frac{\Delta f}{f_o} = -\frac{\Delta M}{\rho_q \tau q}
\]

where $\Delta M$ is the change in the areal mass density in g/cm$^2$ on the surface of the resonator with $\Delta M$ positive meaning addition of mass, $\rho_q$ is the density of quartz (2.65g/cm$^3$), and $f_o$ is the frequency before $\Delta M$ has been applied to the surface of the resonator plate.

### 1.5 Combination of the three effects

In equations 1.2 and 1.3 it is assumed that the surface film causing the change in frequency is uniform across the actively vibrating region of the crystal. Also $\Delta M$, $\Delta S$, and $\Delta T$ must be small enough to ensure that the simple proportional relations used in equations 1.1-1.3 hold.

A good approximation for judging the applicability of equations 1.1-1.3\cite{30} is for $\Delta f/f_o$ to be $<10^{-2}$. Larger ratio's can be handled but are beyond the scope of this work.

The basis for the multiple resonator measurements depends on the assumption that all three effects described by equations 1.1-1.3 can be superimposed linearly.
Figure 1.1: Typical frequency-temperature curves for the AT-cut (member of the YXL, ϕ family of quartz crystallographic cuts).
Figure 1.2: Calculated values of the constant K for the popular YXL, $ family of quartz crystallographic cuts.
Although there has been some work relating temperature effects on equation 1.2 [31], there is no published evidence for there being strong second order effects which would invalidate the assumption. It is further assumed that there is a choice of crystallographic cuts for as many as three resonators that have the same pre-dominant $b_n$ in equation 1.1 for small temperature excursions about $T_o$.

Since there are three independent variables, $\Delta T^n, \Delta S,$ and $\Delta M$, we need three resonators to provide sufficient information to solve for all three variables.

The choice of three resonators with different crystallographic cuts then allows the general case to be expressed by the following system of three equations in three unknowns.

$$\frac{\Delta f_1}{f_{o1}} = b_{1n} \Delta T^n + K_1 \frac{\Delta S_1}{\tau_{1q}} - \frac{\Delta M_1}{\rho \tau_{1q}} \quad \ldots \quad (1.4)$$

$$\frac{\Delta f_2}{f_{o2}} = b_{2n} \Delta T^n + K_2 \frac{\Delta S_2}{\tau_{2q}} - \frac{\Delta M_2}{\rho \tau_{2q}} \quad \ldots \quad (1.5)$$

$$\frac{\Delta f_3}{f_{o3}} = b_{3n} \Delta T^n + K_3 \frac{\Delta S_3}{\tau_{3q}} - \frac{\Delta M_3}{\rho \tau_{3q}} \quad \ldots \quad (1.6)$$

We have used two resonators to measure stress and mass simultaneously, represented by equations 1.4 and 1.5. This is made possible by the use of a dummy crystal, in the same irradiation environment, with a Cr-Al thermocouple which allows us to determine the crystal temperature and therefore the $b_n \Delta T^n$ contribution.

There are then two unknowns and only two resonators necessary. The resonators chosen for the experimental work were the AT- and BT-cuts, because of their small temperature coefficients and their
availability.

The resulting equations are,
\[
\frac{\Delta f_1}{f_{1o}} = K_1 \frac{\Delta S_1}{\tau_{1q}} - \frac{\Delta M_1}{\rho_{\tau_{1q}}} \quad \ldots \ldots (1.7)
\]
and
\[
\frac{\Delta f_2}{f_{2o}} = K_2 \frac{\Delta S_2}{\tau_{2q}} - \frac{\Delta M_2}{\rho_{\tau_{2q}}} \quad \ldots \ldots (1.8)
\]

In the present case the ion bombardment acts over the same penetration depth in both identical films; thus
\[
\Delta M_1 = \Delta M_2 = \Delta M,
\]
\[
\Delta S_1 = \Delta S_2 = \Delta S,
\]
and equations 1.7 and 1.8 can be manipulated to obtain \(\Delta S\) and \(\Delta M\) in terms of the experimental observables \(\Delta f_1\) and \(\Delta f_2\).

The result is,
\[
\Delta M = \rho_q K_1 K_2 \left( \frac{K_1 - K_2}{f_{o1} f_{o2}} \right) \begin{bmatrix}
\frac{\Delta f_1 \tau_{1q}}{f_{o1}} - \frac{\Delta f_2 \tau_{2q}}{f_{o2}}
\end{bmatrix}
\]
and
\[
\Delta S = \frac{1}{(K_1 - K_2)} \begin{bmatrix}
\tau_{1q} \Delta f_1 \tau_{2q} \Delta f_2
\end{bmatrix}
\]

A computer program written in Basic aided rapid computation of the experimental results obtained.

The use of two resonators as suggested above in equations 1.7 and 1.8 to measure stress and mass was dubbed the 'double resonator technique', by EerNisse[27,28,32-34], we have dubbed our method the 'triple resonator technique', as we include a dummy in order to ensure that all the results are taken at the same temperature.
1.6 Experimental details.

Several pairs of 6MHz resonator crystals (AT and BT-cut) were coated with approximately 1µm of the material under interest.

An AT-cut resonator, a quartz resonator dummy with a flattened Cr-Al thermocouple placed on its surface and a BT-cut resonator, with their original holders, were mounted side by side onto a stainless steel plate (see figure 1.3).

A 1x3cm ion beam aperture followed by a crystal defining aperture allowed ions to bombard only the active area of the resonators and minimise the heat input to the crystals. The ion beam was focused and scanned both horizontally and vertically to ensure uniformity over the entire beam defining aperture. Secondary electron suppression was used for accurate ion counting. Vacuum during ion bombardment was better than 10⁻⁶ torr.

Resonator frequencies were measured with a simple oscillator circuit (figure 1.4) and a frequency counter for each of the two resonators. The circuit was designed so that all the ion current passing through the aperture was measured, including that impinging on the resonator plates. Temperature rise of the crystals was monitored with the thermocouple on the dummy resonator. Data were taken by recording the two resonator frequencies, bombarding to a pre-determined ion fluence, waiting till the temperature recovered before recording the new frequencies, and repeating the cycle (see figure 1.5).

The d.c. output of the Comark thermometer was fed into a simple comparator circuit (figure 1.6). This activated an l.e.d. at the appropriate d.c. level, to ensure that the readings were constantly taken at the same reference temperature.

All the crystals used, were specified and obtained from the two
companies listed below.

(1) Marconi, Specialised Component Division, Essex
and (2) The Quartz Crystal Company, New Malden, Surrey.
Figure 1.3: Sample holder set-up for quartz crystal resonators.

Figure 1.4: Typical quartz crystal oscillator circuit.
Figure 1.5: Experimental set-up for taking quartz crystal frequency data. Measurements are taken in situ.

Figure 1.6: Simple comparator circuit for easier measurement of a reference temperature.
CHAPTER 2. Rutherford Backscattering Spectrometry (R.B.S)

Theory and experimental details.

2.1 The technique.

The R.B.S analysis technique has been thoroughly explained by many authors[35,36].

This technique was used in the random mode to determine:

(1) The implanted oxygen profile.
(2) The implanted range and standard deviation of oxygen in evaporated aluminium films.
(3) The concentration of oxygen in the implanted layer.
(4) The thickness of implanted and anodized oxides formed.
(5) The stoichiometry of the oxides formed.

and (6) The presence of undesirable impurities.

All the information was obtained without causing significant damage to the sample.

2.2 Mass analysis.

Rutherford Backscattering is used in surface analysis to provide quantitative mass and depth information. The method involves bombarding a target, in vacuum, with a collimated, monoenergetic beam of light ions, usually of helium or hydrogen.

The present study employed 1.5 MeV helium ions. Most of the ions penetrate several microns into the target and come to rest but a few will collide with target atoms and will undergo elastic, wide-angle scattering by the coulomb repulsion of the atomic nuclei.

If such a scattering event is purely elastic with no introduction
of a nuclear reaction then the energy of the scattered ion can be found
from the conservation law. This energy is given by,

$$ E_{\text{m}} = K_{\text{m}} E_{\text{o}} = \left[ \frac{M_1 \cos \theta + (M_2^2 - M_1^2 \sin^2 \theta)^{1/2}}{M_1 + M_2} \right]^2 E_{\text{o}} \quad \text{...(2.1)} $$

where $K_{\text{m}} = \text{Kinematic factor}$
$M_1 = \text{mass of ion}$
$M_2 = \text{mass of target atom}$
$\theta_{\text{s}} = \text{scattering angle}$
and $E_{\text{o}} = \text{incident energy of ion}$

The above equation gives the energy of an ion scattering from a
surface atom as a function of the mass of the target atom.

2.3 Depth analysis.

If the ion penetrates the target surface it will lose energy to
the electrons of the target atoms by ionisation and excitation and
after scattering it will lose further energy along its outward path.
The ion will therefore leave the target surface with energy $K_{\text{m}} E_{\text{o}} - \Delta E$
where $\Delta E$ is the energy lost by the ion on its path into and out of the
target. To a first approximation the energy loss is proportional to
the depth 't', of the scattering event so that,

$$ \Delta E = [S].t $$

where $[S]$ depends on $K_{\text{m}}$ and the energy loss $dE/dx$ per unit path length
for the particular target material.

2.4 Concentration Analysis.

The backscattering yield from a depth 't', is proportional to the
area density of scattering centres at that depth. Therefore the number
of backscattered ions which can be related to scattering from a certain
type of atom at depth 't', will give a measure of the atomic
concentration at that depth.

The scattering process due to Coulomb interactions was treated classically by Rutherford[35] and can be expressed in terms of a differential scattering cross-section,

\[
\frac{d\sigma}{d\Omega} = \left[ \frac{z_1 z_2 e^2}{2E\sin^2 \theta} \right]^2 \left[ \cos \theta + \left\{ \frac{1-(M_1/M_2 \sin \theta)^2}{1-(M_1/M_2 \sin \theta)^2} \right\}^{1/2} \right]^2
\]

where \( z_1 \) = atomic number of ion
\( z_2 \) = atomic number of target atom
\( e \) = electronic charge
\( \theta \) = laboratory scattering angle
and \( E \) = energy of ion prior to scattering

\( \frac{d\sigma}{d\Omega} \) is usually abbreviated to \( \sigma \) or \( \sigma(E) \).

The important consequence of equation 2.1 is that the cross-section for elastic backscattering is proportional to the square of the atomic number of the target atom. Thus the method is very sensitive when used to detect a heavy impurity near the surface of a light substrate. The sensitivity for detection of gold atoms is around \( 10^{12} \) atoms cm\(^{-2} \).

For light atoms the backscattering yield is greatly reduced and where the substrate is of a heavier material the contribution from the light impurity will be superimposed on the spectrum from the substrate.

From scattering theory the number of ions detected due to single scattering from a heavy impurity at depth 't', is given by,

\[
C = \rho \frac{d\sigma}{d\Omega}(E) \ dt \ Q \ \Omega
\]

where \( \rho \) = density of impurity atoms
\( \frac{d\sigma}{d\Omega} \) = scattering cross-section
\( dt \) = thickness of layer under consideration
\( Q \) = total number of ions striking
and $\eta$ = solid angle of detector

The smearing out of the impurity peak and the front edge of the continuum (figures 2.1 and 2.2) is a result of detector resolution. In general silicon surface barrier detectors have energy resolutions in the range 12 to 20keV(F.W.H.M). This is equivalent to a depth resolution of the order of 20 to 30nm.

2.5 Theoretical R.B.S spectra.

Theoretical plots of the samples of interest are shown in figures 2.1 and 2.2 of Al$_2$O$_3$/Al thin film on a carbon substrate and a Al$_2$O$_3$ thin film on a aluminium substrate.

These plots were obtained from a University program based on the work of Ziegler et al[36][37].

So far all the above calculations have been performed, assuming that there has been no significant change in the aluminium concentration in the implanted layer. Further it was assumed that the projected range and the standard deviation of the projected range did not change, and also no sputtering took place.

These assumptions are valid for implant doses up to $10^{18}$ ions cm$^{-2}$, due to the extremely slow sputtering rate of the evaporated aluminium. This is attributed to the presence of the native oxide on the aluminium surface.

2.6 Experimental details.

A beam of helium particles at an energy of 1.5MeV, was used for the analysis; the stability of the beam was better than $\pm$1.5keV.
Figure 2.1: Theoretical R.B.S spectra of 10nm $\text{Al}_2\text{O}_3$, 100nm Al, 50nm $\text{Al}_2\text{O}_3$, 100nm Al and 10nm $\text{Al}_2\text{O}_3$ sandwiched together on a carbon substrate.
Figure 2.2: Theoretical R.B.S spectra of 100nm of Al<sub>2</sub>O<sub>3</sub> on a aluminium substrate.
The beam spot size is 1 mm in diameter and is of uniform density; the vacuum pressure was better than $10^{-6}$ torr in the beam line.

The specimen under investigation was mounted on an aluminium backing plate with silver dag, and was held in position by a phosphor bronze spring. The plate was fitted into a threaded PTFE sample holder. From the aluminium backing plate a lead was taken to an earth potential via a high sensitivity current integrator. The current integrator monitored the beam current and supplied pulses to an electronic counter for the total helium dose measurement.

Attached to the front face of the specimen holder, but insulated from it was an annulus of aluminium, to which a negative potential of 300 volts was applied, with respect to earth. This negative bias suppresses any secondary electrons emitted from the specimen but allows the incident and the backscattered particles through unhindered. During analysis the target chamber and the beam line were pumped down to pressures better than $10^{-6}$ torr, using oil diffusion pumps and liquid nitrogen traps, backed by rotary pumps.

The He$^+$ particles scattered, at a wide angle, from the surface and up to a depth of one micron, of the specimen were detected using a silicon surface barrier detector, with an energy resolution of 15 keV (F.W.H.M), set at an angle of 30° to the beam line entry axis. The particles entering the detector, which is reverse biased to 75 volts, produces pulses which are electronically processed by the electronics of the system.

In the present work the parameters, which have been used are listed below:

1. Incident energy of He$^+$ ions, 1.5 MeV ± 1.5 keV.
2. Helium beam current, 3 nA to 10 nA.
(3) Charge collected, 7 to 15 μC.
(4) 512 channels for 1.5MeV.
(5) Detector bias, -75 volts.
(6) Chamber vacuum, 10⁻⁶ torr.
(7) Random mode analysis.

To obtain an accurate calibration, energy per channel, a backscattering spectrum was obtained using a standard sample (<10nm of gold on a silicon substrate) at the commencement of each backscattering session.

All the R.B.S spectra presented were obtained by replotting the average yield of four adjacent channels normalised to 5μC of helium dose, to improve the statistics of the spectra.

2.7 R.B.S sample preparation.

Vitreous carbon blanks, 25mm square, (manufactured by 'Le Carbone', Lorraine, Paris) with a very rough, undulating surface were obtained from the X.P.S research group (University of Surrey).

Once the edges of these blanks were bevelled using a file, the surface was hand lapped on descending grades of emery cloths.

The bevel was necessary to avoid, ripping the lapping fabric and shattering the blanks. These rough blanks were then mounted with green wax (Castylene A71) onto the holders of a Metaserv Universal lapping polisher.

Lapping fabrics impregnated with diamond lapping paste of a grain size of 8μm and 1μm were used consecutively. The samples were lapped in a double circular revolution, with a applied sample force of 97gms at 300rpm. The blanks were lapped for 30 days at each of the two diamond pastes used, with a constant fabric lubrication of clear liquid
paraffin, until a mirror finish was obtained. The blanks were then moved and mounted on a piece of aluminium with green wax with its highly polished surface down. The back surface was first scored into sample sizes with a surgical scalpel and, then the score was deepened by using a junior hacksaw blade, with the wave on the blade ground out. This allowed a fine surface cut to be established. The samples were finally cut out using a ordinary hacksaw blade.

These samples were ultrasonically cleaned for 3 minutes in trichloroethylene and finally vapour cleaned first in, trichloroethylene and finally propan2ol until the surface was free of stains.

These polished carbon samples were then placed into an evaporator and 240mm±5nm of aluminium was deposited using an AT-cut crystal monitor.

Introduction.

Various topographical features have been observed on ion bombarded single phase materials, namely: cones[38-40], grain relief[41], pits[42,43], facets[44], bubbles and blisters[45]. These have been satisfactorily explained in terms of variations in sputtering yield with angle of incidence[46], redeposition of sputtered material[47], collision cascade density effects[48], voids produced by radiation damage[43], and accumulation of a gaseous implant[45].

The formation of gas-filled blisters in the surface region of irradiated solids has been observed by several authors[49-54].

An extensive range of experiments have been performed at different ion bombarding energies, target temperatures and sample structures over different materials[55-60].

Although a large body of experimental information has been obtained, the basic mechanisms underlying the blistering processes are still poorly understood.

A simple model[8] presented here, could explain blistering mechanisms for high energy (>20keV) ion implantation at room temperature.
3.1 Model for mechanism of blister formation.

Electron microscopy observations have shown that the initial bubbles are nearly spherical cavities of sizes between 1.5nm and 4nm [61-64]. The bubble is assumed to maintain the same geometrical shape whilst altering in size. Thereafter the present model assumes that there is coalescence of the initial bubbles leading to a growth of bubbles up to a radius 'b', at a distance 'R_p', from the surface as shown in figure 3.1. Here R_p is the mean depth of the concentration profile.

Since the inert gas in the bubble exerts a pressure normal to its surface, and due to the proximity of the material surface, an anisotropic stress distribution is produced in the host solid. This can result in fracture with the section above the bubble being ejected or partially ruptured.

It is known that, the exact solution for the equilibrium stress produced by the cavity inner pressure in the material surrounding the bubble, when it is near a surface, is mathematically intractable in a three-dimensional case. However Jeffery[65] has obtained the exact solutions for an isotropic semi-infinite medium in the two-dimensional case. Since the cavity can be sectioned by diametral planes perpendicular to the solid surface, any one of them leading to the two-dimensional problem, Jeffery's results are used here to approximately find points of maximum stress.

The pertinent results obtained by Jeffery[65] are briefly explained here. If 'P', is the pressure within the cavity, the tensile stress along the circular cavity is given by

$$\sigma_c = P (1+2\tan^2\theta) \quad \ldots (3.1)$$
A point on the boundary of the cavity is described either by the angle $\phi$ or $\theta$ (see figure 3.1) with 

$$\tan \phi = \frac{b \sin \theta}{\frac{R}{p} - \cos \theta}$$

The resulting function $\sigma(\theta)$ has extremes at $\theta = 0$ and at $\theta = \theta_m = \cos^{-1}(b/R_p)$, the first one being a minimum and the second a maximum.

Therefore the maximum stresses are at B, the points of the tangents drawn from A to the circular boundary. At these points the stress is

$$\sigma_{c \ max} = P \frac{R^2 + b^2}{R^2 - b^2} \quad \ldots (3.2)$$

The stress along the straight edge ($z = R_p$, figure 3.1) is a function of $x$ only and is given by

$$\sigma_{x z} = \frac{R_p}{P} = -4Pb^2 \frac{(x^2 - R_p^2 + b^2)}{(x^2 + R_p^2 - b^2)^2} \quad \ldots (3.3)$$

where the origin of coordinates is at point 0. Maximum tensile stress in this case occurs at point A ($x = 0$), where

$$\sigma_{x \ max} = 4P \frac{b^2}{(R_p^2 - b^2)} \quad \ldots (3.4)$$

If the maximum stresses at A and B are compared it is seen that they are equal when $R_p = \sqrt{3}b$ in which case $\sigma_{c \ max} = \sigma_{x \ max} = 2P$.

According to the considerations immediately following this, two different cases are expected to occur:

1. $R_p < \sqrt{3}b$, in this case the fracture is expected to propagate
along the z axis from point A towards the cavity surface, as sketched in figure 3.2.

(2) $R_p > \sqrt{3}b$, in this case a fracture would develop along the circle resulting from the intersection of the sphere $r=b$ and the cone $\theta=\theta_m$ (figure 3.1), with the fracture propagating through the solid along the walls of this cone as shown in figure 3.3.
Figure 3.1: Sketch of a bubble of radius $b$ at a distance $R_p$ below the material surface. Maximum stresses are exerted on points A and B.
Figure 3.2: Bubble fracture propagating along the z axis from point A towards the cavity surface.

$r_p < \sqrt{3}b$

Figure 3.3: Bubble fracture propagating along the solid through the side walls.

$r_p > \sqrt{3}b$
CHAPTER 4. Anodizing of bulk aluminium.

4.1 The technique.

An anodic oxide film can be produced only on metal which is functioning electrically as an anode.

During electrolysis atomic oxygen is liberated at the anode as a result of the passage of the electric current. The atomic oxygen reacts with the aluminium to form aluminium oxide, which is anchored to the metal surface and remains adherent, forming the anodic oxide film. The anodic oxide film grows in the most direct manner out of the metal itself, this is to say, the initial metallic surface is converted to the oxide film and progressive growth of the latter is derived from the metal itself.

4.2 The Process.

It is generally true to say that the most commonly used, the most universal in application, and the cheapest process is the direct-current Sulphuric acid process where the film thickness ranges up to 30µm. This process produces a colourless oxide film.

4.3 Preparation of samples.

Prior to anodization, 1cm square bulk polycrystalline aluminium samples (99.9% pure) were thoroughly cleaned so that the electrolyte could attack the metal uniformly. For this purpose it is essential to remove any dirt, oil or grease.

Degreasing was carried out in hot trichloroethylene and hot propan2ol vapour, then the samples were etched in a hot sodium hydroxide bath and finally rinsed in distilled water.
The samples, after the final rinsing were then ready for anodizing and were left in clean distilled water until they were transferred to the anodizing bath.

4.4 Dissolving the Anodic film.

This process obviously damages the oxide film, but the underlying metal surface is not affected.

A suitable acid mixture[66] consists of:

48g sodium dichromate, \(Na_2Cr_2O_7\cdot2H_2O\) and
200g 50% phosphoric acid, made up to 1 litre with distilled water.

This bath will dissolve an oxide film 30\(\mu\)m thick in 5 minutes. If the sample is left too long in the solvent solution no great harm is done, since the solvent bath has little action on the underlying metal.

4.5 Experimental details.

Anodizing process  - Sulphuric Acid d.c.process
Details of bath    - \(H_2SO_4\) (conc) and distilled \(H_2O\) made up to a 15% solution.
Working temperature - For hard, colourless films, 10-16\(^\circ\)C
                      for ordinary films , 18-20\(^\circ\)C
                      for thick, absorbant films, 20-22\(^\circ\)C
Electrical data    - The voltage, was kept to 20\(\pm\)1v.
                      the current, for 1\(cm^2\) was 10mA.

To ensure, correct formation of the anodic film the bath was
constantly changed and electromechanically stirred for each sample. The experimental set-up is shown in figure 4.1.
Figure 4.1: The experimental set-up used for the anodization of aluminium samples.

5.1 The Talystep technique.

The 'Talystep', provides a mechanical height measurement by means of a moving stylus transducer. The output of the moving coil transducer is amplified electrically and presented upon a carbon conductive paper strip recorder.

Using the Talystep a 2mm length could be scanned and the profile recorded on a strip chart.

5.2 Experimental considerations for the Talystep.

The sensitivity of this machine (resolution of 2nm) was so great that disturbances on the sample surface due to grit, dust and long undulations in the substrate cause problems when examining very thin films. The former disturbances could be minimised by careful preparation, storage and handling of the samples, but the latter occurred in the original manufacture of the substrate.

The practical maximum resolution of this instrument was found to be 4nm for quartz and aluminium substrates. At such a great sensitivity the position of the step under investigation had to be pre-determined very accurately. This was achieved by placing a coloured marker on the edge of the step with the aid of a light microscope.

The Talystep measurement was used for three significant measurements.

(1) Film thickness calibration

(2) Bombardment profile of the surface

and (3) sputtering measurements.
5.3 Talystep- Sample preparation.

To investigate the swelling of crystalline quartz at low fluences, a 25mm square ST-cut quartz plate was cut into 3mm square quartz samples using a diamond impregnated wire saw.

Half of the area of these samples were protected from the ion beam by a stainless steel shield (refer to figure 5.1).

To investigate the sputtering of quartz at high fluences, a 25mm diameter circular fused quartz (to eliminate radiation damage effects) slice 1mm thick was used. Figure 5.2 shows this second sample and figure 5.3 shows the cleaning process used on all the quartz substrates before a double evaporation to produce a aluminium mesh which served the purpose of conducting away charge from the surface and expose 0.5mm squares of quartz to the ion beam. This disc was then cut into identical sized samples as above.

Both quartz substrates were purchased from 'Gooch and Housego', Cornhill, Ilminster.

5.4 Preparation of T.E.M samples.

A large sodium chloride off-cut single crystal purchased from 'Rank Hilger', Margate, Kent, was cleaved until samples were obtained with a mirror surface finish (1mm cubic).

These were then fixed on double sided tape and evaporated with the metal of interest, to the thickness required using an AT-cut crystal monitor.

After implanting the samples, the metal films were floated off in distilled water onto 3mm copper grids.

Samples were also made by electro-polishing both sides of bulk
aluminium discs. The bath consisted of 5% Perchloric in Methanol at 
\(-45^{\circ}C\) with a potential of +12v and a current between 15-20mA. This was 
found to be a highly inefficient method of producing samples of the 
required standard.
Figure 5.1: Talystep samples for investigation of the swelling of crystalline quartz.

Figure 5.2: Talystep samples for the investigation of the absolute sputtering yield of quartz.

Figure 5.3: Cleaning procedure for all quartz slices. Each chemical is totally soluble in the previous, thereby eliminating any possible source of contamination.
5.5 S.A.W measurements.

The S.A.W layout is shown in figure 5.4. The S.A.W, with its unprotected ultrasonically bonded wires, was subjected to ion bombardment on the designed circuit board, shown in figure 5.5. All metallisation was connected to the current integrator via the 50Ω connectors. Only the area concerned with the S.A.W resonator was bombarded to minimise heat input.

The basic measurement system is shown in block diagrams in figure 5.6. This system enabled the resonant frequency, $f_0$ (150MHz±50Hz), the 3dB bandwidth and the insertion loss to be measured prior to and after ion bombardment. All tracks (made by photolithography), connectors, and interconnecting leads were made to 50Ω specification.

A 50Ω short circuit coupler was used via points A and B, shown in figure 5.6. This enabled the O dB level to be calibrated before each S.A.W measurement.
Figure 5.4: Basic S.A.W layout on the ST quartz substrate.

Figure 5.5: S.A.W device holder and 50Ω circuit board.

Figure 5.6: Basic system required for measurement of a S.A.W device.
CHAPTER 6. Results.

Introduction.

In this chapter the experimental results obtained using various diagnostic techniques are presented.

The results are presented in six parts with parts one, two, four, five and six relate to molecular oxygen bombardment of a S.A.W device. The remaining part, three, relates to the verification of the triple resonator measurement technique.

The first part is concerned with the fate of the implanted oxygen ions for various implantation doses within the energy range of 50 to 400keV, in the aluminium and quartz substrates while the second part deals with the chemical nature of any compounds formed. The third part deals with the verification of the 'triple resonator technique', described in chapter 1. Using the triple resonator technique, the mass loading and the static stress produced by the trapped oxygen ions in the implanted aluminium thin film is investigated in part four.

Surface edge effects and surface texture, produced during implantation, are reported in the fifth part.

The sixth part finally concludes the previous parts by examining the frequency response of a S.A.W resonator implanted with 50keV, $O_2^+$ ions.

The list below indicates the various diagnostic techniques utilized in each section.
(6.1) Implantation - R.B.S and Talystep
(6.2) Chemical and Structural - T.E.M and X.P.S
(6.3) Sputtering and stress - T.R.T
(6.4) Trapped ions and stress - T.R.T
(6.5) Surface Effects - S.E.M
and (6.6) S.A.W measurements - Network analyser.

6.1 Implantation-Distribution and Concentration
of the implanted oxygen.

6.1.1 Oxygen profiles.

Figures 6.1.1 and 6.1.2 show an unimplanted oxygen profile and
the profile obtained after implantation with an atom dose of \(2.5 \times 10^{16}\)
atoms cm\(^{-2}\) at molecular oxygen energies of 50 and 100keV respectively.

It is seen that each spectrum will require the subtraction of its
own background to obtain the true oxygen profile shown as the dotted
line. Angular R.B.S located the first small background peak at the
carbon-aluminium interface while the second was found to be at the
surface. This small surface peak is seen to correspond to the oxygen
signal at the surface and can be concluded to be the oxygen signal from
the native oxide of the aluminium film. The interface peak can be
attributed to oxygen gettering by aluminium during the initial stages
of evaporation or absorption of oxygen on the carbon substrate.

The implanted oxygen profiles obtained from the backscattering
spectra (with their individual backgrounds subtracted) are shown in
figures 6.1.3 and 6.1.4 for the molecular oxygen implant energies of 50
and 100keV respectively. Results for 150keV \(O_2^+\) ions were not obtained
as the oxygen and aluminium profiles were found to interact.
Figure 6.1.1: R.B.S oxygen profile from 50keV $O_2^+$ implanted aluminium.

Figure 6.1.2: R.B.S oxygen profile from 100keV $O_2^+$ implanted aluminium.
Figure 6.1.3: R.B.S oxygen profiles (with no backgrounds) from 50keV $O_2^+$ implanted aluminium.

Figure 6.1.4: R.B.S oxygen profiles (with no backgrounds) from 100keV $O_2^+$ implanted aluminium.
As the implanted dose is increased, the oxygen yield (profile height) increases as shown in figures 6.1.3 and 6.1.4. Saturation of the oxygen yield is reached at a dose of $9 \times 10^{17}$ atoms cm$^{-2}$, for the 100keV molecular implant.

The profiles broaden with increasing atom dose up to a critical dose and then start to narrow. Therefore for any further increase in the implanted atom dose beyond the critical value, the implanted layer becomes thinner. The critical dose was estimated to be $1.8 \times 10^{18}$ oxygen atoms cm$^{-2}$ for the 100keV oxygen molecular implant.

6.1.2 Oxygen concentration in the implanted aluminium layer.

The spectra obtained from room temperature, 50 and 100keV $O_2^+$ implants into the aluminium layer are presented in figures 6.1.5 and 6.1.6 for various doses. The spectra were aligned with the half-maximum point of the leading edge, which defines the aluminium surface. It was observed that as the implanted oxygen dose is increased, the aluminium yield in the implanted surface layer decreases. The reduction in the aluminium yield is indicative of the depth at which the oxygen peak occurs. The profile near the surface remains flat for implant doses greater than the saturation dose.

The oxygen to aluminium ratio was calculated using the area's method[67]. This is presented in figure 6.1.7. All the backscattered spectra were normalised to 5μC.
Figure 6.1.5: R.B.S aluminium profiles from 50keV $O_2^+$ implanted aluminium.

Figure 6.1.6: R.B.S aluminium profiles from 100keV $O_2^+$ implanted aluminium.
Figure 6.1.7: Oxygen / aluminium ratio from backscattered spectrum versus implanted oxygen dose.
6.1.3 Calculated oxygen concentration and range data.

Figure 6.1.8 shows a complete energy spectrum of 1.5MeV Helium ions backscattered from an R.B.S sample implanted with $O_2^+$ ions at a dose of $5 \times 10^{16}$ atoms cm$^{-2}$.

The data from figure 6.1.8 are given in table 6.1.1. From figure 6.1.8 a zeroth-order analysis allows us to calculate the dose, range, and the range distribution of oxygen in aluminium.

We assume the oxygen profile is sufficiently shallow that the surface energy approximation can be used in calculating the stopping cross section and the differential scattering cross section.

The implantation dose can be calculated from the equation below[35], with the implanted oxygen treated as a surface impurity.

The dose of oxygen is then,

$$
(N_t)_{ox} = \frac{A_{ox} \sigma_{ox}(E_o) \xi}{H_{Al} \sigma_{ox}(E_0) [\varepsilon_{Al}]} = 6.4 \times 10^{16} \text{atoms cm}^{-2} \ldots (6.1)
$$

in agreement with the nominal value of the implanted dose.

The maximum concentration of oxygen in aluminium can be estimated from the peak height of the oxygen signal. Using the formula obtained from Chu et al[35] derived for the bulk impurities and data given in table 6.1.1, we have

$$
\frac{N_{ox}}{N_{Al}} = \frac{H_{ox} \sigma_{Al}(E_o) [\varepsilon_{Al}]}{H_{Al} \sigma_{ox}(E_0) [\varepsilon_{ox}]} = 0.063 \text{at.}\% \quad \ldots (6.2)
$$

or $N_{ox} = 3.9 \times 10^{19}$ atoms cm$^{-3}$ using $N_{Al} = 6.02 \times 10^{22}$ atoms cm$^{-3}$.

From the area under the oxygen profile, the oxygen concentration was calculated.
Figure 6.1.8: R.B.S spectra of a 240nm aluminium layer implanted with 100keV $O^+$ ions to a dose of $5 \times 10^{16}$ atoms$\text{cm}^{-2}$ on a carbon substrate.
Table 6.1.1: Data extracted from figure 6.1.8 with backscattering parameters based on the Surface Energy Approximation.

<table>
<thead>
<tr>
<th>Data</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>(H_{Al}) = 1690 cts</td>
<td>(\epsilon_{Al} = 81.10 \times 10^{15} \text{eVcm}^2)</td>
</tr>
<tr>
<td>(H_{ox}) = 38 cts</td>
<td>(\epsilon_{ox} = 82.02 \times 10^{15} \text{eVcm}^2)</td>
</tr>
<tr>
<td>(A_0) = 1005 cts</td>
<td>(c_{ox}/\sigma_{ox} = 0.3516)</td>
</tr>
<tr>
<td>(\Delta E_{ox}) = 70 keV</td>
<td>(K_{ox} = 0.3848)</td>
</tr>
<tr>
<td>((\text{FWHM})_{ox}) = 22.5 keV</td>
<td>(K_{Al} = 0.5726)</td>
</tr>
</tbody>
</table>

Values are for \(E_0 = 1.5\text{MeV}\), normal incidence with \(\theta = 150^\circ\) and \(\chi = 3.09\text{keV}\).
Figure 6.1.9 shows the variation of the calculated oxygen concentration with the implanted oxygen dose. The amount of oxygen in the implanted layer increases with the implanted dose and reaches a saturation.

The uncertainty bars on these graphs were calculated from the standard deviation of the mean value of the data, collected for that dose.

To obtain a concentration profile, we use the stopping cross section factor $[\varepsilon_o]_{\text{Al}}$, which gives an energy to depth conversion for scattering from oxygen in an aluminium matrix.

The peak position of the oxygen is shifted by $\Delta E_{\text{ox}}=70\text{keV}$ below the surface edge, and

$$N_{\text{Al}} R_p = \Delta E_{\text{ox}} /[\varepsilon_o]_{\text{ox}} = 8.526 \times 10^{17} \text{ at cm}^{-2}. \quad (6.3)$$

therefore $R_p=141.5\text{nm}$

when $N_{\text{Al}}=6.02 \times 10^{22} \text{ atoms cm}^{-3}$.

Where $R_p$ is the projected range of the implanted oxygen.

The depth scale in nanometres is more convenient than that in atoms per square centimetre but the latter is useful for backscattering when there is uncertainty in the atomic density. If the implant distribution is assumed to be gaussian, the depth profile can be described by a projected range $R_p$ and a range straggling $\Delta R_p$, which is the standard deviation of the gaussian distribution in depth. The standard deviation, $\sigma$, is related to the F.W.H.M of a gaussian distribution by

$$\text{F.W.H.M} = 2(2 \ln 2)^{0.5} \times \sigma$$

$$= 2.355 \times \sigma$$
Figure 6.1.9: Oxygen concentration from backscattered spectrum versus implanted oxygen dose.
The F.W.H.M of the energy spectrum for oxygen is measured to be 54keV. This F.W.H.M contains not only the depth distribution of the oxygen, but also the energy resolution of the backscattering system and the energy straggling of the He\textsuperscript{II} ions.

The energy resolution of the backscattering system is quite independent of the detected energy and can be measured from the slope of the aluminium step in figure 6.1.8. If we differentiate the step near the aluminium surface, we obtain a negative gaussian (negative because the yield decreases when the energy increases). The F.W.H.M of this negative gaussian is the energy resolution of the backscattering system. This system resolution can alternatively be obtained by simply measuring the energy spread of the step from 12\% to 88\% of the step height. In figure 6.1.8, the energy spread of the aluminium step from 12\% to 88\% of the height is 25.4keV.

The energy straggling of He\textsuperscript{II} ions in aluminium has not been measured but can be estimated from Bohr's theory[35] to be about 3.0keV in the implanted region. The F.W.H.M of this energy straggling is then $2.355 \times 3.0 = 7.0$keV.

From the measured F.W.H.M of oxygen, it is necessary to deconvolute the measured F.W.H.M system resolution (25.4keV) and the energy straggling (7.0keV). Since all three distributions are assumed to be gaussian, the deconvolution process is simply a subtraction in quadrature:

$$F.W.H.M(\text{corrected}) = \sqrt{(54)^2 - (25.4)^2 - (7.0)^2} = 47.14\text{keV}.$$  

This value represents the real spread of oxygen in the energy
scale. It can be readily converted into a depth scale by using the equation below[35].

\[ \Delta R_p = \frac{\text{FWHM(corrected)}}{2.355N_{\text{Al}}} [\varepsilon_{\text{ox}}]^\text{Al} = 40.5\text{nm} \]

Table 6.1.2 compares experimental range data with theoretical L.S.S[68] and PRAL[69] range statistics.

Up to this point our analysis has been based on the surface energy approximation[35]. That is, we have evaluated the stopping cross section \([\varepsilon_{\text{ox}}]^\text{Al}\) at a surface energy \(E_0=1.5\text{MeV}\).

If we use the mean energy approximation[35] then,

\[ [\varepsilon_{\text{ox}}]^\text{Al} = K_{\text{ox}} \varepsilon(E_{\text{in}}) + \frac{1}{\cos\theta_2} \varepsilon(E_{\text{out}}) \ldots (6.4) \]

To obtain the average energies \(E_{\text{in}}\) and \(E_{\text{out}}\) we use the symmetric mean energy approximation:

\[ E_{\text{in}}=E_0-1/4\Delta E \quad \text{and} \quad E_{\text{out}}=E_1+1/4\Delta E \quad \text{where} \quad E_1=KE_0-\Delta E \]

By substituting these energies into equation 6.4 for \([\varepsilon_{\text{ox}}]^\text{Al}\), we have \([\varepsilon_{\text{ox}}]^\text{Al}=82.24 \times 10^{-15} \text{eVcm}^2\). The new stopping cross section factor is only 0.3% larger than \([\varepsilon_{\text{ox}}]^\text{Al}=82.02 \times 10^{-15} \text{eVcm}^2\) calculated from the surface energy approximation (see table 6.1.3). Therefore, the new range and range straggling will be 0.3% lower than the values obtained.

The results of the two analyses, one performed by the surface energy approximation and the other by the mean energy approximation, are summarised in table 6.1.3.

For a higher-order calculation there can be a correction for the total dose of implanted oxygen atoms. In equation 6.1, both \(\sigma_{\text{Al}}\) and \(\sigma_{\text{ox}}\) are evaluated at a surface energy \(E_0=1.5\text{ MeV}\).
Table 6.1.2: Experimental and theoretical range data.

<table>
<thead>
<tr>
<th>$O_2^+$ Energy (keV)</th>
<th>Experimental $R_p$ (nm) $\Delta R_p$ (nm)</th>
<th>L.S.S $R_p$ (nm) $\Delta R_p$ (nm)</th>
<th>PRAL $R_p$ (nm) $\Delta R_p$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>61.7 25.8</td>
<td>49.2 21.8</td>
<td>55.3 25.9</td>
</tr>
<tr>
<td>100</td>
<td>141.5 40.5</td>
<td>100.3 37.0</td>
<td>107.6 42.5</td>
</tr>
</tbody>
</table>

Table 6.1.3: Approximations used in the analyses of figure 6.1.8 for $\varepsilon$ values obtained from Chu et al [35].

<table>
<thead>
<tr>
<th>Method</th>
<th>Incoming Energy (keV)</th>
<th>Outgoing Energy (keV)</th>
<th>$[\varepsilon]_{ox}^{Al}$ $(10^{15} \text{eVcm}^2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface Energy Approximation.</td>
<td>$E_0 = 1500$</td>
<td>$K \cdot E_0 = 577$</td>
<td>82.02</td>
</tr>
<tr>
<td>Symmetrical Mean Energy Approximation.</td>
<td>$E_{in} = 1482$</td>
<td>$E_{out} = 525$</td>
<td>82.24</td>
</tr>
</tbody>
</table>
Since the oxygen signal area $A_{ox}$ is distributed over an energy interval, we should evaluate $\sigma_{ox}$ at the various energies. If a fixed value of $\sigma_{ox}$ is to be taken, $\sigma_{ox}$ should be evaluated at $E$ (the energy immediately before scattering) rather than at $E_0$, such that

$$E = E_0 - NR_0 (E_{in}) = 1458.7\text{keV}$$

The scattering cross section is related to energy by

$$\frac{\sigma_{ox}(E)}{\sigma_{ox}(E_0)} = \frac{E^2}{E_0^2} = 1.06 \quad \ldots \ldots \text{(6.5)}$$

Therefore, the total implanted dose is 6% lower when calculated with energy $E$ than when calculated with the surface energy $E_0$.

### 6.1.4 Comparison of anodized films to an implanted film.

Figure 6.1.10 shows the backscattered profiles obtained from three anodized films. A small amount of sulphur contamination of the films was detected.

The energy loss, $(\Delta E)$, was measured using the Rutherford backscattering technique and the thickness was evaluated by dissolving the anodic film (section 4.4)and using a 'Talystep'. R.B.S calculations (appendix 2) agree well with the Talystep thickness measurements. In Table 6.1.4, the results obtained from the spectra (figure 6.1.10) are shown with the calculated data.

Table 6.1.5 compares an R.B.S sample implanted with 100keV $O_2^+$ ions, to a dose of $2.325 \times 10^{18}\text{ atoms cm}^{-2}$, with the three anodized aluminium specimens.
Figure 6.1.10: R.B.S profiles of anodized bulk aluminium samples with various oxide thicknesses.
<table>
<thead>
<tr>
<th>Anodized film</th>
<th>$\Delta E_{\text{ox}}$ (keV)</th>
<th>$\Delta E_{\text{Al}}$ (keV)</th>
<th>DATA--Calculated $(\text{eVcm}^2 \times 10^{15})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>a. 700</td>
<td>55.8</td>
<td>65.1</td>
<td>$\varepsilon_{\text{Al}_2\text{O}_3} = 221.3$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\varepsilon_{\text{Al}<em>2\text{O}<em>3} (E</em>{\text{ox}} E</em>{\text{O}}) = 251.844$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\varepsilon_{\text{Al}<em>2\text{O}<em>3} (E</em>{\text{Al}} E</em>{\text{O}}) = 251.046$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$[\varepsilon_{\text{O}}]_{\text{Al}_2\text{O}_3} = 375.96$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$[\varepsilon_{\text{Al}}]_{\text{Al}_2\text{O}_3} = 416.60$</td>
</tr>
<tr>
<td>b. 1600</td>
<td>130.2</td>
<td>148.8</td>
<td></td>
</tr>
<tr>
<td>c. 2500</td>
<td>198.4</td>
<td>229.4</td>
<td></td>
</tr>
</tbody>
</table>

Table 6.1.4 : Comparison between a R.B.S sample implanted at 100keV with a oxygen dose of $2.325 \times 10^{18}$ atoms/cm$^2$ and three anodized aluminium specimens.
<table>
<thead>
<tr>
<th></th>
<th>Oxide thickness</th>
<th>O/Al ratio</th>
<th>O/Al ratio</th>
<th>$H_{Al}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(nm)</td>
<td>area's method</td>
<td>height's method</td>
<td>counts</td>
</tr>
<tr>
<td><strong>Anodized films</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>70</td>
<td>1.51</td>
<td>1.58</td>
<td>599</td>
</tr>
<tr>
<td>b</td>
<td>160</td>
<td>1.40</td>
<td>1.49</td>
<td>620</td>
</tr>
<tr>
<td>c</td>
<td>250</td>
<td>1.45</td>
<td>1.41</td>
<td>640</td>
</tr>
<tr>
<td><strong>Implanted Sample.</strong></td>
<td>100-130</td>
<td>1.47</td>
<td>1.56</td>
<td>605</td>
</tr>
</tbody>
</table>

Table 6.1.5: Comparison of anodized samples with an implanted sample.
6.1.5 Talystep measurements.

Molecular oxygen ions were implanted in ST-cut quartz samples (see figure 5.1), with various ions, doses and implant energies. The volume of the implanted region increases and the height 'e', of the resulting step at the boundary of this region has been measured.

Figure 6.1.11 shows how this parameter changes with normal incident, $O_2^+$ ion energy. The dose of ions for each energy being $10^{16}$ atoms cm$^{-2}$. Results from P. Hartemann and M. Morizot[16] are also shown, where several species of ions have been implanted in (Y-X) quartz. The dose being $10^{16}$ atoms cm$^{-2}$ at 100keV.

Figure 6.1.12 shows the variation of the height 'e', with oxygen atom dose at $O_2^+$ energies of 50, 100 and 400keV. P. Hartemann and M. Morizot[16] have only measured the dose effect of 100keV helium into (Y-X) quartz and this is also shown in figure 6.1.12.

The sputter rate of quartz and the expansion of the aluminium after oxygen bombardment was obtained by initially measuring the height of the SiO$_2$/Al step, 'b' (see figure 5.2). Height 'a', was measured after dissolving the implanted aluminium film by immersing the sample in hot sodium hydroxide. Thus the expansion of the aluminium after bombardment was obtained by subtracting the measurement 'a', and the initial height of the aluminium from the measurement 'b'.

From the value of 'a', the absolute sputter yield for quartz was calculated for all three implant energies and these are shown in figure 6.1.13. The expansion of the aluminium layer for all three energies are shown in figure 6.1.14. The theoretical curves are calculated on the simple assumption that all the implanted oxygen formed aluminium oxide ($Al_2O_3$) in the aluminium film, with a density in the range of 3.5 to 4.0gcm$^{-3}$. 
Figure 6.1.11: Height 'e', of the swelling of the quartz implanted region shown as a function of the incident ion mass and energy.

Figure 6.1.12: Height 'e', of the quartz implanted surface versus incident ion dose.
Figure 6.1.13: Absolute sputter yield of quartz for various molecular oxygen implant energies.

Figure 6.1.14: Expansion of the aluminium layer versus incident oxygen dose for 50, 100 and 150 keV molecular oxygen ions.
6.2 Chemical and Structural analysis-
for $O_2^+$ implanted aluminium films.

6.2.1 T.E.M investigation of crystal structure.

Aluminium films were examined by electron diffraction before and after oxygen implantation.

The transmission diffraction patterns were utilised to determine the crystal structure. Interplanar spacing ('d'-values) were obtained from the relation $d = \lambda L / r$ where $r$ is the radius of the diffraction ring, $L$ is the effective specimen to plate distance (75cms in our case) called the camera constant, and $\lambda$ is the wavelength of the radiation, 0.00285nm for 160keV electrons. $\lambda$ is given by the expression[70] below,

$$\lambda \, (\text{nm}) = \frac{0.01226}{E^{0.5}(1 + 0.9788 \times 10^6 E)^{0.5}}$$

The electron diffraction data obtained from the implanted aluminium thin films are shown in table 6.2.1.

Unbombarded aluminium films indicated oxide 'd', values but with lower ring intensities. All the films were found to be polycrystalline before and after implantation.

Table 6.2.2 shows ring data obtained from a thin (100nm) anodized aluminium film lifted off a carbon substrate. The table shows two broad bands indicative of an amorphous structure. The bands are formed by oxide lines that have overlapped.
<table>
<thead>
<tr>
<th>Evaporated aluminium film</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental 'd',values.</td>
<td>Identification</td>
</tr>
<tr>
<td>2.67</td>
<td>Al</td>
</tr>
<tr>
<td>2.25</td>
<td>oxide</td>
</tr>
<tr>
<td>1.60</td>
<td>oxide</td>
</tr>
<tr>
<td>1.36</td>
<td>oxide</td>
</tr>
<tr>
<td>1.03</td>
<td>Al</td>
</tr>
<tr>
<td>1.01</td>
<td>oxide</td>
</tr>
</tbody>
</table>

Table 6.2.1 : Diffraction data from implanted aluminium films.

<table>
<thead>
<tr>
<th>Anodized aluminium film</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental Identification 'd',values.</td>
<td></td>
</tr>
<tr>
<td>1.425-1.900</td>
<td>Al$_2$O$_3$,Al</td>
</tr>
<tr>
<td>2.137-1.816</td>
<td>Al$_2$O$_3$</td>
</tr>
</tbody>
</table>

Table 6.2.2 : Diffraction data from a lifted anodized aluminium film.
6.2.2 X.P.S investigation for oxide formation and recoil implantation.

Figure 6.2.1 shows the aluminium spectrum produced by a 1cm$^2$ sample consisting of a pattern of 0.1mm aluminium squares on a fused quartz substrate implanted with $1 \times 10^{18}$ oxygen atoms cm$^{-2}$, at an ion energy of 100keV. The dual peak of the aluminium signal comprises of metallic and oxidised aluminium for various oxygen doses. It is seen that the implanted oxygen slowly depletes the metallic aluminium signal until only the trivalent aluminium signal can be detected.

The aluminium squares were then stripped off by immersing in hot concentrated sodium hydroxide for fifteen minutes. The X.P.S spectra was found to be identical to the pre-etched samples except for the lack of aluminium signals. No metallic aluminium was detected in the stripped sample, but a very small level of trivalent aluminium was observed. The same result was also obtained by implanting an identical specimen to a dose of $7 \times 10^{17}$ atoms cm$^{-2}$ with 100keV Ar$^+$ ions.

To eliminate the possibility of the stripping of the aluminium layer being incomplete. Identical unimplanted samples were stripped in hot concentrated sodium hydroxide for two, three and four minutes. The aluminium content was found to be zero in all cases.

The Auger parameter[71], for silicon was calculated in all the above cases to determine the possible change in the silicon chemical state. Its value was found to be 225.2eV, consistent with the SiO$_2$ state.

No surface contamination of any samples was detected prior to or after ion implantation.
Figure 6.2.2: X.P.S results from an aluminium film before and after oxygen implantation.
6.3 Verification of the Triple Resonator technique

Sputtering and Stress.

Introduction.

It is necessary to verify the resonator technique owing to our development of the original experimental technique used by EerNisse[27].

Two materials were chosen for investigating the effects of ion dose on the sputtering yield and stress of thin films;

(1) Gold, where a considerable body of sputtering data exists[72-79] and we do not expect results to be complicated by the existence of a surface oxide.

and (2) Germanium, to represent covalently bonded semiconductors.

Data on sputtering yield[80,81] and topographic effects[82] are readily available.

Both sets of results are used to demonstrate the reliability of the triple resonator technique in interpreting the presence of surface effects.
6.3.1 Gold results.

Results for 50keV Ar\textsuperscript{+} ions implanted into polycrystalline Au at a total sample ion current density of 1\(\mu\text{Acm}^{-2}\) are presented in table 6.3.1 as raw frequency shift data and shown, versus argon dose in figure 6.3.1 for AT and BT-cut quartz crystals. Figure 6.3.2 shows the change in areal mass density in gcm\textsuperscript{-2} on the surface of the quartz resonator versus argon dose.

The accumulated integrated lateral stress and the sputtering yield calculated from the raw frequency shifts are listed in table 6.3.1. Figures 6.3.3 and 6.3.4 show the variation in sputter yield and the lateral stress with argon dose. The sputter yield slowly diminishes, being 22 atoms ion\textsuperscript{-1} at a dose of 5\times10\textsuperscript{14} ions cm\textsuperscript{-2} to 17 atoms ion\textsuperscript{-1} at a dose of 6.5\times10\textsuperscript{16} ions cm\textsuperscript{-2}. The magnitude of the lateral stress (figure 6.3.4) is very low, but appears to peak at a dose of around 4\times10\textsuperscript{16} ions cm\textsuperscript{-2}.

Examination with X.P.S and electron microprobe showed no evidence of argon loading of the Au surface. T.E.M analysis of thin evaporated Au films, lifted off NaCl crystals showed that the Au remained polycrystalline after bombardment. Plates 6.3.1 and 6.3.2 show the Au surface topography, observed in a Cambridge Joel S250, of the Au film before and after bombardment, no gross changes were observed.

A backsputtered deposit of Au from the quartz resonators was observed on the back of the crystal defining aperture (figure 1.3). This is shown in plate 6.3.3.
<table>
<thead>
<tr>
<th>Argon dose ($10^6$ ions cm$^2$)</th>
<th>Accumulated $\Delta f_{[AT]}$ (Hertz)</th>
<th>Accumulated $\Delta f_{[BT]}$ (Hertz)</th>
<th>Sputter Yield (atoms ion$^{-1}$)</th>
<th>Lateral Stress ($10^6$ dyne cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>297</td>
<td>199</td>
<td>22</td>
<td>-0.04</td>
</tr>
<tr>
<td>1.0</td>
<td>590</td>
<td>398</td>
<td>22</td>
<td>-0.12</td>
</tr>
<tr>
<td>2.0</td>
<td>1123</td>
<td>763</td>
<td>21</td>
<td>-0.29</td>
</tr>
<tr>
<td>5.0</td>
<td>2731</td>
<td>1884</td>
<td>20.3</td>
<td>-1.10</td>
</tr>
<tr>
<td>10.0</td>
<td>5354</td>
<td>3735</td>
<td>19.9</td>
<td>-2.72</td>
</tr>
<tr>
<td>15.0</td>
<td>7956</td>
<td>5546</td>
<td>19.7</td>
<td>-3.98</td>
</tr>
<tr>
<td>20.0</td>
<td>10504</td>
<td>7303</td>
<td>19.5</td>
<td>-5.00</td>
</tr>
<tr>
<td>25.5</td>
<td>12940</td>
<td>9004</td>
<td>18.9</td>
<td>-6.26</td>
</tr>
<tr>
<td>31.0</td>
<td>15591</td>
<td>10797</td>
<td>18.7</td>
<td>-6.86</td>
</tr>
<tr>
<td>35.0</td>
<td>17482</td>
<td>12053</td>
<td>18.6</td>
<td>-6.97</td>
</tr>
<tr>
<td>39.0</td>
<td>19345</td>
<td>13280</td>
<td>18.5</td>
<td>-6.95</td>
</tr>
<tr>
<td>45.0</td>
<td>22055</td>
<td>15046</td>
<td>18.2</td>
<td>-6.66</td>
</tr>
<tr>
<td>51.0</td>
<td>24680</td>
<td>16736</td>
<td>18.0</td>
<td>-6.11</td>
</tr>
<tr>
<td>55.0</td>
<td>26398</td>
<td>17817</td>
<td>17.9</td>
<td>-5.42</td>
</tr>
<tr>
<td>61.0</td>
<td>28927</td>
<td>19349</td>
<td>17.6</td>
<td>-3.60</td>
</tr>
<tr>
<td>65.0</td>
<td>30560</td>
<td>20346</td>
<td>17.5</td>
<td>-2.53</td>
</tr>
</tbody>
</table>

Table 6.3.1: Measurement of sputtering yield and integrated lateral stress for 50keV Ar$^+$ on Au using the triple resonator technique.
Figure 6.3.1: Argon bombardment of gold;

Frequency shift versus argon dose.
Figure 6.3.2: Argon bombardment of gold;

Areal mass change versus argon dose.
Figure 6.3.3: Argon bombardment of gold;

Sputter yield versus argon dose.
Figure 6.3.4: Argon bombardment of gold; Accumulated lateral stress versus argon dose.
Plate 6.3.1 Gold layer; as deposited

Plate 6.3.2 Gold layer; after 50keV, $6.5 \times 10^{16}$ Ar$^+$ atoms cm$^{-2}$. 
Plate 6.3.3 Crystal defining aperture; showing a backspattered gold deposit.
6.3.2 Germanium results.

Results for 100keV Ar⁺ ions implanted into amorphous Ge at a total sample ion current density of 1.5μAcm⁻² are presented in table 6.3.2 as raw frequency shift data, and are shown, versus argon ion dose in figure 6.3.5.

Figure 6.3.6 shows the change in Ge areal mass density. The accumulated integrated lateral stress and the sputter yield are also listed in table 6.3.2 and shown as a function of argon ion dose in figures 6.3.7 and 6.3.8. Figure 6.3.7 is seen to consist of three regions. Initially the sputter yield rises to 3.7 atoms ion⁻¹ at a dose of 10¹⁶ argon ions cm⁻². Indicating either a vast change in material composition due to loading of the substrate with implanted argon or more probably the removal of a surface oxide with a low sputtering yield. The second region in figure 6.3.7 rises slowly from 3.7 atoms ion⁻¹ at a dose of 10¹⁶ argon ions cm⁻² but with a large scatter of sputter yield results. This could be the combination of argon loading and a change in surface topography. The final region beyond 4.4 atoms ion⁻¹ at 5×10¹⁶ argon ions cm⁻² shows a sputter yield smoothly increasing to 4.6 atoms ion⁻¹ at 3×10¹⁷ argon ions cm⁻².

Figure 6.3.8 shows the linear increase of the lateral stress with the increase in argon dose for doses above 10¹⁶ argon ions cm⁻². This is indicative of incident argon ions loading[27] the substrate. At doses less than 10¹⁶ argon ions cm⁻² the lateral stress shows a relaxation, consistent with the removal of an oxide surface layer. T.E.M results are shown in plates 6.3.4 to 6.3.6. The structure, before and after argon bombardment of the Ge film was found to be semi-amorphous as can be seen from the diffraction pattern(plate 6.3.4).
<table>
<thead>
<tr>
<th>Argon dose (ions cm$^{-2}$)</th>
<th>Accumulated Δf [AT] (Hz)</th>
<th>Accumulated Δf [BT] (Hz)</th>
<th>Sputter Yield (atoms ion$^{-1}$)</th>
<th>Lateral Stress (10$^6$ dyne cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>7</td>
<td>31</td>
<td>1.9</td>
<td>- 0.36</td>
</tr>
<tr>
<td>5.0</td>
<td>147</td>
<td>154</td>
<td>3.9</td>
<td>- 0.75</td>
</tr>
<tr>
<td>10.0</td>
<td>350</td>
<td>310</td>
<td>4.2</td>
<td>- 1.03</td>
</tr>
<tr>
<td>20.0</td>
<td>729</td>
<td>634</td>
<td>4.3</td>
<td>- 2.03</td>
</tr>
<tr>
<td>32.0</td>
<td>1146</td>
<td>1013</td>
<td>4.3</td>
<td>- 3.41</td>
</tr>
<tr>
<td>40.0</td>
<td>1596</td>
<td>1309</td>
<td>4.6</td>
<td>- 3.42</td>
</tr>
<tr>
<td>50.0</td>
<td>1856</td>
<td>1595</td>
<td>4.4</td>
<td>- 4.93</td>
</tr>
<tr>
<td>70.0</td>
<td>2634</td>
<td>2310</td>
<td>4.5</td>
<td>- 7.60</td>
</tr>
<tr>
<td>90.0</td>
<td>3342</td>
<td>2970</td>
<td>4.5</td>
<td>- 10.16</td>
</tr>
<tr>
<td>100.0</td>
<td>3740</td>
<td>3311</td>
<td>4.5</td>
<td>- 11.20</td>
</tr>
<tr>
<td>130.0</td>
<td>4869</td>
<td>4329</td>
<td>4.5</td>
<td>- 14.83</td>
</tr>
<tr>
<td>180.0</td>
<td>6765</td>
<td>6019</td>
<td>4.5</td>
<td>- 20.66</td>
</tr>
<tr>
<td>200.0</td>
<td>7553</td>
<td>6715</td>
<td>4.5</td>
<td>- 22.99</td>
</tr>
<tr>
<td>240.0</td>
<td>9139</td>
<td>8159</td>
<td>4.6</td>
<td>- 28.27</td>
</tr>
<tr>
<td>280.0</td>
<td>10692</td>
<td>9563</td>
<td>4.6</td>
<td>- 33.31</td>
</tr>
<tr>
<td>300.0</td>
<td>11433</td>
<td>10251</td>
<td>4.6</td>
<td>- 35.95</td>
</tr>
</tbody>
</table>

Table 6.3.2: Measurement of sputtering yield and integrated lateral stress for 100keV Ar$^+$ on Ge using the triple resonator technique.
Figure 6.3.5: Argon bombardment of germanium;
Frequency shift versus argon dose.
Figure 6.3.6: Argon bombardment of germanium;
Areal mass change versus argon dose.
Figure 6.3.7: Argon bombardment of germanium;
Sputter yield versus argon dose.
Figure 6.3.8: Argon bombardment of germanium;

Accumulated lateral stress versus argon dose.
Argon bubbles in the Ge film were observed above an argon dose of $3 \times 10^{15}$ argon ions cm$^{-2}$ (plate 6.3.6). Some structure seen in the T.E.M micrographs (plates 6.3.5 and 6.3.6) was due to the cleaved NaCl substrate.

Figure 6.3.9 shows the spectrum obtained from E.P.S (Electron Probe Spectroscopy) measurements carried out on the Ge coated quartz crystal surfaces, before and after implanting. It is seen that after implantation, argon is detected in the Ge surface. The variation and saturation in detected argon counts by the probe with the implanted argon dose in bulk Ge samples is shown in figure 6.3.10. The detected argon counts were found to saturate at an argon dose of $10^{17}$ ions cm$^{-2}$. X.P.S (X-ray Photo-electron Spectroscopy) results indicated the absence of surface contamination. Figure 6.3.11 demonstrates, using X.P.S, the presence of a surface oxide (GeO$_2$) from the chemical shift of the Ge peak. A small trace of argon was also detected in the Ge surface. Angular X.P.S showed that the oxide layer on the germanium surface was depleted of argon. Plates 6.3.7 and 6.3.8 shows the S.E.M micrographs of the Ge surface obtained, before and after bombardment. The smoothing in topography after argon bombardment can be clearly seen. This is markedly different to the case for Au films where little change can be detected, if anything there is a slight trend towards a roughening of the surface.
Plate 6.3.4 Diffraction pattern for an implanted Ge film.
(unimplanted films were identical)

Plate 6.3.5 T.E.M micrograph of an unimplanted Ge film.
mag100K.

Plate 6.3.6 T.E.M micrograph of a argon implanted Ge film.
mag100K.
Figure 6.3.9 : Argon bombardment of germanium;
Electron microprobe analysis before
and after ion implantation.
Figure 6.3.10: Argon bombardment of germanium; E.P.S results of argon retention versus ion dose.
Figure 6.3.11: Argon bombardment of germanium; X.P.S spectrum for germanium (Ge 3d).
Plate 6.3.7 Germanium layer; as deposited.

Plate 6.3.8 Germanium layer; after 100keV, $3 \times 10^{17}$ Ar$^+$ atoms cm$^{-2}$. 
6.4 Trapped ions and Stress—

oxygen implanted into aluminium.

This section deals with the results obtained from the triple resonator technique for O$_2^+$ implants into aluminium. The aluminium was evaporated onto the resonator surface with a thickness of 700nm±5nm.

The dose dependence of the frequency shift data obtained from the triple resonator technique are shown in figures 6.4.1 and 6.4.2 for O$_2^+$ implant energies of 50, 100 and 150keV.

The theoretical lines in the above figures were calculated assuming that all the oxygen incident on the aluminium film was retained and that no sputtering took place.

Frequency shift results for 50keV O$_2^+$ into aluminium (figure 6.4.1) follow theory up to a dose of $4.5 \times 10^{17}$ oxygen atoms cm$^{-2}$ and then the frequency tends to a constant value. Both results for 100keV and 150keV O$_2^+$ implants, indicate a larger frequency shift than predicted in theory. These results are used to plot figure 6.4.3 where the areal mass density has been calculated for all three energies from the resonator theory. Again the 100keV and 150keV results show a larger than expected increase in detected areal mass change.

The lateral stress as measured in the resonator parameter, $\Delta S$(dyne cm$^{-1}$) for all three oxygen energies is shown in figure 6.4.4.

Plate 6.4.1 shows the relatively smooth quartz crystal surface after evaporation of aluminium, while plate 6.4.2 displays the fibrous surface obtained after oxygen bombardment. This topography is seen at all three ion energies. Surface expansion due to oxide formation appears to be the major cause for the change in topography.

Additional work concerned with the investigation of the stress effect of argon loading the aluminium layer using the triple resonator
technique is shown in Appendix 1. The results of this work were found to contradict previous work of stress related to Kr$^+$ loading of a Au substrate performed by EerNisse[27].
Figure 6.4.1: Oxygen bombardment of aluminium;

Frequency shift versus oxygen dose.
Figure 6.4.2: Oxygen bombardment of aluminium;

Frequency shift versus oxygen dose.
Figure 6.4.3: Oxygen bombardment of aluminium; 
Areal mass change versus oxygen dose.
Figure 6.4.4: Oxygen bombardment of aluminium; Accumulated lateral stress versus oxygen dose.
Plate 6.4.1 Aluminium layer; as deposited.

Plate 6.4.2 Aluminium layer; after 100keV $O_2^+$ ions

\[ (4 \times 10^{17} \text{ oxygen atoms cm}^{-2}) \].
6.5 The effect of $O_2^+$ bombardment at the Al/SiO$_2$ interface.

S.E.M observations.

Grid pattern aluminium films (300nm) were evaporated onto fused quartz specimens. These were coated with a layer of sputtered gold (<10nm) to prevent the build up of charge on the exposed quartz surface in the electron microscope.

Oxygen bombarded specimens displayed blisters in the transition region between the aluminium and the fused quartz. This is shown as areas 'a', and 'b' in plates 6.5.1 and 6.5.2. Area 'a', is the edge of the aluminium film and 'b', is silica originally below the aluminium film but now exposed by lateral sputter etching.

Unimplanted aluminium showed no visible topography at all, but after oxygen implantation it was noted that the surface developed nodules with a mean diameter of 180nm±80nm. This area is shown as area 'c', in the above plates. Any surface scratches in the fused silica also took various surface forms after implantation (see region 'd'). One of these scratches provided a quartz marker for an edge so that the area of interest could be stripped and reinvestigated. This technique is shown as a montage in plate 6.5.3. The surface texture can be seen to increase with bubble proximity in the blistered area.

Various substrate combinations were investigated and this is shown in table 6.5.1.

While table 6.5.2, shows the distribution of blisters with different aluminium thicknesses and oxygen ion energy. The different evaporated aluminium layers were obtained by careful monitoring of a crystal resonator during deposition.

Plates 6.5.4 and 6.5.5 demonstrate visually the drastic effect
of varying the aluminium thickness has on the blister density. When the oxygen range coincides with the thickness of the aluminium layer, blisters are seen over the entire aluminium surface.

Plate 6.5.6 shows a partially defoliated 3μm radius blister. This larger blister can be seen to be a coalescence of smaller bubbles, as described in section 3.1. The rupture seems likely to have originated as described in figure 3.2 (section 3.1) for no side rupturing was ever observed.
Plate 6.5.1 Aluminium(300nm) step on fused quartz after bombardment with 100keV \( O_2^+ \) ions

\( (4 \times 10^{17} \text{ oxygen atoms cm}^{-2}). \)

Plate 6.5.2 Continuation of the above step.
Al-SiO₂ sample implanted with 100keV O⁺ ions
(2.8×10⁻¹⁸ oxygen atoms cm⁻²)

Plate 6.5.3 A aluminium-quartz edge, before and after stripping.
<table>
<thead>
<tr>
<th>Film and substrate</th>
<th>blistering</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$O_2^+$</td>
</tr>
<tr>
<td></td>
<td>(100 keV, $1 \times 10^4$ ions cm$^{-2}$)</td>
</tr>
<tr>
<td>Al on SiO$_2$</td>
<td>Yes</td>
</tr>
<tr>
<td>Al on Si</td>
<td>Yes</td>
</tr>
<tr>
<td>Al on C</td>
<td>Yes</td>
</tr>
<tr>
<td>Al on Al</td>
<td>No</td>
</tr>
<tr>
<td>Au on C</td>
<td>No</td>
</tr>
<tr>
<td>Al edges 1 mm above SiO$_2$</td>
<td>No</td>
</tr>
<tr>
<td></td>
<td>messy edges.</td>
</tr>
</tbody>
</table>

Table 6.5.1: Material composition investigation of edge blistering.
Table 6.5.2: Blister distribution with aluminium thicknesses.

<table>
<thead>
<tr>
<th>Oxygen dose energy (at. cm(^{-2}))(keV)</th>
<th>L.S.S. range (nm)</th>
<th>PRAL range (nm)</th>
<th>Al thickness deposited (nm)</th>
<th>Average number of blisters per (\mu m^2)</th>
<th>Mean diameter (nm)</th>
<th>Standard deviation (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(4 \times 10^{17}) 50</td>
<td>100.3</td>
<td>107.6</td>
<td>58</td>
<td>100</td>
<td>620</td>
<td>200</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>115</td>
<td></td>
<td>580</td>
<td>220</td>
</tr>
<tr>
<td>(4 \times 10^{17}) 75</td>
<td>151.3</td>
<td>168.4</td>
<td>61.3</td>
<td>33</td>
<td>909</td>
<td>180</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>141</td>
<td></td>
<td>682</td>
<td>200</td>
</tr>
</tbody>
</table>
Plate 6.5.4 Al(141nm) on quartz bombarded with 150keV $O_2^+$ ions ($4\times10^{17}$ oxygen atoms cm$^{-2}$).

Plate 6.5.5 Al(61.3nm) on quartz bombarded with 150keV $O_2^+$ ions ($4\times10^{17}$ oxygen atoms cm$^{-2}$).
Plate 6.5.6 Al(141nm) on quartz bombarded with 150keV O$_2^+$ ions (4x10$^{17}$ oxygen atoms cm$^{-2}$).

The S.E.M micrograph shows a ruptured blister made up of a coalescence of smaller bubbles.
6.6 S.A.W measurements-

$O_2^+$ implanted S.A.W resonator.

This section deals with the change in frequency response of a S.A.W resonator after various $O_2^+$ doses at an implant energy of 50keV.

The measurements were obtained as explained in section 5.5. The results are shown in table 6.6.1 and a typical frequency response spectra is shown in plate 6.6.1.

From table 6.6.1, the insertion loss is seen to deteriorate from 2dB to 6.5dB after a oxygen dose of $10^{15}$ atoms cm$^{-2}$. The 3dB bandwidth is relatively constant fluctuating slightly around a median of 46kHz.

As the implanted oxygen dose is increased the resonant frequency is found to increase by 81kHz, after a oxygen dose of $4 \times 10^{16}$ atoms cm$^{-2}$, and then fall by 526kHz to resonate at 149.445MHz after a total oxygen dose of $3 \times 10^{17}$ atoms cm$^{-2}$. This frequency change is shown in figure 6.6.1 with earlier results from James and Wilson[3].

The side lobes on the frequency response of the device was found to increase by 10%, changing slightly each time the insertion loss deteriorated.
Table 6.6.1: Results obtained from a S.A.W resonator implanted with 50KeV molecular oxygen ions.
Plate 6.6.1 Typical frequency response from an unimplanted S.A.W resonator.
Figure 6.6.1: Oxygen bombardment of a S.A.W device; Frequency shift versus oxygen dose.
CHAPTER 7 Discussions and Conclusions.

7.1 Physical and Chemical effects of the implanted oxygen ion.

During oxygen bombardment the crystalline quartz substrate was observed to swell (figure 6.1.12) for all oxygen ion energies. This swelling is due to amorphisation[16]. The density of quartz being 17% higher than that of amorphous silica. This lowering of material density will thus manifest itself as a swelling. For oxygen the curve of quartz swelling versus ion energy (figure 6.1.11) is a straight line and the swelling 'e', may be considered as a function of the form,

\[ e = A(R_p + 2\Delta R_p) \]

where \( R_p \) is the projected range
\[ \Delta R_p \] is the standard deviation
and \( A_p \) is a constant.

'A', for our case oxygen, has a calculated value of 0.114.

The insensitivity of the swelling, 'e', to oxygen atom dose (figure 6.1.12) is due to saturation of damage at a dose lower than the lowest value measured; \( 3 \times 10^{14} \) ions cm\(^{-2} \). Some evidence of the final stages of damage saturation can be seen for the two higher energies.

The dramatic dose effect observed by Hartemann and Morizot[16] is due to the high penetration depth of helium ions in quartz resulting in fewer displacement collisions per unit depth, and therefore a lower rate of damage accumulation per unit volume.
The table below, from figure 6.1.13, shows the absolute sputter yield for quartz for three molecular oxygen implant energies.

<table>
<thead>
<tr>
<th>$O_2^+$ Energy (keV)</th>
<th>Sputter yield of quartz</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>0.13</td>
</tr>
<tr>
<td>100</td>
<td>0.08</td>
</tr>
<tr>
<td>150</td>
<td>0.05</td>
</tr>
</tbody>
</table>

The aluminium layer was also observed to swell for all three oxygen atom energies. This expansion is independent of ion energy. We suggest that the expansion results from the creation of $Al_2O_3$ and is dependent only on the amount of oxygen implanted and is therefore independent of depth and profile. The discrepancy between experimental and theoretical points in figure 6.1.14 can be attributed to surface roughness or to a lower density in the case of the layer formed by ion implantation compared to that of crystalline $Al_2O_3$. Data for doses above $10^{18}$ atoms cm$^{-2}$ seem to show evidence of saturation due to surface sputtering. The talystep results of figure 6.1.14, therefore seem consistent with the growth of stoichiometric $Al_2O_3$.

From figure 6.1.4 it can be seen that as the implanted oxygen dose is increased, the yield (profile height) increases. The measured oxygen area and the calculated oxygen concentration in the implanted layer both increase with dose and saturate when a stoichiometric $Al_2O_3$ surface layer is formed. The reduction in layer thickness for high doses is due to surface sputtering. It was observed that as the implanted oxygen dose is increased, the aluminium yield in the implanted surface layer decreases. The dip in the aluminium yield is indicative of the depth at which the oxygen peak occurs. The profile near the surface becomes flat for implant doses greater than the
saturation dose. From figure 6.1.7 it can be seen that the stoichiometric ratio of 1.5 (ie Al$_2$O$_3$) was not exceeded and that Al$_2$O$_3$ is formed at a dose of $1.2 \times 10^{18}$ atoms cm$^{-2}$ for a molecular oxygen energy of 100keV.

The computed experimental range and standard deviation values are larger than the L.S.S statistics by 9% to 41% and the PRAL statistics by 4.7% to 31.5% (table 6.1.2). The computed PRAL statistics can be seen to give a slightly better fit to the experimental data. These discrepancies can be attributed to the inaccuracy of the range theories for light ions and possibly enhanced penetration due to the phase structure of the films. Analysis performed by the surface energy approximation and by the mean energy approximation yield values of range and range straggling that are 3% lower in the case of the mean energy approximation (due to the stopping cross section factor being 3% larger). We conclude that for 100keV O$_2^+$ the surface energy approximation is adequate for this analysis of depth distributions since $\Delta E$ is small compared to $E$ and $\epsilon$ changes very little over $\Delta E$.

Table 6.1.5 shows that there is good agreement with R.B.S profiles obtained from anodized and implanted samples. The area's and height's method[67] are in good agreement. The profile height of the surface aluminium ($H_{Al}$ in figure 6.1.10) is a good indication that the oxygen concentration in the implanted and anodized films has saturated to the same level.

A small trace of sulphur trapped in the oxide lattice of the anodized samples was detected on the R.B.S spectra (figure 6.1.10). This is due to disassociation of H$_2$SO$_4^+$ liberation of SO$_2$ and atomic oxygen at the anode.
7.2 The nature of the implanted oxide.

The T.E.M results for the oxygen implantation were difficult to quantify owing to the irregular granular nature of the implanted layer and its greater than optimum sample thickness (200nm). However they do demonstrate that, unlike the amorphous anodic oxide films, a polycrystalline oxide is formed. This is in contradiction to earlier results[83]. Recent results on the implantation of α-Al_2O_3 single crystals[84] indicate that Al_2O_3 is not turned amorphous by implantation of 10^{17} cm^{-2} Cr to depths of 0.1 μm and amorphous layers can be produced in crystalline Al_2O_3 under two implantation conditions[85].

At relatively low doses (<5×10^{15} atoms cm^{-2}), an amorphous layer can be formed if implantation is done at liquid nitrogen temperature and at room temperature where much higher doses (>10^{19} atoms cm^{-2}) are necessary to form the amorphous phase. It would therefore appear that the crystal structure of Al_2O_3 is stable under ion bombardment, in our case.

From the X.P.S spectra it was found that the implanted oxygen slowly depletes the metallic aluminium until only the trivalent aluminium can be detected. After 2 minutes of sputter etching of the highest dose sample with 3kV argon atoms, the X.P.S spectrum continued to indicate the presence of trivalent aluminium only.

The detection of trivalent aluminium in the surface of aluminium stripped specimens provided evidence of possible surface diffusion and knock-on implantation of atoms from the deposited aluminium regions.

The state of silicon in the quartz was monitored via the Auger parameter[71] and was found to be undeviating from 225.2eV which is consistent with SiO_2.

The stripped quartz after X.P.S irradiation was found to be
coloured light purple. This is due to the fact that X-rays may cause clear quartz to become smoky[86]. The colouration was found to disappear after heating the sample to $500^\circ$C.
7.3 Sputtering and Stress

7.3.1 The results for Au films.

The table below compares the present work on argon sputtering of gold with those of other workers.

<table>
<thead>
<tr>
<th>Energy (keV)</th>
<th>Sputter Yield, S, Dose</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>small</td>
</tr>
<tr>
<td>Present work</td>
<td>50</td>
</tr>
<tr>
<td>J.F. Singleton[72]</td>
<td>50</td>
</tr>
<tr>
<td>Sigmund[73] (Theory)</td>
<td>45</td>
</tr>
<tr>
<td>Nenadovic et al[74]</td>
<td>50</td>
</tr>
<tr>
<td>Colligon and Patel[75]</td>
<td>38</td>
</tr>
<tr>
<td>Andersen and Bay[76]</td>
<td>45</td>
</tr>
<tr>
<td>Almén and Bruce[77]</td>
<td>45</td>
</tr>
<tr>
<td>EerNisse[78]</td>
<td>45</td>
</tr>
<tr>
<td>Oliva Florio et al[79]</td>
<td>45</td>
</tr>
</tbody>
</table>

The 'small', and 'large', doses referred to in connection with the above are in the region of $10^{14}$-10$^{15}$ ions cm$^{-2}$ and $10^{16}$-10$^{17}$ ions cm$^{-2}$ respectively.

The results show that the present work gives higher values of yield than any other experimentalists. In all the experimental results used for comparison the yield is calculated by measuring the weight loss of the target although Nenadovic et al[74] supported their results with a parallel measurement of collected deposits using spectrophotometry. The weight change due to implanted ions is allowed for but there is an error due to reflection of bombarding ions. This problem has been considered by Andersen and Bay[76] using reflection coefficients measured by Böttiger et al[87] and they find that the error in $S$ is less than 1% in all cases where $S$ is greater than unity.
Andersen and Bay use a term $M_1/M_2$ to correct for the mass of the incident ions where $M_1$ and $M_2$ are the atomic weights of the ion and the target material respectively. The term $M_1/M_2$ is added to their relationship for sputtering yield so it is not significant if the ions are much lighter than the target atoms which is true of the situation under discussion.

It is quite unlikely that the yields measured in the present work are high owing to the initial starting material. Andersen and Bay[76] and Oliva Florio et al[79] utilised evaporated Au films and obtained results in good agreement with us. The other workers used Au foils and obtained much lower sputter yield values. The exceptions are Singleton[72] (his values of yield by activation analysis of sputtered Au deposits of Au foils are in good agreement with the present work) and Colligon and Patel[75] (extrapolation of their sputter yield with energy to 50keV gives a sputter yield of around 15-16).

Neutral components in the ion beam in our case were less than 1% as confirmed by measurements carried out on the University of Surrey, 500keV ion implanter using calorimetry[88].

A further influence on the sputter yield which is especially apparent at high doses will be the development of surface topographical features, an effect which Andersen and Bay have suggested as a possible cause of discrepancy between their work and that of EerNisse[78]. As S.E.M observations have shown, no gross effects were observed in the present work.

Only EerNisse's earlier results[27] indicate that sputtering yields of Au increase with higher ion doses. While the work of Andersen and Bay and Oliva Florio et al agree with the present findings that the sputter yield decreases with increasing argon dose. As no
argon was detected in the bombarded Au by X.P.S analysis we must look elsewhere to explain the decrease in sputter yield with increasing ion dose. We propose that this arises from the variation of sputtering yield with crystal orientation. Those grains oriented favourably for sputtering would be preferentially eroded and so would tend to diminish in surface area leading to a gradual predominance of lower sputtering yield grains.

The kink in the sputter yield graph, figure 6.3.3, at an argon dose of \(2.25 \times 10^{16} \text{ ions cm}^{-2}\) can only be explained by surface contamination of the Au crystal surfaces during an overnight shutdown in the target chamber.

The lateral stress, figure 6.3.4, in argon bombarded Au is very small[27], but a peak stress of \(-7 \times 10^5 \text{ dyne cm}^{-1}\) occurs at a dose of \(2.7 \times 10^{16} \text{ ions cm}^{-2}\). A relaxation of this compressive stress is seen at higher doses. One can speculate that mismatch at grain boundaries due to preferential erosion could be the cause of these small stress effects.
7.3.2 The results for germanium films.

The table below compares the present work with those of others.

<table>
<thead>
<tr>
<th>Energy (keV)</th>
<th>Sputter Yield, $S,$</th>
<th>Dose</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>small</td>
</tr>
<tr>
<td>Present work</td>
<td>100</td>
<td>4.3</td>
</tr>
<tr>
<td>I.H. Wilson et al [80]</td>
<td>100</td>
<td>3.09</td>
</tr>
<tr>
<td>Sigmund [73] (Theory)</td>
<td>100</td>
<td>3.40</td>
</tr>
<tr>
<td>Chose et al [81]</td>
<td>35</td>
<td>3.75</td>
</tr>
</tbody>
</table>

The 'small', and 'large', doses referred to in connection with the above are in the region of $10^{14}\text{--}10^{15}$ ions cm$^{-2}$ and $10^{16}\text{--}10^{17}$ ions cm$^{-2}$ respectively.

The initial rise (region 1, figure 6.3.7) of the sputter yield versus argon dose is due to the presence of a surface oxide ($\text{GeO}_2$) confirmed by X.P.S analysis.

Angular X.P.S analysis shows that the surface oxide is 4.2nm in thickness. This is in good agreement with an estimate of 4.0nm from the dose to reach the end of region 1 of the quartz oscillator sputtering yield curve (figure 6.3.7). Angular X.P.S also showed that argon was almost undetectable in the oxide layer which indicates that the mobility of argon is much higher in GeO$_2$ than in Ge.

In region 2 E.P.S results show that the argon concentration increases by an order of magnitude reaching saturation at the end of this region ($10^{17}$ ions cm$^{-2}$). The saturation dose correlates well with that predicted assuming sputtering to the depth of the peak in the original argon profile. In this region one observes fluctuations in the sputter yield. We suggest that these fluctuations arise from retention of argon in bubbles [82] followed by release as the eroding
surface reaches the bubble layer. The presence of the bubbles were confirmed by T.E.M analysis of thin germanium films. The slow increase in sputter yield in region 3 is interpreted as resulting from changes in surface topography (smoothing) once a structure that enables a constant rate of argon release is established. The end of region 1 (sputter removal of the oxide) correlates exactly with a change in slope of the lateral stress versus dose curve (figure 6.3.8). However the fluctuations in sputtering yield seen in region 2 and the saturation in argon concentration at the end of region 2 are not reflected in variations in the slope of the ΔS versus dose curve. One can only speculate that changes in bubble structure and surface topography possibly due to the presence of voids[82] compensate for the saturation in argon concentration.
7.4 Stress and loading of implanted oxygen ions in aluminium.

Results of the triple resonator measurements for 50keV \( \text{O}_2^+ \) into aluminium are presented in figure 6.4.1 as raw frequency shifts versus implanted atomic dose. The frequency shifts follow theory up to a dose of \( 4.5 \times 10^{17} \) atoms cm\(^{-2} \) and then the frequency increase starts to saturate. The primary cause of this saturation is sputtering with a resultant reduction in the number of trapped implanted oxygen ions in the aluminium film. Figure 6.4.2 shows results for 100keV and 150keV \( \text{O}_2^+ \) implants. Both indicate a larger frequency shift than predicted in theory. These results are used to plot figure 6.4.3 where \( \Delta M \) (areal mass density) has been calculated for all three energies from the double resonator theory. The 100keV and 150keV results show a larger than expected increase in detected areal weight. This can only be accounted for if a compressive stress normal to the crystal surface is present. This compressive stress increases with increasing incident ion energy.

Increasing the ion energy increases the range and range straggling of the incident ions. We conclude that the compressive stress depends on the oxygen depth profile.

Results from Arrowsmith et al[89] for the internal stress measured in anodic oxide during anodizing, indicate that for an oxide thickness less than 9\( \mu \)m at 20\(^\circ\)C (or 7\( \mu \)m at 60\(^\circ\)C) the internal stress will be compressive.

The fluctuation in \( \Delta M \) for 100keV could be due to a relaxation of the stress in the implanted film. A relaxation of the stress in the anodic film after a period of ten to fifteen minutes was observed by
Arrowsmith et al[89].

The lateral stress, $\Delta S$, (double resonator parameter) for all three energies is shown in figure 6.4.4. All show an almost insignificant lateral stress. A very slight lateral tension can be measured for the 150keV results.

Plates 6.4.1 and 6.4.2 show the aluminium surface before and after 100keV oxygen bombardment. A fibrous expansion of the surface is seen at all the oxygen energies. This is considered to be due to anisotropic growth of the polycrystalline oxide.
7.5 Interface blistering.

The blistering mechanism seen for thin aluminium films on quartz depends upon the presence of an interface. The blisters seen after oxygen bombardment form at the aluminium-quartz interface which acts as a sink for the implanted oxygen atoms. Blisters are always seen near the edge of the aluminium layer where the layer thickness is of the same magnitude as the range of the implanted oxygen. The quantity of oxygen trapped at the interface will be the greatest where the interface depth equals the oxygen projected range. Thus the maximum blistering occurs when the depth of the interface equals the projected range of the incident ions. The mismatch of aluminium oxide (synthesis) and aluminium crystal structures may be considered as an additional factor to the formation of these blisters.

Larger blisters were found to be a coalescence of smaller bubbles. The large blister seen in plate 6.5.6, is a half spherical sphere with a blister cap radius of 1.5μm.

From equation 3.4, from section 3.1, for 150keV O$_2^+$ ions. A fracture is predicted by theory to propagate along the z axis, figure 3.2, from the point 'A', towards the cavity surface as seen in plate 6.5.6.
7.6 S.A.W performance.

As the aluminium layer defining the S.A.W resonator was only 200nm thick, a molecular oxygen ion energy of 50keV was chosen as seen in sections 7.4 and 7.5 to minimise stress effects owing to oxide formation and blistering.

From table 6.6.1, the initial rise in the S.A.W frequency response can be attributed to a reduction of the effective mass loading of the quartz resulting in an increase in surface wave velocity. The mass reduction is due to the amorphisation and swelling of the crystalline ST quartz between the aluminium stripes. As the densities of aluminium and quartz are nearly identical it would be reasonable to assume that wave velocities in the two materials would be the same. Based on the above assumptions, the height of the aluminium above the quartz surface after implantation can be considered to be the effective depth of the metallic loading. Also it is known that the velocity of the surface wave in amorphous quartz is 9% higher[14] than crystalline quartz, principally as a result of lower density.

The amorphous height in this case is only 10nm (figure 6.1.11, section 6.1.6) and gives a reduction in aluminium loading of 5%.

James[14] gives the shifts to the stop/pass band frequency due to amorphization of the quartz with argon ions as,

\[
\frac{df}{dE} = 167 \text{MHz} = 120 \pm 25 \text{kHz} \quad 100 \text{keV}^{-1}
\]

\[
= 1.5 \times 10^{16} \text{ argon atoms cm}^{-2}
\]

This gives a expected shift of 70kHz, if normalised to 25keV oxygen, this then agrees well with the 81kHz measured for an oxygen atom dose of \(4 \times 10^{16} \text{ cm}^{-2}\). The rise to 81kHz is then interpreted as the saturation of the acoustic wave velocity to the amorphisation of the
implanted quartz.

The drop to 54kHz of the frequency change at a oxygen dose $8\times10^{16}$ atoms cm$^{-2}$ may be attributed to an increase in surface loading. The damage and therefore the thickness of the amorphized layer has saturated and the implanted quartz is sputtering at a faster rate than the aluminium[6].

The sudden and spectacular drop in the resonant frequency at $1.5\times10^{17}$ oxygen atoms cm$^{-2}$ cannot be attributed to stress effects due to oxide formation although a weight increase in surface loading owing to trapped oxygen atoms obviously occurs. The drop can only be explained by the presence of edge blisters at the aluminium-quartz interface (section 7.5). The interface blistering set up stresses at the edges of the aluminium fingers which in turn causes a static stress bias in the quartz surface, and effectively increases the mass loading and slows the acoustic wave.

The gradual reduction of the resonant frequency thereafter is due to oxide formation and the difference in the sputtering yield of the quartz and aluminium. Both effects causing an increase in the effective mass loading of the ST quartz substrate.

The insertion loss can be seen to deteriorate from 2.2dB at a oxygen dose of $10^{15}$ atoms cm$^{-2}$ and saturate at 6.5dB at $2\times10^{17}$ atoms cm$^{-2}$. Obviously this is an undesired effect. This phenomenon has not been investigated but possible reasons could be:

(1) The loss of the piezoelectric effect in the amorphous regions between the transducer electrodes,

(2) Interface blistering setting up additional scattering centres,

and (3) Deposition of a thin metallic layer as a result of forward
sputtering from the ion beam aperture plate, and or redeposition of the aluminium thin film networks under the influence of energetic ions. Hemphill[90] has observed large surface wave attenuation for metallic films of only 3-10nm in thickness.

The side lobes observed in the complete frequency response in plate 6.6.1 arise from a source of time delayed signal. This occurs when the surface wave signal is partially reflected from the receiving transducer back towards the transmitter where it is again partially reflected back to the receiver. Thus it makes three transits between transducers compared with the single transit of the main signal, and hence is termed the 'triple transit', signal[1].

The level of triple transit signal relative to the main signal depends on the insertion loss of the filter, the structure of the transducers and on the electrical terminations of the transducers. Thus as the insertion loss deteriorates the relative level of triple transit will rise, and this problem can impose a limit on the lowest level of insertion loss usable for a given application.
7.7 Conclusions.

The degree of amorphisation of crystalline quartz is linearly dependent upon the energy of the incident ion.

Surface swelling measurements, R.B.S, T.E.M, and X.P.S all indicate that ion implantation of oxygen into aluminium at energies between 25 and 75keV (50 to 150keV, for molecular oxygen) result in the synthesis of aluminium oxide. The oxygen concentration in the implanted layer saturates when $N_{Ox}/N_{Al}=1.5$. At higher doses a stoichiometric surface layer of aluminium oxide is formed, and sputtering acts to reduce the layer thickness. The oxide grows as crystalline regions of aluminium oxide in a polycrystalline aluminium matrix.

The implanted region exerts a compressive stress, normal to the surface of the substrate. This results from the mismatch of the aluminium oxide and aluminium crystal structures. The mismatch becoming significant above an oxide thickness of 72.6nm (ie $R_{p}+2\Delta R_{p}$ for 50keV $O_2^+$ ions).

The triple resonator technique for determining sputtering yields and surface stress in deposited thin films has been demonstrated using thin films of gold and germanium.

The gold films showed no argon retention and very low levels of lateral stress. The sputtering yield diminished with increasing ion dose due to preferential sputtering of grains with a high sputtering yield orientation.

The germanium films were semi-amorphous, with a 4nm surface oxide. After argon bombardment bubbles formed with no change in the semi-amorphous structure of the films. The measured sputtering yield
versus ion dose was divided into three regions; removal of oxide, periodic gas release and surface smoothing. The surface stress increased linearly with ion dose once the surface oxide had been removed.

Blister formation (in oxygen bombarded aluminium-quartz structures) was found to be a result of oxygen accumulation at the interface. Large blisters being a coalescence of smaller bubbles. The theory was found to agree well with the experimental work. To avoid blister formation, in our case, edges must be as vertical as possible and the incident ions must be kept away from the interface.

The experiments have demonstrated the ability of high and low energy incident ions to trim the operating frequency of passive velocity dependent (S.A.W) structures.

The deterioration of the insertion loss is a factor that cannot be ignored when considering the degree of frequency shifting required. Increased surface wave attenuation warrants further investigative work, but selective area ion implantation in order to avoid bombardment of the transducer networks may reduce the undesirable effect.
APPENDIX 1.

Additional experiments performed with the triple resonator technique.

This section is divided into two parts. The first part(1A) deals with the mass loading and lateral stress caused by implanting argon ions into an evaporated aluminium film. While the second part(1B) is concerned with the angular variation of the sputtering yield (Sθ) of gold and germanium. Both results were obtained using the triple resonator technique.

1A. T.R.T results for argon implanted into aluminium.

This section deals with the results obtained from the triple resonator technique for 100keV Ar⁺ implanted into a 1µm film of aluminium evaporated onto the resonator surface.

The frequency shift data versus argon atom dose are shown in figure 1A. Figure 2A shows the change in areal mass density and the accumulated lateral stress versus argon atom dose.

The theoretical lines in the above figures were calculated assuming that all the argon incident on the aluminium film was retained and that no sputtering took place.

Electron microprobe analysis showed the presence of argon in the aluminium film. The aluminium surface was examined before and after argon bombardment, with a cambridge Joel S250, and no gross changes were observed.
1A. Discussion.

The variation of the areal mass density with argon dose gives values larger than expected (figure 2A). This can only be accounted for if a small additional compressive stress normal to the crystal surface is present. The areal mass density is seen to saturate at around $10^{17}$ argon ions cm$^{-2}$. The primary cause of this saturation is sputtering with a resultant reduction in the number of trapped implanted argon ions in the aluminium film. This is reflected by a saturation of the lateral stress in the aluminium film also shown in figure 2A. The values of lateral stress are small compared to the values obtained by EerNisse[1A].

From our previous work (section 7.4) it is reasonable to postulate that an increase in the detectable level of lateral stress would follow an increase in the depth profile of the implanted ion. EerNisse[1A] detected a maximum lateral stress of $-26 \times 10^5$ dyne cm$^{-1}$ when 98% of the Kr ion profile lay in 22.8nm ($R_p+2\Delta R_p$, PRAL[2A] range statistics) of Au.

The measured maximum value of lateral stress, determined from figure 2A, happens to be only $+3 \times 10^5$ dyne cm$^{-1}$, with 100keV argon ions implanted into aluminium the ion profile lies within 157.4nm of aluminium(PRAL range statistics). The causes for this major discrepancy is the difference in the ion-substrate system studied and our development of the original experimental technique used by EerNisse[1A]. The main differences in our experimental procedure was; crystal surfaces were flat and not plano and compensation for ion implanted temperature effects were allowed for.

CRYSTAL FREQUENCY SHIFTS (hertz)

ION : Ar⁺
TARGET : Al
ENERGY : 100 keV

ARGON ATOM DOSE (ions cm⁻²)

Figure 1A: Frequency shift data versus argon atom dose.
**Figure 2A:** Areal mass density and accumulated lateral stress versus argon atom dose.
1B. S(θ) characteristics for Au and Ge.

The crystals for the triple resonator technique were mounted as previously described (section 1.6). The sample holder was then placed on a rotating assembly. The whole assembly could be rotated accurately (±0.5°) to facilitate bombardment at any value of ion incidence, θ, between 0 and 90°. The assembly was made such that all the incident ion current was measured (even at θ=90°).

Electron suppression was achieved with a suppression plate curved around the sample holder.

Measurements for Ge were taken after the initial GeO₂ layer had been sputtered away.

The results obtained for 50keV argon bombardment of Au are shown in figure 1B with a theoretical curve calculated by Wilson[1B]. The results for 100keV argon on Ge, with a theoretical curve[1B], are also plotted in figure 2B.

1B. Discussion.

A good fit between experimental and theoretical is obtained for 50keV argon into Au for θ<70°. For θ>70° the experimental value of S(θ) rises above that predicted theoretically. We can attribute this to the effect of surface roughness which leads to a mean (microscopic) value of θ somewhat less than the set (macroscopic) value.

The results for 100keV argon on Ge are also plotted with earlier results[1B] obtained by scanning electron microscopy. The theoretical fit at S(θ) and the value at θ_max agree well with the experimental results, but the predicted value of S(θ)_{max} is 20% lower. This discrepancy is due to experimental artefacts such as argon bubbles and changes in surface topography.

Figure 1B: $S(\theta)$ characteristic for gold.
Figure 2B: $S(\theta)$ characteristic for germanium.
APPENDIX 2.

R.B.S calculations.

In calculating $\epsilon$, [1] for an aluminium oxide matrix we assume Bragg's rule[1] and we must consider as the unit of the compound one molecule of $\text{Al}_2\text{O}_3$ with its associated atoms:

$$\epsilon_{\text{Al}_2\text{O}_3} = 2\epsilon_{\text{Al}} + 3\epsilon$$

$$\epsilon_{\text{Al}_2\text{O}_3}(E_0) = 2(48.34) + 3(41.54) = 221.3 \times 10^{-15}\text{eV cm}^2.$$

$$\epsilon_{\text{Al}_2\text{O}_3}(K_{\text{Ox}}E_0) = 2(54.92) + 3(47.33) = 251.844 \times 10^{-15}\text{eV cm}^2.$$

$$\epsilon_{\text{Al}_2\text{O}_3}(K_{\text{A1}}E_0) = 2(53.403) + 3(48.08) = 251.046 \times 10^{-15}\text{eV cm}^2.$$

$\theta = 150^\circ$, $K_{\text{Ox}} = 0.3848$, $K_{\text{Ox}}E_0 = 577.2\text{keV}$, $K_{\text{A1}} = 0.5726$, $K_{\text{A1}}E_0 = 859\text{keV}$.

All the $\epsilon$ data are obtained from Chu et al [1].

$$[\epsilon_{\text{o}}]_{\text{Al}_2\text{O}_3} = K_{\text{Ox}}\epsilon_{\text{Al}_2\text{O}_3}(E_0) + 1/\cos(180-\theta) \epsilon_{\text{Al}_2\text{O}_3}(K_{\text{Ox}}E_0) = 375.96 \times 10^{-15}\text{eV cm}^2$$

$$[\epsilon_{\text{o}}]_{\text{Al}_2\text{O}_3} = K_{\text{A1}}\epsilon_{\text{Al}_2\text{O}_3}(E_0) + 1/\cos(180-\theta) \epsilon_{\text{Al}_2\text{O}_3}(K_{\text{A1}}E_0) = 416.60 \times 10^{-15}\text{eV cm}^2$$

$N_t = \Delta E_{\text{Al}}/[\epsilon_{\text{o}}]_{\text{Al}_2\text{O}_3} = 3.57177 \times 10^{17}\text{mols cm}^{-2}$,

$N_t = \Delta E_{\text{Ox}}/[\epsilon_{\text{o}}]_{\text{Al}_2\text{O}_3} = 3.46313 \times 10^{17}\text{mols cm}^{-2}$, mean value = 3.51745 \times 10^{17}\text{mols cm}^{-2}.

$\rho_{\text{Al}_2\text{O}_3} = 4.0$ (max) g cm$^{-3}$ or 3.5 (min) g cm$^{-3}$.

$$= 2.36 \times 10^{22}$$(max) mols cm$^{-3}$ or $2.066 \times 10^{22}$ (min) mols cm$^{-3}$.

Therefore the thickness, $t$, of the anodized aluminium films are,

a. $t = 73.7\text{nm (max)}$ or $64.6\text{nm (min)}$.

b. $t = 170.3\text{nm (max)}$ or $149.0\text{nm (min)}$.

c. $t = 261.0\text{nm (max)}$ or $228.5\text{nm (min)}$.

REFERENCES

1. W.H.Haydl, P.Hiesinger, R.S.Smith, B.Dischler and K.Heber,
   Proc.IEEE,Freq.control symposium (1976),346-357.

2. D.W.Parker,

3. S.James and I.H.Wilson,
   Electronic Letts, October(1979), Vol.15, No.21, 683.

4. P.Hartemann and M.Morizot,

5. S.Chereckdjian and I.H.Wilson,

6. J.G.Perkins,

7. E.P.EerNisse,
   Proc.3rd Inter.Conf.on Ion Impl.in Semi.and other mats., NY, 1972,

8. O.Auciello,
   Rad.effects (1976), vol.30, 11-16.

9. R.G.Musket and D.W.Brown,
   IBM,M, Cornell, USA. (1984) to be published.

10. S.S.Gill and I.H.Wilson,

11. A.R.Bayly,
    J of Mat.Sci. (1972), 404-412.

12. I.H.Wilson,

13. S.K.Das and M.Kaminsky,

14. S.James,

15. W.Ashby,
    E4 project, Univ.of Surrey, Dept. of Electrical Eng. (1978).

16. P.Hartemann and M.Morizot,
17. P. Hartemann,

18. W. H. Haydl and P. S. Cross,

19. W. H. Haydl and P. S. Cross,

20. G. Volluet,

21. H. L. Garvin and R. D. Weglein,

22. H. I. Smith, R. C. Williamson and W. T. Brogan,

23. J. DeKlerk and E. F. Kelly,

24. D. McKeown,

25. E. P. EerNisse,

26. H. H. Andersen and H. Bay,

27. E. P. EerNisse,

28. E. P. EerNisse,

29. E. P. EerNisse,

30. Physics of thin films,

31. C. D. Stockbridge,
edited by K. H. Behrndt.

32. E. P. EerNisse,

33. E. P. EerNisse and S. T. Picraux,

34. E. P. EerNisse,
35. W.K. Chu, J.W. Mayer and M.A. Nicholet, 

36. J.F. Ziegler and W.K. Chu, 

37. Biersack and Ziegler, 

38. I.H. Wilson, 
Rad. Effects., 18, (1973) 95.

39. I.H. Wilson, 

40. W. Hauffe, 

41. W. Hauffe, 

42. I.S.T. Tsong and D.J. Barber, 

43. S. Chereckdjian and I.H. Wilson, 

44. R.S. Nelson and D.J. Masey, 

45. S.K. Das, M. Kaminsky, and G. Fenske, 

46. G. Carter, J.S. Colligon, and M.J. Nobes, 

47. J. Belson and I.H. Wilson, 

48. P. Sigmund, 

49. R.S. Barnes and D.J. Mazey, 

50. M. Kaminsky, 
51. W. Primak,  

52. L. H. Milaceck, R. D. Daniels and J. A. Cooley,  

53. W. Bauer and G. J. Thomas,  

54. G. Carter and J. Colligon,  

55. J. Roth, R. Behrisch and B. M. U. Scherzer,  

56. J. G. Martel, R. St.-Jacques, B. Terreault and G. Veilleux,  

57. S. K. Erents and G. M. McCracken,  

58. S. K. Das and M. Kaminsky,  

59. S. K. Das and M. Kaminsky,  

60. M. Kaminsky and S. K. Das,  

61. R. S. Barnes,  
   Phil. Mag., 5, 635, (1960).

62. J. H. Evans,  

63. R. S. Nelson,  
   Phil. Mag., 9, 343, (1964).

64. M. Kaminsky, S. K. Das and G. Fenske,  

65. G. B. Jeffery,  
   Phil. Trans. R. Soc. Lond., 221, 265, (1921).

66. Huber and Schiltknecht,  

67. S. S. Gill,  
   PhD, Univ. of Surrey, Dept. of Electrical Eng., June (1980).

68. J. Lindhard, M. Scharff and H. E. Schiott,  
69. J.P.Biersack and J.F.Ziegler,

70. P.J.Goodhew,
Electron Microscopy and Analysis, Wykeham Science series.

71. R.H.Wert and J.E.Castle,

72. J.F.Singleton,
Phd, Univ of Surrey, Dept. of Electrical Eng.,(1979).

73. P.Sigmund,

74. T.M.Nenadovic,Z.B.Fotiric, and T.S.Dimitrijevic,

75. J.S.Colligon and M.H.Patel,

76. H.H.Andersen and H.L.Bay,

77. O.E.Almén and G.Bruce,

78. E.P.EerNisse,

79. A.R.Oliva Florio, E.V.Alonso, R.A.Baragiola and J.Ferron,

80. I.H.Wilson, S.S.Todorov and D.S.Karpuzov,

81. D.Ghose, D.Basu and S.B.Karmohapatro,

82. I.H.Wilson,

83. R.Kelly,

84. H.Naramoto, C.W.White, J.M.Williams, C.J.McHargue, O.W.Holland,
M.M.Abraham, and B.R.Appleton,

85. C.W.White, G.C.Farlow, C.J.McHargue, M.P.Angelini, P.S.Sklad,
M.B.Lewis and B.R.Appleton,
IBMM,Cornell, USA.,(1984) to be published.
86. A. Heising, 
Quartz Crystals for Electrical Circuits, Van Nostrand Com. 
Inc. USA. (1946).

87. J. Bøttinger, J. A. Davies, P. Sigmund and B. Winterbon, 

88. P. L. F. Hemment, 

89. D. J. Arrowsmith, E. A. Culpan and R. J. Smith, 
Proc. Symp. Anodizing aluminium, Univ. Aston, Birmingham, April (1976), 
Aluminium Federation, Portland House, London.

90. R. B. Hemphill, 