DEVELOPMENT OF QUARTZ RESONATOR TECHNIQUES FOR THIN FILM MEASUREMENTS

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Presented for consideration for the degree of Doctor of Philosophy in the department of Electronic and Electrical Engineering.

April 1999

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ABSTRACT

The objective of the current work has been to develop a system which will allow continuous monitoring of areal mass density, lateral stress, and temperature during a process with real time presentation of results making possible either manual or automated control of the process. The system uses three quartz resonators of different crystallographic cuts (AT cut, BT cut and SC cut) in the same environment. The development of an algorithm to solve a system of equations representing a complete representation of the temperature characteristics of the three resonators is presented. This is followed by an analysis of the potential accuracy of the system and the limitations imposed by the assumptions made in the mathematical models of the system. Sputtering yields were verified using Rutherford backscattering analysis. Experimental apparatus including the physical mounting of the resonators in an experimental environment, details of the oscillator circuitry and frequency counter, and use of a personal computer for data acquisition and control are described. The results presented show, in addition to the mass change and lateral stress build-up which occur when sputtering a gold film with an argon ion beam, the radiation induced temperature rise and the radiation induced stress caused by temperature gradients. An experiment using beams of Sb\(^+\) at 50keV and Sb\(_2\)^+ at 100keV has been used to demonstrate the enhancement of sputtering yield that occurs when Au films are bombarded with monomers and dimers of Sb at the same energy per atom. Results are compared with simulations using both the TRIM program and molecular dynamics code.
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DEDICATION
I dedicate this work to my wife Angela who always believed I would finish and to the memory of our daughter Stephanie and of my parents John and Alice who sowed the seeds for a lifetime of learning.

ACKNOWLEDGEMENT
I would like to acknowledge the support of all my co-workers in The Department of Electronic and Electrical Engineering at the University of Surrey. I would like to single out Chris Jeynes, John Mynard and my supervisors Ian Wilson, Ken Stephens, Roger Webb and Brian Sealy for all their help and encouragement over the years. Thank you, everyone.
The subject of this thesis is the development of quartz resonator based techniques for in-situ measurements of mass change, lateral stress change and temperature of thin films during ion implantation processes. The initial focus was on development of suitable apparatus, algorithms and procedures which would allow automated real time measurements during implantation. After initial experiments which attempted to define a system and prove the validity of that system, several areas of application were explored. This led to a study of the literature on sputtering and simulation of sputtering and identification of areas where the techniques developed could provide additional experimental knowledge about the stress behaviour in thin films during implantation and sputtering.

Section 1.1 details the development of quartz resonators as sensors in thin film processes. Following a look at the development of the general topic of atomic collisions in solids in section 1.2, sections 1.3 and 1.4 present brief summaries of the development of sputtering theory and simulation of sputtering from the literature respectively. Particular attention is paid to sputtering by high mass ions and ionised clusters or molecules where nonlinear effects become important or predominant. Section 1.5 presents a brief overview of Rutherford backscattering analysis.

The first two sections of chapter 2 describe the experimental investigation of physical changes on quartz
resonators and development of the oscillator circuitry. The focus was on gaining an understanding of problem areas and development of a system which would produce reliable data. This is followed by a section describing the mathematical equations used to represent the three resonator system and the algorithms developed for their solution. The development of the software is covered in the last section.

The development of the experimental apparatus and experimental procedures are described in chapter 3.

The results of two experiments using argon to sputter gold films, the second of which also used Rutherford backscattering (RBS) to verify the sputtering yields, are presented in section 4.1. This includes a closer look at the sources of error especially in the measurement of stress. Section 4.2 describes an attempt to use the system to monitor implantation of oxygen into silicon nitride in a Plasma Immersion Ion Implanter (PIII).

Over the last two decades, there has been growing interest in development of the theory of collisions between energetic particles and solids (Andersen, 1993 and Thompson, 1981a). The work on the interaction between energetic clusters of atoms and solids has been of increasing interest. Section 4.3 describes an experiment using beams of Sb\(^+\) at 50keV and Sb\(_2\)\(^+\) at 100keV which demonstrates the enhancement of sputtering yield that occurs when Au films are bombarded with monomers and dimers of Sb at the same energy per atom. Also described are the
results of the first stage of an experiment looking at the effect of temperature on the sputtering yields of Sb\(^+\) and Sb\(_2^+\).

In section 4.4 the results are compared with those found in the literature and with molecular dynamic and binary collision approximation simulations.

The final chapter summarises the main conclusions of the work and discusses several ways in which the work might be continued.

1.1 QUARTZ RESONATORS AS THIN FILM SENSORS.

The use of quartz crystals to produce high stability oscillators was already being explored in the 1920s and by the mid 1930s the use of the AT-cut resonator was well established for transmitter frequency control (Terman, 1937, Section 70). During the second world war research workers identified many other useful cuts of quartz and the production of millions of units for use in military radio equipment had refined manufacturing techniques to the point that stabilities of a few parts per million over normal ambient temperatures and years of use were possible. (Heising, 1946)

The AT-cut and BT-cut resonators were developed theoretically and experimentally from the rotated Y-cut family of resonators of which they are a part to produce resonators which had a low coefficient of frequency change with temperature and which would oscillate reliably in the desired thickness shear mode. The orientation of the AT-
Figure 1.1
The AT- and BT-cuts in quartz relative to the major and minor rhomb faces. The X-axis is normal to the plane of the diagram. The r- and R-faces make an angle of 38°13' with the Z-axis. (Bottom, 1982)

cut and BT-cut resonator crystals relative to the quartz crystal axes are shown in figure 1.1. The sensitivity of the shape of the frequency versus temperature curves to changes in the angles relative to the Z axis are shown in figure 1.2.

A significant part of this work was the development of suitable holders which would minimise the side effects produced by changes in mechanical stress and loading. The development of deposited metal electrodes directly onto the crystal surfaces and the optimisation of the electrode shapes led to subsequent development of the resonators as sensors (Lu, 1984).

The first reported work on the use of a quartz crystal resonator for measurement of the thickness of thin films was by Sauerbrey (Sauerbrey, 1957 and Sauerbrey, 1959)
Figure 1.2a
Frequency-temperature curves for the AT-cut operating at 4 MHz vs. the angle of orientation. (Bottom, 1982)

Figure 1.2b
Frequency-temperature curves for the BT-cut at different values of the angle $\theta$. (Bottom, 1982)
summarized in Lu, 1984). Sauerbrey established an approximately linear relationship between mass change and frequency change for thin films deposited onto quartz resonators. This was based on the assumption that for small mass change, the addition of foreign mass can be treated as an equivalent mass change of the crystal itself. This is expressed as

$$\Delta f = -C_f m_f$$

where $\Delta f = f_c - f_q$, $C_f = 2f_q^2/\rho_q v_q$ and $m_f$ is the mass of the added film and where $f_c$ is the resonant frequency of the resonator with the added film, $f_q$ is the resonant frequency of the resonator without the added film, $\rho_q$ is the density of the quartz and $v_q$ is the propagation velocity in the quartz. Since $C_f$ is proportional to the square of the frequency, it is apparent that it will only be valid over a limited change in frequency. Behrndt and Love (Behrndt, 1961 and Behrndt and Love, 1962) suggested that the slope be defined as $C_f' = 2f_c^2/\rho_q v_q$ making

$$\Delta f = -C_f' m_f.$$  

This provided a correction which was useful for repeated small changes in mass but which still did not allow for a continuous change of slope during a large change of mass. If the above equation is written in differential form and integrated,

$$dm_f = -\left(\rho_q v_q/2f_c^2\right)df_c$$  \hspace{1cm} (3)

$$\int_0^{m_f} dm = -\left(\rho_q v_q/2\right)\int_{f_q}^{f_c} \left(1/f_c^2\right)df_c$$  \hspace{1cm} (4)

the result is

$$m_f = (\rho_q v_q/2)(1/f_c - 1/f_q).$$  \hspace{1cm} (5)
This shows that the mass change is proportional to the change in period with a constant slope which is determined only by the physical constants of the quartz. This equation was found to agree well with experimental data for large changes in mass if the material being deposited had an acoustic impedance near to that of the quartz. Theoretical models were developed (Lu and Lewis, 1972) which yielded the following equations relating the mass-frequency relationship to the acoustic impedance of the deposited film.

\[
\frac{\rho_f t_f}{\rho_q t_q} = \tan^{-1}(Z \tan \pi F) \quad \frac{\pi Z(1-F)}{n}
\]

(6)

where \(\rho_f\) and \(\rho_q\) are the densities and \(t_f\) and \(t_q\) the thicknesses of the film and the quartz respectively, \(Z\) is the ratio of the acoustic impedance of the deposited film relative to that of the quartz crystallographic cut being used and \(F = \left( \frac{f_q - f_c}{f_q} \right) / f_q\)

(7)

An examination of these effects shows that for added mass less than about 10% of the crystal mass, the deviations from the linear approximation are small for most materials.

EerNisse (EerNisse, 1972) showed that by using AT-cut and BT-cut quartz resonators in the same environment, the stress and mass effects of thin films deposited on their surfaces could be separated. This was because the stress coefficients of the two cuts were approximately the same in magnitude but opposite in sign. The equation relating frequency changes to changes in mass and stress is

\[
\frac{\Delta f}{f_0} = KAS \quad \frac{\Delta M}{\rho_q t_q}
\]

(8)
where \( f_0 \) is the starting frequency, \( \rho_q \) is the density of quartz and \( t_q \) is the thickness of the quartz.

\[ K_{AT} = 2.75 \times 10^{-12} \text{ cm}^2/\text{dyne} \text{ and } K_{BT} = -2.65 \times 10^{-12} \text{ cm}^2/\text{dyne} \]

EerNisse (EerNisse, 1975) suggested the use of a three resonator system to measure mass, stress and temperature simultaneously. The third resonator proposed was another AT-cut resonator with a different temperature characteristic. He suggested using the predominant term in the temperature effects series expansion

\[ \Delta f/f_0 = a_1\Delta T + a_2\Delta T^2 + a_3\Delta T^3 + \ldots \quad (9) \]

to represent the temperature effect of each resonator in a system of three equations in three unknowns. Each of the three equations takes the form

\[ \Delta f/f_0 = a_n\Delta T^n + K\Delta S/t_q - \Delta M/\rho_q t_q. \quad (10) \]

where \( n \) is the number of the predominant term in the temperature effects series expansion.

Chereckdjian (Chereckdjian, 1984) used a third dummy resonator in the same environment with a fine wire thermocouple attached to establish a reference temperature at which all readings were taken to minimize the temperature effects.

1.2 ATOMIC COLLISIONS IN SOLIDS (Townsend et al, 1976)

When an energetic atom or ion encounters a solid surface it loses energy to the atoms of the solid until its energy is reduced to the average energy of the surrounding atoms. The three main processes of energy loss are (1) direct collisions between the ion and a screened nucleus,
(2) excitation of electrons bound in the solid and (3) charge exchange processes between the ion and the atoms of the solid. All three processes are energy dependent and so make different contributions to the energy loss along the path of the ion. The total energy loss of an incoming ion is the sum of the losses due to the three processes. The three processes can be treated separately to simplify the analysis and it will be seen later that depending on the energy of the incoming ion and the ion and atom species involved, one process will frequently be dominant. The range of the incoming ions is of major interest for implantation processes because the goal of the process is frequently to achieve a desired concentration of the ion species at a particular depth. Also of interest when implanting into crystalline solids is the introduction of damage to the crystal structure caused by the atomic collisions which occur as the incoming ion loses energy. Of particular interest to the work presented in this thesis are processes which cause mass and stress changes in the films. Mass loss will be caused by sputtering where the incoming ion transfers enough energy to the atoms of the target material to remove some of them from the target surface. Changes in stress in films can be made by displacements in the film caused by collisions of the ion as it slows down and loses energy. Sputtering will be discussed in section 1.3.

In the energy range between 5 and 500 keV the dominant energy loss for heavy ions is by elastic interactions
Figure 1.3
A collision between two particles in a laboratory co-ordinate system. (Townsend et-al, 1976)

Figure 1.4
A collision between two particles in a centre of mass frame co-ordinate system. (Townsend et-al, 1976)
between the ion and a screened nucleus. We can approach the problem by considering two body events in a centre of mass coordinate system to predict the energy loss, $T$, the cross section for energy transfer, $d\sigma_{\text{nuclear}}$, and the angle of scattering. The trajectory of the particles for a two body collision event is shown in figure 1.3 for a laboratory frame and the equivalent collision in a centre of mass frame is shown in figure 1.4. In the laboratory frame the momentum must be

$$M_1 u_1 = (M_1 + M_2) v_{0\text{H}}.$$  \hspace{1cm} (11)

This is equivalent to moving the particle $M_2$ in the centre of mass frame at a velocity

$$u_2 = - \frac{M_1 u_1}{(M_1 + M_2)}.$$  \hspace{1cm} (12)

In an elastic collision both energy and momentum are conserved so

$$M_1 u_1^2 + M_2 u_2^2 = M_1 v_1^2 + M_2 v_2^2$$ \hspace{1cm} (13)

and

$$M_1 u_1 - M_2 u_2 = M_1 v_1 - M_2 v_2$$ \hspace{1cm} (14)

which implies

$$u_1 = v_1 = \frac{M_2 u_1}{M_1 + M_2}$$ \hspace{1cm} (15)

and

$$u_2 = v_2 = \frac{M_1 u_1}{M_1 + M_2}.$$ \hspace{1cm} (16)
Figure 1.5
Vector diagrams of the velocities which relate the two coordinate systems. (Townsend et-al, 1976)

Referring to the vector diagrams shown in figure 1.5 enables us to relate the angles in the two systems by

\[ V_2 \cos \phi + V_2 \cos \theta_2 = u_2 \quad (17) \]
\[ V_2 \sin \phi = V_2 \sin \theta_2 \quad (18) \]

which can be reduced to

\[ \sin \phi = \tan \theta_2 (1 - \cos \phi). \quad (19) \]

The recoil energy of the struck atom is the energy transferred \( T = E_2 = \frac{1}{2} M_2 v_2^2 \) but

\[ v_2^2 = 2(1 - \cos \phi) \frac{M_1^2 u_1^2}{(M_1 + M_2)^2} \quad (20) \]

so

\[ T = \frac{4M_1 M_2}{(M_1 + M_2)^2} E_1 \sin^2 \left( \frac{\phi}{2} \right) \quad (21) \]

which makes the upper limit for energy transfer in a head on collision

\[ T_{\text{max}} = \frac{4M_1 M_2}{(M_1 + M_2)^2} E_1. \quad (22) \]
In order to treat ion/atom collisions as classical elastic collision events it is necessary to choose a form for the repulsive potential, \( V(r) \), between the incoming ion and a target atom, where \( r \) is the interparticle separation, in order to calculate a scattering angle. Historically the Coulomb, Bohr and Born-Mayer potentials were of this form. The Coulomb potential is the repulsive force between the two nuclei ignoring any screening effect by the associated electrons and is expressed analytically by

\[
V(r) = \frac{Z_1 Z_2 e^2}{r} \tag{23}
\]

where \( Z_1 \) and \( Z_2 \) are the atomic numbers of the atoms involved, \( e \) is the electronic charge and \( r \) is the separation of the atoms. The Coulomb potential gives good results where collisions in which \( 0 < r < a_B \) predominate, where \( a_B \) is the radius of the first Bohr orbit in hydrogen (\( =0.53 \) Å). The Born-Mayer potential is expressed analytically as

\[
V(r) = A \exp(-r/b) \text{ where } A \text{ and } b \text{ are constants.}
\]

The Born-Mayer potential gives good results where collisions in which \( r > a_B \) predominate. The Bohr screened Coulomb potential expressed analytically as

\[
V(r) = \frac{Z_1 Z_2 e^2}{r} \exp(-r/a) \tag{24}
\]

gives better results over the range where \( r \) is of the same order as \( a_B \) but falls off too quickly for large values of \( r \). A variation of the screened Coulomb potential (Lindhard, Scharff, Schiott, 1963) known as the LSS potential gives
good results for most applications. The LSS potential is expressed analytically as

\[ V(r) = \frac{Z_1 Z_2 e^2}{r} \phi_{\text{TF}}(r/a) \]  

(25)

where \( \phi_{\text{TF}}(r/a) \) is the Thomas-Fermi screening function expressed analytically by Lindhard as

\[ \phi_{\text{TF}}(r/a) = 1 - (r/a)[(r/a)^2 + 3]^{-1/2} \]  

(26)

where \( a \sim a_{\text{b}}(Z_1 Z_2)^{-1/6} \). A comparison of various proposed interatomic potentials is shown in figure 1.6.

![Figure 1.6](image)

A comparison of various proposed interatomic potentials between two copper atoms. (Townsend et-al, 1976)

The development of a universal screening potential is described by Ziegler et-al (1985). Figure 1.7 compares this universal screening potential with other interatomic potentials in terms of a screening function, \( \Phi_0 \). The defining equations are given in the figure.
Figure 1.7

The reduced screening function has been fitted to the analytic expression shown above with four exponential terms. This screening function is identified as \( \Phi_U \), a universal screening function with its argument, \( x \), being defined as \( x = \frac{r}{a_u} \), where \( a_u \) is the universal screening length shown above. (Ziegler et al., 1985)

The LSS cross section for nuclear collisions is appropriate for all values of \( Z_1 \), \( Z_2 \), \( M_1 \), \( M_2 \). It is therefore sensible to relate the cross section to dimensionless energy and range parameters \( \varepsilon \) and \( \rho \),

\[
\varepsilon = \frac{a M_2}{Z_1 Z_2 e^b (M_1 + M_2)}
\]

(27)

\[
\rho = \frac{4 \pi a^2 M_1}{R N M_2 (M_1 + M_2)^2}
\]

(28)

where \( R \) is the range, and \( N \) the number of atoms per unit volume.

The stopping cross section, \( \sigma \), is related to these parameters by
Figure 1.8
The differential cross section for elastic nuclear collisions. The calculation from the LSS theory using a Thomas-Fermi potential approaches the Rutherford scattering cross section at high energy. For comparison the cross section for an inverse square law potential is also shown. The cross section and energy axes are plotted in terms of universal functions (see text). (Townsend et-al, 1976)

The universal curves computed from this expression are shown in figures 1.8 and 1.9. Figure 1.8 is a plot of the differential cross section computed by LSS using a Thomas-Fermi model to give $d\sigma$ in terms of energy transfer as

$$
\frac{d\varepsilon}{d\rho} = \sigma \frac{(M_1 + M_2)}{4\kappa e^2 Z_1 Z_2 M_1} .
$$

(29)

$$
d\sigma = \frac{k\alpha^2}{2t^{1/2}} f(t^{1/2}) dt
$$

(30)

since

$$
t = \varepsilon^2 \sin^2 \left( \frac{\phi}{2} \right) = \varepsilon^2 \left( \frac{T}{T_{\text{MAX}}} \right) .
$$

(31)
Figure 1.9
Nuclear and electronic stopping cross sections in reduced units. The curved line is the nuclear cross section computed from the LSS theory of figure 1.8. Electronic stopping is proportional to velocity and for comparison the cross section for the inverse square law potential is also shown. (Townsend et-al, 1976)

It can be seen that the LSS and Coulomb potentials predict the same scattering cross sections at high energies where we measure Rutherford scattering. In the intermediate energy range there is also some agreement with the cross section predicted by the inverse square potential.

Figure 1.9 shows the universal cross section curve in terms of the cross section and velocity of the primary ion. Here the elastic (nuclear) energy losses are compared with the inelastic energy losses.

The universal screening function presented in figure
1.7 can be used to compute a universal reduced nuclear stopping function, $S_n$, which is shown in figure 1.10 where it is compared with nuclear stopping functions using other interatomic potentials.

We can also use a classical approach when considering the inelastic energy loss from the passage of the ion through the electronic cloud of the target atom. Again one can trace the historical approach from the early theory of Bohr (1913) where he considered a fully ionised atom striking a second ion. The primary ion will be stripped of all its electrons if it is moving at a higher velocity than the electrons of the K shell ($v > Z_1^e Z_2^e / h$) so the rate of energy loss will depend on the closeness of approach to the second atom and thus the number of electrons which can be excited. Bohr wrote the energy loss as

$$\frac{dE}{dx}_{\text{electronic}} = \frac{4\pi Z_1^2 e^4}{mv^2}$$

where $B$ is a measure of the penetration through the electron shells.

There is no universal curve which describes the electronic loss for all ion pairs, as there is for elastic collisions, and for amorphous materials a good approximation is to assume the energy loss is proportional to the ion velocity. The Lindhard, Scharff (1961) formulation is

$$\frac{dE}{dx}_{\text{electronic}} = \xi e \frac{8\pi e^2 N_a Z_1 Z_2}{(Z_1^{2/3} + Z_2^{2/3})^{3/2}} \frac{v}{v_0}$$

where $v$ is the velocity, $v_0$ the Bohr velocity ($Z_1^e Z_2^e / h$) and
Universal reduced nuclear stopping calculated using the universal screening potential shown in figure 1.7. The result is shown in reduced co-ordinates in the spirit of LSS theory but with the screening length of LSS theory, $a_L$, being replaced with that of figure 1.7, $a_u$. The reduced nuclear stopping power calculations are shown as small circles over the 8 decades of energy. Through these points has been fitted the analytic formula identified in the figure as: Universal Nuclear Stopping. This function agrees with the calculated nuclear stopping within a few percent. Also shown are the nuclear stopping calculations based on the four classical atomic models. (Ziegler et-al, 1985)

Numerically $\xi \sim Z^{1/6}$. When written in terms of $\varepsilon$ and $\rho$ the electronic energy loss is

$$\frac{d\varepsilon}{d\rho}_{\text{electronic}} = k\varepsilon^{1/2} \tag{34}$$

with

$$k \approx \frac{0.079 Z_1^{1/6} Z_1^{1/2} Z_2^{1/2} (M_1 + M_2)^{3/2}}{(Z_1^{2/3} + Z_2^{2/3})^{3/4} M_1^{3/2} M_2^{1/2}} \tag{35}$$
that is, a linear energy loss with velocity and a proportionality constant a function of each ion pair.

The cross section for transfer of an electron from one ion to another is a maximum if the ion velocity is close to the orbital velocity of the electron. This is a well defined process for inner shell electrons but as the ion slows down the outer electron shells will offer a range of states suitable for charge transfer, particularly for heavy ions. For light ions Bohr (1948) proposed capture and loss cross section as

$$\sigma_{\text{capture}} \sim 4\pi a_B^2 Z_1^2 Z_2^{1/3} (v_0/v)^5$$

$$\sigma_{\text{loss}} \sim \pi a_B^2 Z_1^{-1} Z_2^{2/3} \left(\frac{v_0}{v}\right)$$

whereas for heavy ions Bohr and Lindhard (1954) suggest

$$\sigma_{\text{capture}} \sim \pi a_B^2 Z_1^2 Z_2^{1/3} \left(\frac{v_0}{v}\right)^3$$

$$\sigma_{\text{loss}} \sim \pi a_B^2 Z_1^{1/3} Z_2^2 \left(\frac{v_0}{v_1}\right)^3.$$  \hfill (36)

If $v_1$ is the velocity of outer electrons on the moving ion then for heavy ions the capture and loss cross sections are symmetric about $Z_1$ and $Z_2$. Charge exchange losses represent a small fraction of the total energy losses, typically a few percent.

The preceding theories indicate the mechanisms of energy loss so we are now able to predict the total path covered by the ion as it is brought to rest from an initial energy $E_0$. It is

$$R_{\text{total}} = \int_{0}^{E_0} \frac{-dE}{(dE/dx)_{\text{total}}}.$$  \hfill (40)

At high energies, where electronic losses dominate, the
particle is only slightly deflected but at the end of the path the elastic nuclear collisions produce large angle scattering. A more useful measure of range, because it relates directly to the depth profile of the implanted ions, is the projected range, \( R_p \), defined as the average component of range perpendicular to the target surface. The early theory of Lindhard and Scharff (1961) provides an approximate relation between the total and projected ranges in the case of nuclear stopping as

\[
\frac{R_{\text{total}}}{R_p} \approx 1 + \frac{M_i}{3M_t} \quad (41)
\]

The discussion so far has assumed an amorphous target. When the target is crystalline and the direction of the incoming ions is aligned or nearly aligned with the crystal structure, some of the ions will enter the target at locations where the probability of a nuclear collision is greatly reduced so they will travel deeper into the target before coming to rest. This is known as channelling. The channelled ions are steered through the channel by glancing angle collisions with the atoms surrounding the channel and are thus subjected to electronic losses over a relatively large distance before losing enough energy to be deflected into a non-channelled direction.

We have looked at what happens to an incoming ion as it loses energy and comes to rest in a target. In the process of losing energy it has collided with a large number of target atoms to which it has transferred enough energy to make them into moving particles which in turn
will collide with other target atoms. The entire series of collision events resulting from a single ion entering a target is known as a collision cascade. Some of these collisions will result in atoms of the target arriving at the surface with enough energy to leave the surface. This is known as sputtering. Also associated with the collision cascade is damage to the target atomic structure in the form of vacancies and interstitials. It is this target damage which produces stress in the target material.

The subject of the interatomic repulsive potentials has been discussed. The attractive potentials which oppose them in a solid become important when dealing with events at the surface. For sputtering calculations a planar surface binding energy, $U_0$, is considered adequate for single atom events. $U_0$ is of the order of a few eV for metals and acts on the component of velocity perpendicular to the surface. The energy and angle of the particle leaving the surface will be

$$E' = E - U_0,$$  \hspace{1cm} (42)

$$\cos \theta' = \frac{(E \cos^2 \theta - U_0)/(E - U_0)}{1/2}$$  \hspace{1cm} (43)

where $E$ and $\theta$ are the energy and angle before leaving the surface and $E'$ and $\theta'$ are the energy and angle after leaving the surface.

1.3 SPUTTERING THEORY  \hspace{1cm} (Thompson, 1981a)

Linear cascade theory (Sigmund, 1969) predicts that the sputtering yield is linearly dependent on the energy deposited into elastic collision events at the target
The general result from collision cascade theory, assuming a planar surface barrier potential, gives the calculated sputtering (Sigmund, 1969) yield, $S_0$, as

$$S_0 = \frac{\Delta x \cdot F_p(0, E, \eta)}{\pi^2 U_0}$$

where ($F_p$ is the spatial distribution of deposited energy, $E$ is the incident ion energy, $\eta$ is the cosine of the angle between the incident ion path and the surface normal,) $U_0$ is the surface binding energy and $\Delta x$ is a depth over which the deposited energy contributes to $S_0$. Linear cascade theory assumes that all collisions are between a moving atom and a stationary atom. When the number of target atoms set into motion in a collision cascade is such that this assumption is no longer valid the collision cascade gradually becomes a high density cascade. High density cascade effects show up as a departure from this model; i.e. a much higher sputtering yield, $S_h$, is measured than is predicted by the model.

The "thermal" spike model (Thompson and Nelson, 1962), (Nelson, 1965) and (Kelly, 1977) was a significant step in the development of theoretical treatments of the enhancement of sputtering yield due to high density cascade effects. The early (Thompson and Nelson, 1962) supposition was that, as a result of the collision cascade, a momentary localized large increase in "temperature" occurs such that surface atoms are emitted via evaporation. It was later (Johar and Thompson, 1979) argued that the high rate of
energy deposition in the surface region manifests itself as a collisional spike which causes a reduced surface binding energy leading to enhanced sputtering yields. Models were then developed to describe the initial "temperature" distribution and its time evolution. Thermal sputtering can be subdivided into two separate processes on the basis of time; prompt thermal (\(10^{-12}\) to \(10^{-11}\) s) after ion impact, and slow thermal, which occurs on a time scale \(>10^{-10}\) s. The total sputtering yield is the sum of the yield due to the linear cascade, \(S_c\), and the yield due to thermal effects, \(S_{\text{Thermal}}\). The prompt thermal regime corresponds to the time necessary for the energy deposited into atomic motion to be distributed to all atoms in the cascade volume. The slow thermal regime corresponds to a time scale sufficiently long for atomic motion and electronic excitation to reach equilibrium. However, by this stage of the cascade quenching, the cascade volume will have almost returned to the macroscopic target temperature so thermal emission would only be expected for the most volatile materials. For this and other reasons, it is concluded that a contribution to sputtering by a prompt thermal process is subject to serious objections. (Thompson, 1981a)

In a similar model (Sigmund and Claussen, 1981), the spike volume is treated as gas-like; i.e. the kinetic energy distribution of the atoms is described by Maxwell-Boltzmann statistics and energy transport is determined by a temperature dependent thermal diffusivity, \(K\), obtained from kinetic gas theory as (Sigmund, 1974)
\[ K = \frac{25}{48} \left( \frac{kT}{\lambda_0 a^2 \pi N_2} \right)^{1/2} \]  

(45)

where \( k \) is Boltzmann's constant, \( \lambda_0 = 24 \) and \( a = 0.0219 \) nm are constants appropriate to the approximate Born-Mayer potential applied to low energy recoils. Assuming a cylindrical spike geometry with initial spike width \( \langle \rho_0^2 \rangle^{1/2} \) and an initial temperature distribution based again on current cascade theory, the heat conduction equation

\[ \frac{\partial T}{\partial t} = K \frac{\partial^2 T}{\partial x^2} \]  

(46)

can be solved. Then, as in the previous model, the integrated evaporation flux yields the thermal sputtering yield. This is found to be

\[ S_{Th} = \frac{0.036 \lambda_0 a^2 F'_D(0,E,\eta)^2}{U_0^2 f\left( \frac{U_0}{\theta_v} \right)} \]  

(47)

where \( F'_D(0,E,\eta) \) is the energy deposited per unit path length (taken for calculational purposes as the value at \( x=0 \)) and \( f(\xi) = (1+\xi^2) \exp(-\xi) + \xi^3 \int^\infty (e^{t/t}) \, dt \) where \( \theta_v = \frac{F'_D}{2\pi N} \langle \rho_0^2 \rangle \) is the bulk deposited energy density. Since \( \theta_v \propto F'_D \), then \( S_{Th} \propto F'_D^m \), where \( m \) is somewhat greater than 2. For molecular ion sputtering we note that \( S_{mol}/nS_{atom} \propto n^3 \). This model then predicts good qualitative agreement with the experimentally observed (Thompson, 1981b) \( \sim F'_D^3 \) dependence of yield enhancement above \( S_c \) values of around 10 and also with experimentally observed (Johar and Thompson, 1979) molecular enhancement factors.

The concept of a critical sputtering yield, above which non-linear behaviour occurs was also adopted in a
collisional model extended to accommodate very high sputtering yields. (Thompson, 1981b) The basic requirements considered in modifying the collisional model are now discussed.

i) For $S_{\text{h}}$ values greater than the critical values, as obtained from the onset of non-linear sputtering, atoms will be sputtered from layers that originally lay beneath the surface layer and are uncovered as the sputtering proceeds during the cascade propagation. Then as $S_{\text{h}}$ increases, the depth from which sputtered atoms may originate increases. This is consistent with cascade produced experimentally observed surface topography in the form of craters. Thus, the deposited energy which would participate in sputtering is that integrated over the depth of the craters, $h_{s}$, i.e.

$$S_{\text{h}} = \frac{1}{n_{0}U_{0}} \int_{0}^{h_{s}} F_{0}(x,E,n)dx$$  \hspace{1cm} (48)$$

where $S_{\text{h}}$ is now the non-linear sputtering yield. Assuming that the craters formed have a hemispherical geometry, $h_{s}$ is determined from $S_{\text{h}}$ as $h_{s} = ((3/2)S_{\text{h}}/N_{0})^{1/3}$. The agreement between $S_{\text{h}}$ and $S_{\text{h}}$ is reasonably good but as the incident ion energy increases, $S_{\text{h}}$ is consistently greater than $S_{\text{h}}$ for all ions. This can be qualitatively explained by the following additional requirements in a modified collisional model.

ii) The surface binding energy may not have a unique value in the presence of a high density cascade and significant reductions are reasonable for two reasons. First, it has been observed that a significant factor of sputtered particles evolve as clusters of two or more atoms. These
clusters are consistent, both with crater formation and a reduced binding energy per atom for emission from the surface. Secondly, the presence of defects created in the surface by the collision cascade could effectively reduce the average surface binding energy.

iii) The development of surface craters would be responsible for producing higher measured sputtering yields than corresponding to a planar surface. Such an increase has been measured (Whitton et al, 1980) and discussed theoretically (Thompson, 1981b).

Another approach to modelling the high density cascade effects was to use a shock wave model described conceptually by Carter (1979) as follows: As a heavy ion traverses a solid it loses energy at the rate of some hundreds of electron volts per atomic layer which is initially to a very few atoms. These atoms will recoil with forward directed momentum but with a substantial translational component to the projectile path, at very high velocity $10^3$ - $10^5$ m/s. Such velocities greatly exceed the speed of sound (at which normal thermal transport processes occur). Under such high velocity conditions the transport processes may no longer be treated as those pertinent to a uniform or weakly perturbed gas but must be associated with shock wave propagation. It is thus suggested that the core of the spike is a source of continuously developing shock fronts and that the atoms in this core initially possess very high mean energies (hundreds of eV). Characteristics of shock fronts are that
they rapidly dissipate into the surrounding medium until transforming to normal sound waves and that the shock front layer thickness is very small. Rarefaction waves also move into the shock fronts from the surrounding medium and are held to be responsible for the backwards ejection (sputtering) of solid material under hypervelocity impact. One may approach the problem (of making quantitative predictions of the energy transport processes involved) in a crude kinematic manner as follows. We assume that projectile deposits \( \sim 1000 \text{ eV/atomic layer} \). Then because there is a collective collision process, the effective energy for atomic displacement may be much reduced, perhaps to the order of 1 eV (i.e. of the magnitude of the atomic heat of melting) as compared to the single collision displacement energy of 15-35 eV per atom. One estimate of the number of atoms displaced in this plane is \( \approx 500 \) i.e. the extent of the displacement process would encompass \( \approx 20 \) atomic distances. In view of the preferential forward motion of the initially struck atoms, which would be partly off-set by backward moving recoils originating from deeper layers, it would be estimated that the shocked volume would possess an effective cross-sectional area of the order of \( 10^{-14} \text{ cm}^2 \). The time for distribution of the initial energy would be determined by the velocities of the slowest moving atoms at the boundary of the shock say \( 10^3 \text{ m/s} \), and a collision distance of \( 10^{-10} \text{ m} \), i.e. \( 10^{-13} \) secs. In this shock period the atoms are moving with energies in the range 1-100 eV (velocities between \( 10^2 \) and \( 10^4 \text{ m/s} \)) so that the flux
of atoms across any plane lies in the region of $10^{30}$ atoms cm$^{-2}$ sec$^{-1}$. The number of atoms 'ejected' during the shock is thus $\approx 10^{30} \cdot 10^{-14} \cdot 10^{-13} = 1000$ which may be identified with the sputtered atom yield if the surface binding energy is reduced to zero or has a low value, which seems plausible in the absence of atomic order in the shocked region.

Kitazoe and Yamamura (1980) developed the shock wave model based on numerical solution of hydrodynamic equations. This approach was found to agree well with experimental data if the cascade density was high enough to make the hydrodynamic assumptions valid.

The temperature dependence of sputtering yields was explored experimentally by Nelson (1965) whose results showed a constant sputtering yield for Au irradiated with 45 keV Xe$^+$ ions between $-180^\circ$C and $500^\circ$C. At higher temperatures the sputtering yield rose to about double the lower temperature value at $950^\circ$C. It was later shown (Besocke et al, 1982) that there is a small rise in sputtering yield, about 10% from $30^\circ$C to $800^\circ$C, but that the large rise in yield above $500^\circ$C reported by Nelson (1965) was entirely due to evaporation. The temperature dependence of the sputtering yield and the temperature evolution during spike processes were explored in greater depth by Sigmund and Szymonski (1984). The conclusions of interest are 1) that the ambient temperature has limited effect on the high temperature part of the sputtering process which is predominant when "spike" conditions exist and 2) that the ambient temperature as well as beam current
density effects in conjunction with thermal time constants relating to the sample and its mounting can have a significant effect on the low temperature part of the sputtering process which lasts for a much longer time.

In a review of nonlinear effects Andersen (1993) summarized later developments of sputtering theory and experimental results and the developments in computer simulation of cluster impacts which will be covered in the following section. Andersen (1993) concludes that spike theories generally provide the best explanation of the processes involved in high density cascade sputtering, that cluster emission may play a substantial role and that the existing data does not allow differentiation between different spike models.

1.4 COMPUTER SIMULATION OF SPUTTERING PROCESSES

Computer simulation of atomic collisions in solids are traditionally divided into fully interacting or molecular dynamics (MD) simulations and simulations based on the binary collision approximation (BCA) in which only one collision is treated at a time. The development of simulation of atomic collisions in solids is treated in depth by Andersen (1987). Much of the development centred on the development of realistic interaction potentials for projectile-target and target-target interactions. The subject of inelasticity also received attention. Early simulations used the hard sphere approximation which gave reasonably good results for lower energies. For higher
energies the inclusion of electronic energy losses produced simulation results more in line with experimental results though the level of contribution is uncertain especially at intermediate energies. Surface and bulk binding energies are also important input parameters for BCA simulations especially if realistic results for sputtering yields are required.

In a review paper on collisional sputtering under cluster impact, Andersen (1993) notes the rapid growth of interest in simulation of cluster impacts after his review paper on simulation of atomic collisions in solids (Andersen, 1987). The understanding of the time evolution of sputtering yield and the energy distribution of sputtered atoms and particles versus time has been greatly enhanced by simulation of the processes especially the understanding of the "spike" phase (Shapiro and Tombrello, 1991, Colla and Urbassek, 1997 and Shapiro, 1997). Some conclusions drawn from these simulation studies are: 1) dimer impacts lead to greater surface disruption than monomer impacts and the polar angle distributions of ejected atoms exhibit larger forward components for dimer impacts than for monomer impacts which is consistent with more second layer atoms escaping the target (Shapiro et al, 1985). The disruption of the surface layer tends to lower the surface binding energy, which leads to higher yields for dimer impacts. 2) Surface disruption alone is insufficient to explain the excess yields. The energy distribution of the extra ejected particles (1 to 10 eV)
under molecular-ion bombardment leads to the explanation that the nonlinear effects are due to emission from collisional spikes (collision cascades dominated by collisions between moving atoms) enhanced by excess surface disruption.

The main program now used for BCA simulations of amorphous materials is TRIM, first published for range calculations by Biersack and Haggmark (1980), but later extended fully to cover collision cascades including the motion of recoils (Biersack and Eckstein, 1984). Many versions of TRIM have been used. Ziegler et al. (1985) gave a detailed description of a version called TRIM 85. Subsequent refinements of TRIM are compared with regard to sputtering yields in Smith (1997) where a factor of 2 difference in the sputtering yield of Argon into Nickel is shown between TRIM 89 and TRIM 95. The main differences arise because of the way in which the electronic energy loss is included. In TRIM 89, this loss is subtracted after the collision whereas in later versions it is subtracted before the collision. The results of BCA calculations used for sputtering calculations are also sensitive to the way collisions at the surface are handled. The agreement with experimental results is good for Argon and Xenon into Nickel but results for heavy ions into heavy targets (Sb into Au), where non-linear effects due to cascade overlaps become significant, predict sputtering yields which are lower than experimental observations by a factor of 2 or more. (See section on experimental results.)
While MD simulations for sputtering are still sensitive to the values used for inter-atomic potentials and to the way events at the surface are handled, they can give reasonable results for heavy ions into heavy targets. The main limitation is in the amount of computer time required to follow each event for sufficient time to include particles sputtered late in the cascade development. For the study of cluster ion impacts, especially of larger clusters, these problems are compounded by the need to use targets containing a large numbers of atoms.

1.5 RUTHERFORD BACKSCATTERING ANALYSIS

(Townsend et al, 1976, Chapter 8)

Rutherford backscattering analysis (RBS) is a primary tool for analysis of near surface composition and is therefore especially useful for analysis of the results of other ion beam processes which affect the same near surface region. The technique allows identification of the mass of the target atoms, their depth, and their concentrations to a depth of up to a few microns depending on the target materials and concentrations involved. In this work, RBS was used to provide an independent measurement of the thicknesses of the gold films on the quartz resonators, to provide an independent measure of ion doses, and to measure the composition and thickness of the oxygen implanted silicon nitride films.

1.5.1 Mass Determination
Rutherford backscattering (RBS) is the backscattering of incident high energy (1 to 2 MeV) light ions (H\(^+\) or He\(^+\)) resulting from elastic collisions with target atoms. Consider first collisions with atoms at the surface. The probability of interaction (the cross section) is related to the atomic numbers of the target and incident ion, and the energy of the incident beam. The energy of the particles scattered from the surface is \( E = KE_0 \) (49)
\[
K = \left( \frac{M_1 - M_2}{M_1 + M_2} \right)^2
\]
where \( K \) is for a 180\(^\circ\) scattering angle and \( E_0 \) is the incident ion energy, \( M_1 \) is the mass of the incoming ion and \( M_2 \) is the mass of the target atom. For a scattering angle of \( \theta_s \),
\[
K = \frac{M_1^2}{(M_1 + M_2)^2} \left[ \cos \theta_s + \left( \frac{M_2^2}{M_1^2} - \sin^2 \theta_s \right)^{1/2} \frac{M_2^2}{M_1^2} \right]^{1/2}
\]
(50)
Therefore, for a fixed detector position, the energy of the scattered ion depends on the mass of the struck atom for events at the target surface.

1.5.2 Depth Determination

Let us now look at scattering events from target atoms below the surface. As the incident ion passes through the target it loses energy through electronic stopping so that its energy when an elastic scattering event occurs is reduced by an amount determined by the stopping power. The scattered ion loses further energy, again determined by the stopping power, on its return path to the surface. Using published values for the stopping powers (Ziegler et al, 1985) allows calculation of the depth of the scattering
event. The energy of the ions scattered from a depth $x$ can be expressed as

$$E(x) = K \left[ E_0 - \int_x^0 S(E)dx \right] - \int_0^x S(E)dx$$ (51)

where $S(E)$ is the stopping power, $K$ and $E_0$ are as defined above, and the angles are as defined in figure 1.3. For depths of 1 or 2 microns over which the stopping power is approximately constant with depth we have

$$E(x) = K E_0 - x \left[ S(E_0) K + S(E) \frac{\cos \theta_1}{\cos \theta_2} \right]$$ (52)

solving for $x$ in microns with $E$ and $E_0$ in MeV and $S(E)$ in $\text{MeV/(mg cm}^2\text{)}$ gives

$$x = \left( \frac{K E_0 - E(x)}{\cos \theta_1} \right) \frac{1}{10 \rho} \left[ S(E_0) K + S(E) \frac{\cos \theta_1}{\cos \theta_2} \right]$$ (53)

where $\rho$ is the density of the target in $\text{gm/cm}^3$.

1.5.3 Concentration Determination

The back scattering yield from a depth $'x'$, 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 $'x'$, will give a measure of the atomic concentration at that depth. The Rutherford cross section is simply related to $Z_1$, $Z_2$, the incident beam energy $E_0$ and the scattering angle $\theta_s$ by

$$\sigma \propto \left( \frac{Z_1 Z_2^2}{E_0} \right)^2 \frac{1}{\sin^4 (\theta_s/2)}$$ (54)

When $E_0$ is expressed in MeV the differential cross
section is given by

\[ \frac{d\sigma}{d\omega} = 1.296 \left( \frac{Z_1 Z_2}{E_0} \right)^2 \left( \frac{M_1 + M_2}{M_2} \right)^2 \frac{1}{\sin^4 \left( \frac{\theta_s}{2} \right)} \text{mb/sr} \]  

(55)

for particles of mass \( M_1 \), charge \( Z_1 e \) striking target atoms of mass \( M_2 \), charge \( Z_2 e \) where \( \omega \) is the solid angle of the detector. The value of \( \frac{d\sigma}{d\omega} \) for a particular combination of \( Z_1, Z_2 \) and \( E_0 \) may therefore be calculated with a high degree of accuracy for a given scattering angle. A small correction (about 4% at laboratory scattering angles of 164°, assuming the primary ion is helium) should be applied to the differential cross section to allow for recoil of the target atoms.

1.5.4 Collection, Presentation and Interpretation of Data

Backscattered ions are detected by a silicon surface barrier detector which produces a voltage pulse proportional to the energy of each incident ion reaching the detector. A pulse height analyser digitizes the height of each pulse and logs the number of pulses occurring in each channel. Each channel represents a small band of energies relating to the mass and depth of the scattering atom and the number of pulses occurring in a channel can be related to the concentration of a scattering atom of known mass at a particular depth. Data is presented graphically as a spectrum with energy channels on the horizontal axis and number of counts on the vertical axis as shown in figure 1.11. The system can be calibrated using known samples or directly from some prior knowledge of the sample being measured. If the total incident ion dose is known,
then absolute concentration can be measured. For simple targets with only 1 or 2 known constituents, interpretation of the spectra is relatively easy. A widely used technique for interpretation of spectra is to generate theoretical spectra of likely solutions and compare them with the spectrum of the sample. The subtraction of the spectrum of known key constituents is used to identify trace or unknown constituents. The technique called simulated annealing (SA) because of its analogy with annealing of crystalline materials has recently been adapted to "solve" complex RBS spectra (Barradas et al, 1997). With only a knowledge of the constituents present, the algorithm generates a large number of possible concentration profile combinations and compares the resulting spectra with the sample spectrum. Each comparison generates a $\chi^2$ (chi-squared) value representing a weighted distance between the proposed solution and the sample data. As solutions are generated which produce lower values of $\chi^2$, the search space is narrowed slowly to find better and better fits to the data. Because of the large number of solutions generated, the result is usually a better fit than what would generally be accepted as a good fit using human generated possible solutions.
Figure 1.11
RBS spectrum of a gold film on a quartz substrate.
2. INITIAL EXPERIMENTAL WORK

2.1 THE EFFECTS OF PHYSICAL CHANGES ON QUARTZ RESONATORS

2.1.1 Initial Investigations

The first approach to the problem of compensating for the temperature effects on the resonant frequency of the quartz resonators was to try to find a measurable parameter of the quartz resonators which was independent of temperature but which had some predictable response to changes in mass and stress. The temperature dependence of the bandwidth of a quartz resonator used as a transmission filter was explored for AT-cut and BT-cut resonators. The experimental setup and initial measurements are shown in figure 2.1. The radio frequency generator, frequency counter and oscilloscope were standard laboratory instruments. A "10X" probe was used on the oscilloscope to minimise capacitive loading of the circuit. It was found that the bandwidth under specified conditions did not change with temperature as shown in figure 2.2. The bandwidth was, however, affected by stray capacitance as shown in figure 2.3. This could be a significant problem in applications where the resonators are to be placed in a high vacuum environment where the resonators might be some distance from the oscillator circuits. One side of each resonator was then coated with a 900 Å film of gold and the bandwidths remeasured as shown in figure 2.4. The bandwidth of the AT-cut resonator increased from 1500 Hz to 1725 Hz corresponding to a change in resonant frequency of 14040 Hz. The bandwidth of the BT-cut resonator increased
Figure 2.1 Circuit for measurement of resonator bandwidths.
from 414 Hz to 583 Hz corresponding to a change in resonant frequency of 949 Hz. Because of the shape and location of the gold film deposited, some of this change could have been due to a change in capacitance between the electrodes. Further investigation of this effect would require establishing the linearity of the change in bandwidth with change in mass and the independence of the bandwidth from stress effects. These measurements were made on only one resonator of each crystallographic cut so it would be necessary to establish the spread of bandwidths for several units of each cut before coming to any conclusions about the usefulness of this technique. If the above conditions could be established and the frequency versus temperature characteristics of the two resonators are known, it should be possible to determine the changes in mass, stress and
Figure 2.3
Effect of shunt capacitance on AT-cut.

Output Amplitude (εV)

5.992 5.994 5.996 5.998 6.000

C (Thousands)

Frequency (kHz)

□ 0pF + 10pF ◇ 33pF △ 100pF

Figure 2.4
Bandwidth change with 80 nm gold film.

Output Amplitude (εV)

7.0 6.0 5.0 4.0 3.0 2.0 1.0

Relative Frequency (kHz)

AT Before + AT After ○ BT Before △ BT After
temperature from the changes in resonant frequency and bandwidth of the two resonators. The accuracy of this method would be limited by the small change in bandwidth being used to compensate a much larger change in resonant frequency. In light of the possible limitations of this method, further investigation was not continued as investigation of the three resonator system seemed more promising.

2.1.2 The Three Resonator System

The use of three resonators to compensate for both stress and temperature was originally proposed by EerNisse. (EerNisse, 1975) The idea of developing the three resonator system occurred while reading about the properties of SC-cut quartz resonators. (Ballato, 1977 and Brice, 1985) The SC-cut is a doubly rotated cut developed to minimise stress effects and hence to make resonators which were not affected by stresses in the mounting structures or by vibration. A further advantage was minimisation of frequency changes caused by temperature gradients during periods of rapid temperature change. The properties which were particularly interesting were: (1) The stress coefficient approaches zero and (2) The change of frequency with temperature is similar to the AT-cut resonators but the inflection point is at approximately 90°C instead of 40°C. These properties suggested that the SC-cut resonator would be a good choice as the third resonator in a three resonator system to measure mass, stress and temperature over an extended temperature range.
A summary of the important physical constants of AT-cut, BT-cut and SC-cut resonators is shown in table 2.1. The mass constants give a mass sensitivity of approximately $2 \times 10^{-8}$ gm cm$^{-2}$ Hz$^{-1}$ for 5 MHz resonators. For gold films, this is approximately 10 Hz/Å change in film thickness. The stress constants give a stress sensitivity of approximately $2 \times 10^3$ dynes cm$^{-1}$ Hz$^{-1}$ for 5 MHz resonators.

<table>
<thead>
<tr>
<th>Resonator</th>
<th>Mass Constant (kHz mm)</th>
<th>Stress Constant (cm$^2$/dyne)</th>
<th>Temp. Char.</th>
</tr>
</thead>
<tbody>
<tr>
<td>AT-cut</td>
<td>1664</td>
<td>$2.75 \times 10^{-12}$</td>
<td>cubic</td>
</tr>
<tr>
<td>BT-cut</td>
<td>2549</td>
<td>$-2.65 \times 10^{-12}$</td>
<td>quadratic</td>
</tr>
<tr>
<td>SC-cut</td>
<td>1800</td>
<td>approx. zero</td>
<td>cubic</td>
</tr>
</tbody>
</table>

Table 2.1 Physical Constants of Resonators

Measurement of the frequency versus temperature characteristics of several resonators of each crystallographic cut indicated that there are significant differences between resonators of the same cut. This was especially noticeable with the BT-cut resonators where some resonators had a turning point at around 20°C and others at around 50°C as shown in figure 2.5a. The main difference between different SC-cut resonators was the value of the linear term (coefficient $F$ in equation 58) of the equation of frequency as a function of temperature as shown in figure 2.5b. For AT-cut resonators the coefficient of the cubic term (coefficient $A$ in equation 56) in the equation of frequency as a function of temperature varied noticeably between resonators as shown in figure 2.5c.

It was also noticed that some resonators did not
FIGURE 2.5a
DIFFERENCES BETWEEN BT-CUT RESONATORS

FIGURE 2.5b
DIFFERENCES BETWEEN 90-CUT RESONATORS
always return to the same frequency following a temperature run from ambient to around \(90^\circ C\) and back to ambient but when left at ambient for several days without being otherwise disturbed would return to their original frequency. This was more noticeable with the AT-cut resonators and was most likely to be caused by stress buildup during the run. There is also a possibility that the effect was caused by moisture absorption in the electrode film as measurements were taken in air.

2.2 THE EFFECTS OF OSCILLATOR CIRCUITRY

In order to obtain frequency versus temperature data on real samples of AT-cut, BT-cut and SC-cut resonators, a small temperature controlled chamber was built for use between ambient temperature and \(100^\circ C\). Work was also done
to develop an oscillator circuit which operated reliably and repeatably with all three crystallographic cuts of resonators and which did not require any retuning for different frequency resonators. This was done to assure that frequency change information would not be affected by the oscillator circuit. Some difficulty was encountered with SC-cut resonators oscillating in the b-mode instead of the c-mode. Both modes are quasi-shear modes and the activity of the two modes is nearly the same. The undesired b-mode frequency is about 10% higher than the desired c-mode frequency. It is possible excite both modes simultaneously. The b-mode temperature characteristic is nearly linear with a slope of $-25\text{ppm/}^\circ\text{C}$. (Bottom, 1982 p. 228) Some resonators refused to oscillate in the c-mode at some temperatures. This was initially overcome by experimenting with the oscillator circuit as suggestions for guarding against operation in the b-mode are in opposition to the requirement of minimum oscillator circuit effect on operating frequency. It was later found that adding a parallel tuned circuit tuned to the b-mode frequency in series with the resonator to act as a trap allowed all of the SC-cut resonators to work reliably through the required temperature range.

Another requirement of the oscillator circuitry was that they be isolated from the frequency measurement circuitry to allow current collection during ion bombardment for dose measurement. The final oscillator circuit is shown in figure 2.6.
Because the circuit was to be used with the resonators in a vacuum chamber, the circuits were tested with about 30 cm of lead between the resonators and the oscillator circuits to test the effect of lead spacing and position on frequency. Initially, the frequency shifts were of the order of hundreds of hertz when lead spacing and position were changed. It was found that placing a 10 pF capacitor at the resonator end of the lead in series with the resonator reduced the changes to the order of tens of hertz. It was also found that the reduction of stray shunt capacitance on the resonator improved the reproducibility.

![Figure 2.6 Oscillator circuit - with isolation](image-url)
of the shape of the temperature characteristics of the resonators. The change in shape of the temperature characteristics of AT-cut and SC-cut resonators are shown in figures 2.7 and 2.8. The change was minimal with the BT-cut resonators. With some resonators, there were areas of the frequency versus temperature curve where there was significant deviation from the usual smooth quadratic or cubic shape when the resonators were loosely coupled to the oscillator circuit through a short length of cable. As these may be a function of absolute frequency rather than an anomaly in the temperature characteristic, they could be a source of error at specific points during an experiment where the frequency is changing due to changes in mass or stress. The trap added to the SC-cut oscillator to prevent b-mode oscillation also improved this problem so it is

![Figure 2.7](image-url)
Figure 2.8

SCS Temperature Characteristic

likely that the problem was caused by b-mode interference with c-mode operation.

Another factor which could affect the accuracy of results is the drive level of the resonator. (Bottom, 1982, p220) The oscillator circuits were designed to have a low gain and coupling to the resonator was kept to the lowest value which was consistent with reliable oscillation. It was later found that the gain was too low to support oscillation of some BT-cut resonators following deposition of thicker (> 3000Å) gold films. Increasing the gain solved the problem.

2.3 THE MATHEMATICAL PROBLEM

A study of the properties of SC-cut quartz resonators (Ballato, 1977 and Brice, 1985) revealed the following
useful properties: (1) The stress coefficient approaches zero, and (2) The change of frequency with temperature is similar to the AT-cut resonators but the inflection point is at approximately 90°C instead of 40°C. These properties suggested that the SC-cut resonator would be a good choice as the third resonator in a three resonator system to measure mass, stress and temperature over an extended temperature range. The measured temperature effects for a set of commercially available AT, BT, and SC cut resonators is shown in Figure 2.9. These were the first set of resonators used for algorithm development and the first experimental work. The system of equations representing the three resonators is:
These equations are linear in $\Delta M$ and $\Delta S$ and non-linear in $T$. The solution algorithm utilizes the fact that temperature will be a continuous function so that a reasonable estimate of temperature will always be the temperature at the last sample interval. The solution is iterative until the estimated temperature matches the calculated temperature to some predetermined maximum error, usually $\pm 1^\circ C$. Convergence usually occurs in less than four iterations for each data point. Uncorrected differences in mass change produce an unphysical temperature profile and eventually a failure to converge. A temperature profile which is consistent with the implantation conditions and convergence throughout an experiment are indicative of a well configured system and good data but the stress change information is easily masked by differences in mass change between the resonators. The order of solution is based on the estimated temperature so that an unambiguous solution for temperature will always result. This is accomplished by not solving for temperature using an equation which is near its turning point. A flow chart for the solution algorithm is shown in Figure 2.10. This solution algorithm depends on choosing the resonators so that the turning point of the BT-cut resonator occurs at a lower temperature than the turning point of the SC-cut resonator. The curves for the resonator sets chosen for the second and third
experiments are shown in figures 2.11 and 2.12. In the
final version of the program, the equation of the SC-cut
resonator is approximated by a quadratic with no linear
term while it is being used to solve for temperature at
temperatures below the turning point. The more exact cubic
equation is used to solve for mass at higher temperatures
where the BT-cut equation is being used to solve for
temperature.

A test data set was produced using data from a typical
sputtering yield run (Chereckdjian, 1984) with a
superimposed exponential temperature rise to represent
sample heating by radiation during the run. This data set
was used to verify the convergence of the solution
algorithm.

An analysis of the various constants for the system
establishes the potential accuracy of the system.

\[
\begin{align*}
\Delta S_{AT} & \text{ for } 1 \text{ Hz change } = 1.7 \times 10^3 \text{ dynes/cm} \\
\Delta S_{BT} & \text{ for } 1 \text{ Hz change } = -2.9 \times 10^3 \text{ dynes/cm} \\
\Delta M_{AT} & \text{ for } 1 \text{ Hz change } = -1.2 \times 10^{-8} \text{ gm/cm}^2 \\
\Delta M_{BT} & \text{ for } 1 \text{ Hz change } = -2.0 \times 10^{-8} \text{ gm/cm}^2 \\
\Delta M_{SC} & \text{ for } 1 \text{ Hz change } = -1.9 \times 10^{-8} \text{ gm/cm}^2
\end{align*}
\]

For gold films:

\[
\begin{align*}
\Delta f_{AT} & = 156 \text{ Hz/nm} \\
\Delta f_{BT} & = 95 \text{ Hz/nm} \\
\Delta f_{SC} & = 102 \text{ Hz/nm}
\end{align*}
\]

For temperature matching and convergence to 0.5°C, potential
accuracy is of the order of $\pm 3 \times 10^4$ dynes/cm and for gold
films $\pm 0.1$nm. This is based on a maximum temperature slope
Figure 2.10 Flow chart for the solution algorithm.

1. AT - cut equation
2. BT - cut equation
3. SC - cut equation

ET - Estimated Temperature
CT - Calculated Temperature
Figure 2.11 Temperature Characteristics
Second set of resonators

Figure 2.12 Temperature Characteristics
Third set of resonators
of 20 Hz/°C between 20°C and 80°C. At temperatures near 40°C the accuracy could be better by a factor of 5 or more while at temperatures above 100°C or below 0°C the accuracy would be limited by the temperature slope and the matching of the temperatures of the three resonators.

A problem arises with the accuracy of the lateral stress measurements if differences in the surfaces of the three resonators cause the mass change to be different on the three resonators. A later experiment used RBS to quantify the differences in mass change allowing compensation and therefore improved accuracy in the lateral stress measurements.

2.4 SOFTWARE DEVELOPMENT

Initial software for testing the algorithms was written in BASIC which was good for interactive debugging and quickly trying different approaches. Considerable time was spent trying to make the BASIC programs interact through DOS in real time with the frequency counter connected to the RS 232 port. The real time programs were then rewritten in C and compiled using a TURBO C compiler. Program listings are included in the appendices.

The functions required of the real time program are as follows:

1. Control timing of readings.
2. Provide the control characters for the frequency counter.
3. Read initial frequencies and ambient temperature to
provide an automatic zeroing function to compensate for any changes in frequency due to rearrangement of resonator leads or short term exposure of resonators to experimental conditions during set-up.

4. Process data returning from the frequency counter into:

   a) raw data values for display and storage on disc,
   b) calculated results for printing.

Storage of the raw data rather than the calculated results allows for recovery of data in the case where the real time program cannot cope with the data being generated. This proved to be valuable during the calibration run when it was found that the sputter yield on one of the resonators was lower than on the other two and that the sample interval which was originally chosen as 1 minute proved to be too long to handle rapid changes in temperature. By analysing the raw data it was found that changing one constant in the program and inserting interpolated data where the temperature was changing rapidly allowed the data collected during an all day run on the accelerator to give useful results.
3. EXPERIMENTAL APPARATUS AND PROCEDURE

3.1 DESCRIPTION OF EQUIPMENT

3.1.1 The Frequency Measurement and Data Logging System

The important features of the oscillator circuits shown in figure 2.6 are that the circuits are isolated from the frequency counter to allow charge collection and current monitoring and that they are designed to have a minimum effect on the oscillating frequency of the resonators. This is described in more detail in the section on circuit effects. It is necessary to insure that the resonators are wired so that the electrode receiving charge has a current path to the charge monitor.

The frequency counter is a microprocessor based unit with a four channel input multiplexer. All control functions and results are transmitted via an RS232 interface making it easy to integrate the counter with a personal computer running real-time programs. A block diagram of the frequency counter is shown in figure 3.1. The input comparators convert the input sine wave signals of around 300 mV into TTL compatible logic levels. The digital multiplexer, under control of the microprocessor, then selects one of the signals for presentation to the programmable counter. Two four digit counters are connected in tandem giving 8 digits of resolution. The third counter is programmed as a timer which provides an accurate 1 second gate for the input signal. A single ASCII character sent to the counter initiates a reading from a particular channel. The response is a string of
ASCII characters identifying the channel, frequency and units. The real time PC program converts the character string into a number representing the frequency in Hertz. The final calibration was done using a laboratory frequency counter which had a specified accuracy of 1 part in $10^5$ after 1 year. This would mean that the absolute accuracy of the frequency measurements cannot be guaranteed to be better than ±50 Hz at 5 MHz. Stability was checked both for warm-up drift and shifts during operation in a normal lab environment. Warm-up drift was around 20 Hz at 5 MHz during the first two hours after a cold start. Thereafter, readings were stable within ±2 Hz over several hours. Since the duration of a normal experiment is no longer than 8 hours and the information of interest is frequency change rather than absolute frequency, the errors introduced by
the frequency counter should be no more than a few hertz provided the counter is allowed to warm up for at least 2 hours before starting an experiment.

Temperature measurements were made using a thermistor probe with a specified accuracy of ±0.2°C between 0°C and 70°C. Circuitry was developed to present temperature information as a frequency to the fourth channel of the frequency counter allowing automation of all measurements. Figure 3.2 shows the temperature to frequency conversion circuit. The frequency of oscillation is 1/4RC. The thermistor resistance is approximately proportional to 1/T over a limited range so choosing appropriate values for \( R_i \)

![Figure 3.2. Temperature to Frequency Converter](image-url)
and $C_1$ gives a nearly linear relationship between temperature and frequency between $20^\circ C$ and $90^\circ C$ as shown in figure 3.3. The overall accuracy of the temperature measurements is $\pm 3^\circ C$ between $20^\circ C$ and $100^\circ C$. For experiments involving temperatures between $100^\circ C$ and $150^\circ C$ a two segment piecewise linear approximation correction is applied to the raw temperature readings keeping the accuracy within $\pm 4^\circ C$ up to $150^\circ C$.

The real time program in the personal computer reads the frequency data from the three resonators every 30 seconds, displays the frequency data on the screen, calculates and prints the mass change, stress change and temperature, and stores the frequency data on disc for further processing by data presentation software. A data logging program can also be used to display and store the
frequency data without doing any calculations. This is particularly useful where there are problems with convergence due to, for example, differences in sputtering yields between the three resonators as noted in the results section.

3.1.2 The Implanters

3.1.2.1 The 500 keV Implanter

The 500 keV implanter is a low beam current implanter using post acceleration mass analysis which gives very good mass resolution. The layout of the implanter is shown in figure 3.4. All ions extracted from the source are accelerated before mass selection and then only those of

Figure 3.4 The 500 kV Post-Analysis Ion Implanter, illustrating (A) The Cold Penning Source, (B) The magnet field coils to assist in confining the plasma, (C) After the aperture an Einzel lens system, consisting of two extraction plates at common voltages, and an adjustable focusing lens in the centre, (D) The acceleration tube, (E) Following the Beam Profiler a set of quadrapoles, (F) A 90° mass analysing magnet, (G) A Beam Profiler and mass resolving slits, (H) X/Y Scanning and neutral offset followed by a Faraday Cup, and (I) Target chamber with sample.
interest are allowed past the 90° magnet. This provides very good mass separation because the ions pass through the magnet at high energy and hence the difference in bend radii between adjacent species or isotopes is relatively large. An example of the resolution capability was seen when implanting Sb₂ molecules at 100 keV. The mass spectrum taken when setting up the implanter for the experiment showed three separately identifiable peaks at masses 242, 244 and 246 representing Sb₂ molecules consisting of two mass 121 atoms, a mass 121 and a mass 123 atom, and two mass 123 atoms respectively. Because mass separation is done at high energy, a large magnet is required. In the above example, the magnet current was near the maximum available because of the high molecular mass. I would have liked to extend the antimony experiments to include Sb₃ molecules at 150 keV but this was beyond the capability of the magnet. It might have been just possible to achieve an Sb₃ beam at 90 keV but then the lower energy limit of around 40 keV would not allow achieving a 30 keV Sb beam for comparison. The sample chamber is pumped by a diffusion pump and is also equipped with a liquid nitrogen cold finger which together allow implantation to be done at a vacuum level of around 10⁻⁶ torr. Because of the low beam current capability of this implanter, most of the experiments required beam time of the order of a few hours to achieve the required dose.

3.1.2.2 The Danfysik Implanter

The Danfysik implanter has a nominal energy range of
5 keV to 200 keV. It is a high current implanter capable of ion target currents up to 10 mA. A layout diagram for the implanter is shown in figure 3.5. In order to achieve good control of the beam shape at high beam currents and low energies, the beam focusing is done with a magnetic quadrupole triplet lens.

Figure 3.5
Schematic layout of the Danfysik implanter.

The decision to use the Danfysik implanter for the later Sb experiments was because of the beam current and dynamic range limitations of the 500 keV implanter mentioned above.

3.1.2.3 The Plasma Immersion Ion Implanter
Other workers in the department have developed an experimental plasma immersion ion implanter (Kazor et-al, 1994). The application of this implanter is envisaged as being in the formation of electrically useful materials on large substrates for use in large area displays. Figure 3.6 shows the schematic diagram of the plasma immersion implanter. The main components of the system are a magnetron, a quartz window, a plasma chamber, a permanent magnet assembly and a wafer holder. The wafer holder is pulsed at a 50Hz rate with negative pulses of up to 5kV with a pulse width between 5μs and 20μs.

![Schematic diagram of the PIII system. (Kazor et-al, 1980)](image)

During the pulse a positive ion sheath is formed between the plasma and the sample holder. The ions in the sheath are implanted into the sample with a distribution of
energies and angles due to collisions with neutrals in the sheath region. During the pulse off-time, the sample holder is at earth potential and the plasma neutralises any charge build-up on the surface of a non-conducting sample.

It was thought that further information could be gained about the composition of amorphous silicon nitride films from data on the changes in mass and stress during high dose implants of oxygen which would help in characterising the processes. A simple experiment was devised to demonstrate the feasibility of operating the quartz resonators in the plasma environment. The experiment consisted of the following steps:

1. Choose a set of resonators and obtain accurate frequency temperature data.
2. Deposit about 1000Å of amorphous silicon nitride film on one surface of each of the resonators.
3. Measure the thickness and refractive index by ellipsometry and characterise the films by RBS.
4. Implant the samples in the plasma immersion implanter with about $10^{17}$ ions cm$^{-2}$ of O$_{2}$ while monitoring the frequencies of oscillation of the resonators.
5. Repeat the thickness, refractive index and RBS measurements.

The goal of this experiment was to use the mass change information from the resonator measurements in conjunction with the thickness and refractive index measurements made
by ellipsometry to determine the film density and hence the composition using Lorentz-Lorenz correlation curves relating density, refractive index and silicon-nitrogen ratio as shown in figure 3.7 and comparing the data with RBS measurements.

![Figure 3.7](image)

**Figure 3.7**
Typical Lorentz-Lorenz correlation curves for PECVD silicon nitride. (Enomoto, 1980)

3.1.3 The RBS Measurement System

The RBS measurement system uses a 2MeV Van de Graaff generator to produce a nominal 1.5 MeV \( ^4\)He\(^+\) beam. The beam is directed down a beamline, shown in figure 3.8, and passes through a pair of slits. The slit signal obtained is used to provide feedback information on energy and position, which in turn helps to provide energy stabilisation and control within 1 keV. Two apertures are used in the beamline to reduce the beam spot down to
approximately 1 mm in diameter. Several electrostatic plates are present to ensure the beam reaches the target chamber and to provide an offset to remove O^{2+}.

Within the target chamber, the samples are mounted on a computer controlled goniometer, which offers lateral, rotational and tilt movements with reference to the incident beam. The chamber and beamline are typically under vacuum to a pressure of about 10^{-4} torr.

The beam current is measured directly using a current integrator connected to the sample. To reduce the effect of secondary electrons, the sample is elevated to a
potential of 200 V. To convert the charge collection system so that it could be fed to a computer, the output of the current integrator is connected to a counter which has an RS 232 link with the computer providing control of counter functions and reading of counter data.

3.1.4 The Thin Film Deposition Equipment

3.1.4.1 The Evaporator

The gold films were deposited onto the resonators using a general purpose evaporator. The evaporator consists of a vacuum chamber comprising a base under which is mounted a diffusion pump. The filament mountings and sample holder are mounted above the base. The cover is a bell jar which allows viewing of the evaporation process. Pure gold wire was wrapped around a spiral filament which was then attached to screw terminals on the base. The length of gold wire was calculated to give the desired thickness film which was not critical so it was unnecessary to monitor the film thickness during evaporation. The vacuum was pumped down to about $10^{-6}$ torr before applying current to the filament to evaporate the gold wire. The current is slowly increased until the gold starts to melt and then monitored visually until all the gold is evaporated from the filament.

3.1.4.2 The PECVD System

Radio frequency (RF) plasma enhanced chemical vapour deposition (PECVD) is a process that is routinely used in the micro-electronics industry to deposit various types of thin films, (e.g. silicon dioxide, silicon nitride)
especially as the 'gate oxide' in metal oxide semiconductor (MOS) devices. Small quantities of gases such as SiH₄, NH₃, He, Ar, CH₄, N₂, N₂O etc., are fed into the plasma chamber that is held under vacuum, with a maximum of three gases fed in at one time. There is an inbuilt leak detector mechanism before each processing step. The mix of gases is broken up into ionised species and radicals by the application of a 13.56 MHz RF power supply coupled into the system via parallel plate electrodes. The required ion species are then accelerated towards the substrates placed on the bottom electrode by a small dc self bias in the system where they react with each other and the sample to form the film. The thickness of the films produced is of the order of 50 to 100 nm. In chemical vapour deposition (CVD) the substrate must be heated to around 1000°C in order for the chemical reactions to occur. A major advantage of PECVD is that because the RF energy in the plasma ionises the reactants, the substrate can be kept down to around 300°C.

3.1.5 The Ellipsometer

Ellipsometry is the determination of certain physical properties of a surface from measurements of the effect of reflection on the state of polarisation of polarised light. The state of polarisation is described by the relative amplitudes, A, and phase difference, δ, of the P and S waves, the components with the electric vectors in the plane of incidence and perpendicular to it respectively.

The change in the state of polarisation depends on the
complex refractive index of the reflecting surface and the angle of incidence. The presence of a thin film on the surface allows multiple reflections to occur. This complicates the mathematics, but for routine use solutions have been computed for specific conditions. We measure

$$\Delta = (\beta_p - \beta_s)_{\text{reflected}} - (\beta_p - \beta_s)_{\text{incident}},$$

(59)

which is the change in phase, and

$$\Psi = \tan^{-1} \left[ \frac{(A_p/A_s)_{\text{reflected}}}{(A_p/A_s)_{\text{incident}}} \right],$$

(60)

which is the arc tangent of the amplitude change, and from these values the refractive index, $n$, and the thickness, $d$, of the surface film can be determined.

![Figure 3.9](image)

**Figure 3.9**

Layout of the ellipsometer.

The layout of the ellipsometer is shown in figure 3.9. The laser output is linearly polarised. The $\lambda/4$ plate converts it to circular polarisation from which the polariser can select a linearly polarised beam at any angle.
desired. The compensator, which is just another $\lambda/4$ plate, converts it to being elliptically polarised. Depending on the angles of the polariser and compensator, the angle and ratio of the major and minor axes of the ellipse can be chosen at will. In practice, the compensator is kept at $45^\circ$ and the positions of the polariser and analyser are found such that the ellipticity of the incident beam exactly compensates for that produced by reflection, and a null reading occurs at the photodetector. The sets of angles of the polariser and analyser where these null readings occur allow calculation of $\Delta$ and $\Psi$ and hence values of $n$ and $d$.

3.2 EXPERIMENTAL PROCEDURES

3.2.1 Preparation of Resonators

A small temperature controlled chamber was built which allows temperature control between ambient temperature and 100°C. The heated chamber is a cardboard tube about 3 cm in diameter. This tube is surrounded by a layer of copper sheet which is in thermal contact with three 11 watt power resistors. These are then surrounded with several layers of thermal insulation to minimise heat loss. Frequency as a function of temperature data was taken on several resonators of each crystallographic cut. This was done with several configurations of oscillator circuitry until a configuration which produced reproducible results was found. (See section 2.2) Sets of resonators were chosen as described in section 2.3. A set of frequency versus temperature data is then taken on a chosen set of
resonators as a starting data set for the experiment. The frequency versus temperature coefficients for the three resonators are determined by plotting the frequency versus temperature data and the results of a mathematical model of the frequency versus temperature characteristics on the same screen plot and then visually adjusting the coefficients until a good match is found. This process could be performed using a least squares fitting algorithm without ever looking at the data but seeing the data and identifying bad data points or poor data due to resonators either changing modes or ceasing to oscillate or to poor placement of the temperature sensor is a useful step in the validation process for a set of resonators.

The resonators are then cleaned in warm toluene followed by rinses in methanol and AR methanol and blow dried with dry nitrogen. The gold film is then evaporated onto a 9 mm diameter spot covering one electrode of each resonator. The temperature versus frequency data is then retaken to verify that the shape of the characteristic has not changed and that all the resonators still oscillate reliably.

3.2.2 Mounting of Resonators

The experimental apparatus consists of the three resonators mounted as shown in figure 3.10, three identical oscillator circuits with output isolation to allow current monitoring shown in figure 2.6, a programmable frequency counter described in section 3.1.1 and a personal computer. Referring to figure 3.10, the important factors in mounting
the three resonators are that the ion flux is uniform over the three resonators and that the three resonators are exposed to the same temperature environment. The resonators are mounted in a row as close together as possible. There are three identical circular apertures in front of the resonators to limit the exposed area to the active area plus 50%. An electrode is placed between the apertures and the resonators to which a negative potential is applied to suppress secondary electron effects. The beam is raster scanned over an area a little greater than the area required to cover the three apertures to insure a uniform dose on the three resonators.

3.2.3 Dose Measurement

For implantations using the 500 keV accelerator,
charge was collected from the exposed electrode of the resonators using the current integrator which is normally used with that machine. The standard secondary electron suppression arrangement was also used. For the implantation using the Danfysik accelerator, the standard dose measurement system for that machine was used. This consists of four Faraday cups at the edges of the measurement area. The beam scanning is set up so that the four cups receive approximately the same current assuring that the sample area receives a uniform dose. For the later experiments, where RBS was used, dose was also measured by RBS measurement of a silicon sample placed in between two of the resonators during implantation.

3.2.4 Handling of Results

During implantation, frequency data was taken at 30 second intervals on all three resonators and stored by the data logging program. Charge and beam current data was also logged manually during each run. This made it possible to make calculations of instantaneous values of sputtering yield using beam current and rate of mass change data in addition to the average sputtering yield based on total mass change and total dose data. A sample calculation for the instantaneous value is as follows:

Target current = 570 nA = 570 nC/s = 34.2 μC/min.

Dose = 34.2*10^{-6}/1.6*10^{-19} = 2.14*10^{14} ions/min.

For a sample area of 1.3 cm²,

Dose rate = 2.14*10^{14}/1.3 = 1.64*10^{14} ions/min. cm².

Mass rate = -6.25*10^{-7} g/min. cm².
For a gold target,
\[ \frac{6.25 \times 10^{-7}}{(197)(1.67 \times 10^{-24})} = 1.9 \times 10^{15} \text{ atoms/min. cm}^2 \]
Sputtering yield = \[ \frac{1.9 \times 10^{15}}{1.64 \times 10^{14}} = 11.6 \text{ atoms/ion.} \]
The frequency data is first converted into mass change data ignoring stress and temperature effects to identify large differences in sputtering yield between the resonators.
The sputtering yield for the SC-cut resonators, which had a visibly smoother surface, was systematically lower than for the AT and BT cut resonators. Applying a yield correction factor to the mass change for the SC-cut resonator allowed the solution algorithm to converge giving a physically possible solution for temperature and an estimate of the lateral stress behaviour. A later experiment quantified the mass change differences using RBS and hence improved the confidence in the lateral stress measurements which cannot otherwise be differentiated from yield differences between the AT-cut and BT-cut resonators.
The results data file from the solution algorithm is transferred into a spreadsheet program allowing presentation of the results in graphical format with appropriate titles and labels.

RBS analyses were made using a 1.485 MeV \(^4\)He beam with a nominal spot size of 1mm. The RBS detector was at a 165° scattering angle. The energy was stabilised using the system reported previously (Jeynes et al., 1998). Data was taken at a series of points along the electrodes on each sample at each stage of the experiment so any nonuniformity of the film thicknesses could be averaged over each sample.
allowing comparison with the resonator frequency data which is proportional to the average change in mass over the electrode area. The energy thickness was thus determined to an accuracy of about 1.3% giving a final error in the sputtered film thickness determination of typically 0.7nm using a joined half-Gaussian fitting of the differentiated edges as described in (Kimber and Jeynes, 1987). Numerical integration with standard stopping powers (Ziegler et al., 1985) was used to convert energy thickness to g/cm². Film thickness was determined in channels first, where the Au edge was determined with a precision of better than 2*10⁻⁴ for each of the three analysis dates. Using a fixed offset and the (very well determined) Au edge to obtain the energy calibration gives a gain value within 2*10⁻³ of the value obtained from a linear regression on O, Si, and Au edges (with the beam straddling the quartz and the electrode).

The dose was determined absolutely from a silicon sample placed in the same environment using the simulated annealing (SA) algorithm (Barradas et al., 1997) and the pileup correction described in (Jeynes et al., 1997). Note that the silicon is amorphised and a self-consistent fit with SA gives unambiguous answers with an accuracy determined by statistics, stopping of silicon, and the instrument calibration. In this case the error is dominated by the stopping power uncertainty, about 5%. 

4. EXPERIMENTAL RESULTS

4.1 RESULTS FOR ARGON SPUTTERING OF GOLD

4.1.1 Experiment 1

The results from sputtering a gold film with 100 keV and 400 keV argon ions are shown in figure 4.1. Data was taken at one minute intervals. The ion beam was initially turned on and off twice to show the effect of radiation on stress and temperature. The beam current was changed several times to show the effect on temperature. Finally the beam energy was changed from 100 keV to 400 keV to show the effect of additional beam heating on the radiation induced stress. The relationship between beam current, as indicated by rate of mass change, and temperature rise, the radiation induced stress caused by temperature gradients and the build-up of stress due to radiation damage are
shown. Initially, the solution did not converge to a realistic temperature after a few minutes of exposure. This appears to be caused by the difference in surface roughness between the SC-cut resonator which was visually smooth and the AT-cut and BT-cut resonators which were visually dull. Correcting for the difference in sputter yield of the SC-cut resonator, as shown in figure 4.2, produced a convergence indicating a temperature consistent with the implantation conditions. The mass change corrected for stress and temperature as a function of incident charge is shown in figure 4.3. The charge up to 8.3 millicoulombs was deposited as 100 keV argon ions and produced a sputter yield of 11.2 atoms per ion on the AT-cut and BT-cut resonators and a sputter yield of 8.8 atoms per ion on the SC-cut resonator. The charge above 8.3
Corrected for stress and temperature.

Figure 4.3 Mass Loss versus Dose.

milli-coulombs was deposited as 400 keV argon ions and produced a sputter yield of 7.3 atoms per ion on the AT-cut and BT-cut resonators and a sputter yield of 5.7 atoms per ion on the SC-cut resonator. These values compare reasonably well with the values of 11.8 atoms per ion at 100 keV and 6.8 atoms per ion at 400 keV calculated by the TRIM'89 simulation and the values of 10 to 11 atoms per ion at 100 keV reported by Andersen and Bay (Andersen and Bay, 1975).

4.1.2 Experiment 2

It was decided to repeat the gold sputtering experiment using Rutherford Backscattering (RBS) to allow verification of the apparent differences in sputtering yield between the AT-cut and BT-cut resonators which have a roughened surface and the SC-cut resonator which has a
smoother surface. The system of equations representing the
three resonators becomes:

\[ f_{\text{AT}} = f_{\text{AT}} + R_{\text{AT}} \Delta M + P_{\text{AT}} \Delta S + A(T-T_a)^3 + B(T-T_a) \]  (61)
\[ f_{\text{BT}} = f_{\text{BT}} + R_{\text{BT}} \Delta M a_{\text{BT}} + P_{\text{BT}} \Delta S + C(T-T_b)^2 + D(T-T_b) \]  (62)
\[ f_{\text{SC}} = f_{\text{SC}} + R_{\text{SC}} \Delta M a_{\text{SC}} + E(T-T_S)^3 + F(T-T_S) \]  (63)

where \( a_{\text{ef}} \) and \( a_{\text{sc}} \) are the mass normalisation factors relative
to the mass change on the AT-cut resonator which are
determined by RBS. The equations are solved as described
in section 2.3.

The results are summarised in Table 4.1. The
evaporated film thicknesses determined by RBS and the
quartz resonators (QR) are directly comparable. They
differ by about 3%, 8% and 0.7% for the AT, BT and SC cuts
respectively, with the RBS reading systematically low. The
SC electrode is very smooth resulting in very reliable data
within the estimated error, but the BT is very rough. This
gives a large distortion (a tail) in the RBS interface
signal which will bias the midpoint value used. The AT cut
is of intermediate roughness. Thus, the RBS is ignoring
the tail signal, underestimating the thickness.

Large stresses in the deposited films can be
identified and quantified by the same method as used for
the sputtered films. There is no consistent evidence in
the data for there being any quantifiable stress in the
evaporated films. In the sputtered films however, the ion
beam induces stresses into the films which we wish to
measure. The table shows QR thicknesses assuming no
stresses, RBS thicknesses and hence sputtering yields for
the three resonators determined correctly by RBS except for the tailing problem. The QR value for the SC resonator, which is insensitive to stress, is correct. But the AT and BT resonators, which have a roughly equal and opposite stress response, give uncorrected QR values 5% below and above the RBS values, respectively. This internal consistency in the data gives confidence that the RBS sputtering yield measurements are correct, that the implant induces the same stress in the AT and BT resonators and that the evaporated films are effectively unstressed.

Figure 4.4 shows the mass change during implantation for each resonator uncorrected for stress effects. The similarity between the AT and BT cut resonators emphasises that the lateral stress induced by the implantation is masking the sputtering yield differences between these
resonators.

Figure 4.5 shows a fully self-consistent determination of the implantation induced stress using the mass loss values obtained from RBS. The temperature remains essentially constant during this long implantation. The stress builds up linearly in the films with dose, with an end value of $1.4 \times 10^{-3}$ dynes/cm. A 1.3% change in the relative mass change between the AT cut and BT cut resonators produces a 15% change in the stress change value. Solving for stress change using the uncorrected frequency change data from the AT and BT cut resonators gives unphysical tensile stresses demonstrating the necessity for ensuring that the differences in mass changes have been taken into account. There is both a temperature
and a stress drop in the film when the beam is switched off. Figure 4.6 shows a set of RBS spectra for the film thicknesses on the AT-cut resonator for the resonator electrode before deposition, the total thickness following deposition and the total thickness after sputtering.

<table>
<thead>
<tr>
<th></th>
<th>AT</th>
<th>BT</th>
<th>SC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrode Thickness</td>
<td>276.9 nm</td>
<td>158.2 nm</td>
<td>171.9 nm</td>
</tr>
<tr>
<td>Evap. Film Thickness</td>
<td>158.4 nm</td>
<td>179.3 nm</td>
<td>166.4 nm</td>
</tr>
<tr>
<td>Evap. Film Thickness</td>
<td>162.7 nm</td>
<td>194.4 nm</td>
<td>167.6 nm</td>
</tr>
<tr>
<td>Sputtered Film</td>
<td>78.9 nm</td>
<td>89.4 nm</td>
<td>72.0 nm</td>
</tr>
<tr>
<td>Sputtered Film</td>
<td>83.3 nm</td>
<td>85.4 nm</td>
<td>71.6 nm</td>
</tr>
<tr>
<td>Sputtering Yield</td>
<td>9.52</td>
<td>10.79</td>
<td>8.69</td>
</tr>
</tbody>
</table>

Table 4.1. Summary of Results. Au film thicknesses for the three resonators before and after 50keV Ar implantation with a fluence of 4.9*10^16/cm².
A set of RBS spectra for the AT-cut resonator showing the thickness of the gold electrode before deposition of the added gold film, the combined thickness of the electrode and the film, and the combined thickness after sputtering.
4.2 PLASMA IMMERSION ION IMPLANTER RESULTS

This experiment demonstrated the hostility of the PIII environment by overstressing several electronic components so that no real-time data was obtained. However, the benchmark data at the different stages of the experiment could still yield information about the process. The RBS data show very little difference in the composition of the films before and after implantation. The film on the SC-cut resonator was very slightly thinner after implantation indicating that some sputtering occurred. The frequency change information showed a decrease of only 74 Hz which would indicate a very small increase in mass. All this points to an experiment in which very little happened. There was no sign of any significant oxygen in the RBS plots which would indicate that the conditions for implantation were not correct possibly due to charge build up on the surface or the field pattern being disturbed by the resonator electrodes being kept near earth potential.

A second experiment was devised in which the SC cut resonator and a piece of silicon wafer which was coated with silicon nitride at the same time as the resonator were placed in the plasma immersion system without any connecting wires and implanted with about \(10^{17}\) atoms/cm\(^2\) of O\(_2\). Following this experiment, the resonator would no longer oscillate so any contribution of the change in resonant frequency to knowledge about changes in the surface film would be impossible.
4.3 CLUSTER SPUTTERING RESULTS

4.3.1 Introduction

The first experiment involved making a series of runs using both the 2MeV and 500keV implanters to implant carbon and molecules containing multiple carbon atoms at various energies into the gold films on the quartz resonators while monitoring sputtering yield using the three resonator technique previously developed. While some of the data displayed predictable behaviour, the sputtering yields were too low to allow identification of nonlinearities in sputtering yield with molecule size. On reflection, it was decided that carbon was a poor choice because of the low sputtering yield.

The second experiment involved trying to make a series of runs using molecules containing different numbers of iodine atoms at various energies. These molecules were chosen to give better sputtering yields and give data which will allow identification of nonlinear effects. Attempts to obtain a stable beam which contained molecules having multiple iodine atoms were unsuccessful. Looking for an alternative, we decided to try using antimony.

4.3.2 Antimony Experiments

We were successful in obtaining a beam containing both Sb and Sb from which sputter yields at 50keV and 100keV respectively were obtained. At 50keV per atom the yields calculated using collected charge to determine incident dose and quartz resonator frequency data to determine mass of gold lost were 5.1 Au atoms/Sb atom for Sb ions and 9.1
Au atoms/Sb atom for Sb$_2$ ions. TRIM simulations give values around 20 for Sb but the measured values from the literature are closer to 40. The enhancement factor agrees with the values predicted from the literature (Thompson and Johar, 1979). Because the first experiment had been done using gold films which had been deposited with significant doses of carbon, the experiment was repeated after depositing a fresh film of gold on the resonators. The incoming doses were confirmed by co-implanting a silicon sample and measuring the Sb concentration by RBS. The yields were 22 Au atoms/Sb atom for Sb ions and 58 Au atoms/Sb atom for Sb$_2$ ions. The expected values from the literature were 37 Au atoms/Sb atom and 114 Au atoms/Sb atom respectively (Johar and Thompson, 1979). The differences are likely due to the surface roughness and to the buildup of Sb atoms deposited as Sb$_2$ (6 $\times$ 10$^{14}$/cm$^2$) before making the measurements using single Sb atoms both of which would lead to a reduction of yield (Thompson, 1981a). The effect of the surface history on the sputtering yield was demonstrated by the first attempt at this experiment using gold films which had been previously irradiated with about 2 $\times$ 10$^{16}$ carbon atoms/cm$^2$. The results shown in figure 4.7 for Sb and figure 4.8 for Sb$_2$ also show a stress build-up during the runs and the increase in temperature due to beam heating.

4.3.3 Sputtering yield versus temperature

Following on from these initial experiments, I decided to perform a series of experiments to look at sputtering
Figure 4.7 Sb+ into Au.

Energy=50keV Current=90mA/sq cm

Figure 4.8 Sb2+ into Au.

Energy=100keV Current Density=65mA/sq cm
yields of Sb and Sb₄ at energies of 30keV and 60keV respectively and temperatures ranging from those produced by beam heating up to around 150°C. The sample holder was modified by the addition of heaters and the thermistor was attached to the holder. Because of the results of the final experiment using an argon beam where significant differences in sputtering yield between the three resonators were noted, it was decided to use RBS measurements with this experiment also. This provides confirmation of accuracy which allows increased confidence in the stress results. In the first run using a 30 keV Sb beam, sputtering yields were measured at 25°C, 50°C, 100°C and 150°C using a dose of approximately 2*10¹⁶ ions/cm² at each temperature. There were problems with dosimetry for this experiment. The resonators were initially exposed to

Figure 4.9
Sb into Au versus temperature.
an unscanned beam for about 5 minutes before it was noticed that the scanning power supplies had tripped off. The run was restarted and gave good real time mass change information at each temperature but the total thickness change on each resonator as measured by RBS could not be correlated with the total frequency change information. The RBS measurement of the total dose on a co-implanted silicon sample could also have been affected. The total dose as measured on the Faraday cups surrounding the sample was $8 \times 10^{15}$ ions/cm$^2$ while the dose on the silicon sample was measured by RBS to be about $1.4 \times 10^{16}$ ions/cm$^2$. The mass change and temperature data for this experiment is shown in figure 4.9. The calculated sputtering yields using the nominal dose at each temperature are shown in table 4.2.

<table>
<thead>
<tr>
<th>Temperature ($^\circ$C)</th>
<th>Dose (ions/cm$^2$)</th>
<th>Yield (atoms/ion)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>$2 \times 10^{15}$</td>
<td>42</td>
</tr>
<tr>
<td>50</td>
<td>$2 \times 10^{15}$</td>
<td>42</td>
</tr>
<tr>
<td>100</td>
<td>$2 \times 10^{15}$</td>
<td>34</td>
</tr>
<tr>
<td>150</td>
<td>$2 \times 10^{15}$</td>
<td>38</td>
</tr>
</tbody>
</table>

Table 4.2 Sputtering yield at different temperatures for Sb bombardment of Au at 30 keV.

4.3.4 Simulation Results

These results were also presented in (Webb et al, 1999).

Molecular Dynamics simulations were done using MD code which has been described in detail in other publications (Smith et al, 1989 and Harrison, 1988). A brief
description will be given here. The simulation solves the equations of motion simultaneously for each particle and stores information on position, velocity and energy states at different time steps. The program uses the many body potentials of Ackland et al (1990) to model the Au-Au interactions. The Sb-Sb and Sb-Au interactions are modeled by the Universal ZBL repulsive pairwise potential (Ziegler et al, 1985). These interaction potentials do not describe the bonding nature of the Sb-Sb or the Sb-Au particles and so cannot be used to describe the bonding configuration of the implanted Sb ions. Nor will they describe accurately the dissociation of the Sb$_2$ molecule. However, the energy of the interaction with the target surface is of such magnitude that the dynamics are unlikely to be affected greatly by this lack of binding. Also, these potentials are known to give a very good description of the high energy interactions and so, should describe the initiation of the energy exchange with the surface atoms well enough to allow formation of the ensuing collision cascade in the gold target. The gold target is then well described by the many body potential. Periodic boundary conditions are used at the lateral boundaries of the target cell, the surface and bottom layers are considered to be free. This allows sputtering of material and prevents unwanted reflection from the bottom layer of fast moving recoils. In general, the target system is kept large enough to avoid the influence of the edges of the crystal. The target used in this study is a gold lattice arranged into a block 120Å
square, consisting of 30 atomic layers. This contains approximately 25,000 atoms. The initial temperature of the lattice is 0°K. Impacts of Sb and Sb₂ on a single crystal (100) fcc gold surface are considered. A regular array of impact points are used in a symmetry zone of the crystal. Average calculations are made over 164 trajectories for Sb and 328 trajectories for Sb₂. The number of trajectories is not high but by employing regular sampling rather than random sampling, errors are reduced (Harrison, 1988). Orientations of the Sb₂ molecule both parallel and perpendicular to the surface and angles of incidence which were not aligned with the crystal structure were tried to get a feel for the range of values which might go into sputtering from an amorphous or polycrystalline surface for 50 keV Sb into Au and 100 keV Sb₂ into Au using end times of 1 ps per cascade. The energies were chosen to match the energies of the first cluster sputtering experiments. Previous simulation studies of this kind used energies less than 10 keV per bombarding atom (Colla and Urbassek, 1997 and Shapiro and Tombrello, 1991).

The results were characterised by relatively few very high yield events where the impact point was near a column of atoms in the crystal lattice and many low or zero yield events where the impact point was likely to lead to channelling. The number of zero yield events was lower with Sb₂ molecules. Sputtering yield as a function of time for high yield, medium yield and low yield impacts for both Sb and Sb₂ are shown in figures 4.10a and 4.10b.
a) Yield as a function of Time for different impact sites
50keV Sb on Au

b) Yield as a function of time for different impact sites
100keV Sb2 on Au

Figure 4.10
respectively. There is little difference between the two. For the high yield sites the yield increases with time for a long time and is still rising even after 10ps. The principle difference is that the high yield sites occur more frequently in the molecular impact case than in the single atom case. The enhancement in the yield comes from the doubling of the number of high yield sites and the increase in "activity" of the high yield sites. The sputtering yield for single atom Sb impact was found to be 41 atoms/ion and the yield for the Sb\textsubscript{2} to be 109 atoms/molecule or 54.5 atoms Au/incoming Sb atom. For the very high yield simulations of the molecular impacts there is some evidence that there was a containment problem in which a hole was created right through the target region. This will affect the degree of nonlinearity seen in these results and it is likely that the yield will be even higher from the molecular impacts. The velocity distribution of the atoms in the simulation was plotted at 1 ps for selected low, medium and high yield events. As might be expected, there were a higher proportion of high velocity atoms present in the high yield events. The velocity distribution was plotted at a sequence of times up to 1 ps for a high yield event. This was extrapolated to a plot of temperature and yield as a function of time shown in figure 4.11. This further reinforced the conclusion that most of the yield occurs during the initial high temperature "spike" which has dissipated to a slower steady decline after 1 ps.
4.4 DISCUSSION OF RESULTS

The choice of $\text{Sb}^+$ and $\text{Sb}_2^+$ as suitable ions for the experiments was made after trying unsuccessfully to obtain a beam using iodine by looking for an element with similar atomic number for which source material was available. The choice was fortunate in that it allowed direct comparison with previous experiments. The previous experiments used gold films deposited on silicon. These films more nearly represented an ideal planar surface than the gold films deposited on etched quartz which I used. Figures 4.12 and 4.13 show the surfaces of the AT cut resonator before and after implantation respectively. There is clear evidence of crater formation after implantation. Figures 4.14 and 4.15 show the surfaces of the BT cut and SC cut resonators.
Figure 4.12 AT cut Resonator Before Implantation.
Figure 4.14 BT cut Resonator after implantation with $10^{15}$ molecules of Sb$_2^+$ at 100keV followed by $6 \times 10^{14}$ atoms of Sb at 50keV.
Figure 4.15 SC cut Resonator after implantation with $10^{15}$
molecules of Sb$_2$ at 100keV followed by $6 \times 10^{14}$ atoms of Sb at
50keV.
respectively after implantation. As noted in section 4.1, there are significant differences between the surfaces of the different cuts of resonators which lead to differences in sputtering yield between the devices. As in previous experiments, it was necessary to use a correction factor of 7% on the mass constant of the SC cut resonator to achieve a reasonable temperature profile for the experiment. Any difference in the sputtering yield between the AT cut and BT cut resonators will appear as an error in the calculation of the lateral stress. Because the mass change is the predominant factor in this experiment, the expected error in the yield calculations should be mainly limited by the accuracy of the measurement of the ion dose. The difference in dose as measured by collected charge and by RBS of the co-implanted silicon sample was 8% so a worst case accuracy of 10% seems reasonable. A summary of sputtering results and comparison between my results, earlier experimental results and simulation results is shown in table 4.3.
<table>
<thead>
<tr>
<th>Energy</th>
<th>Method</th>
<th>J&amp;T 79</th>
<th>Way 98</th>
<th>MD Norm.</th>
<th>MD Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>45keV Ar&gt;Au</td>
<td></td>
<td>6</td>
<td>7</td>
<td>15</td>
<td>9</td>
</tr>
<tr>
<td>100keV Ar&gt;Au</td>
<td></td>
<td>12</td>
<td>5</td>
<td>7</td>
<td>10</td>
</tr>
<tr>
<td>400keV Ar&gt;Au</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>7</td>
</tr>
<tr>
<td>30keV Sb&gt;Au</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>33</td>
</tr>
<tr>
<td>50keV Sb&gt;Au</td>
<td></td>
<td>17</td>
<td>15</td>
<td>33</td>
<td>23</td>
</tr>
<tr>
<td>100keV Sb&gt;Au</td>
<td></td>
<td>25</td>
<td>20</td>
<td>20</td>
<td>30</td>
</tr>
<tr>
<td>100keV Sb$_2$&gt;Au (vertical)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>114</td>
</tr>
<tr>
<td>100keV Sb$_2$&gt;Au (lateral)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>114</td>
</tr>
</tbody>
</table>

J&T 79 Experimental Data (Johar and Thompson, 1979)
Way 98 Experimental Results Reported in This Work.
MD Norm. I.e.s. Molecular Dynamics Simulation - Normal Incidence.
MD Angle I.e.s. Molecular Dynamics Simulation - 7° off normal 15° rotation.

Table 4.3. Comparison of Simulation Results and Experimental Results.

It can be seen that the TRIM program has been tuned on a regular basis and not always in the direction of a closer fit to reality. The agreement with experimental data has been good for some versions. Figure 4.16 shows the results using TRIM 97 for Ar into Au and Sb into Au for a range of energies and compares them with the experimental data. This comparison bears out the observation that BCA simulations are reasonably good for the lighter ions but not realistic for heavier ions into heavy targets.
Figure 4.16 Simulation Results TRIM 97

Sb & Ar > Au vs. Experimental Data.
5. CONCLUSIONS

The initial work looking at changes in quartz resonator bandwidth or Q with changes in mass loading, temperature and shunt capacitance provided an understanding of the sensitivities and possible usefulness or problems associated with the physical and electrical environment. The original idea was to try to extract sufficient information from two resonators to allow separation of mass change, lateral stress change and temperature effects. The knowledge gained from the initial work was helpful in the design of the oscillator circuits and the overall experimental setup.

The first sputtering experiments using the three resonator system raised doubts about the validity of the lateral stress results because of the sputtering yield differences between the different crystallographic cuts of resonators due to surface texture differences. This prompted the follow on experiment using RBS to verify and quantify the sputtering yield differences. The RBS data was used to correct for the yield differences which allowed determination of lateral stress with greater certainty. Agreement has been shown between two independent measurement techniques in the measurement of sputtering yield. Using the additional information provided by an independent measurement of sputtering yield has allowed a correction to be made for the yield differences and hence compensate for temperature changes and calculate the build-up of lateral stress during sputtering. The cost of the
additional information provided by RBS is not trivial because it requires two sets of RBS data on different days and very careful calibration of the system on each day to provide the required accuracy. The method is applicable to measurements on thin films which can be deposited in place of or over the resonator electrodes.

A technique has been demonstrated which provides an in-situ monitor of changes in areal mass density, lateral stress and temperature for thin film processes. The goal of providing the results in real time during an experiment has not been entirely successful because of the sputtering yield differences between the different crystallographic cuts of the resonators due to surface texture differences. It is possible to provide the mass change results corrected for ambient temperature using the temperature measured by the thermistor, but uncorrected for stress effects, in real-time because this does not require an iterative solution for temperature. This does not provide an indication of, or correction for, temperature change due to beam heating. The use of these techniques for routine work would require having resonators made with the different crystallographic cuts all processed the same way with polished surfaces to minimise the differences between resonators.

The experiments involving the Plasma Immersion Ion Implanter were unsuccessful in that they provided no useful data regarding the processes. Their contribution was only to demonstrate the incompatibility between the plasma
immersion environment and the quartz resonators with or without connecting wires. Careful redesign of the physical details for mounting of a quartz resonator without connecting wires in the PIII could result in useful data about total mass change in the silicon nitride films for an experiment but real time data during implantation doesn’t appear to be feasible.

The experiment measuring the sputtering yields for Au bombarded with Sb at 50keV and Sb₂ at 100keV demonstrated the enhancement of yield using molecular beams and the build up of lateral stress which occurs with even moderate doses. The simulations done using molecular dynamics code provided further insight into the nature and statistics of sputtering.

The final experiment looking at sputtering yields for Sb at 30 keV and Sb₂ at 60 keV for temperatures from ambient to 150°C was inconclusive. The experimental details need to be revised to assure good dosimetry and to use a much smaller dose at each temperature to avoid loading the sample. It would be desirable to alternate between Sb and Sb₂ at each temperature and to repeat the ambient temperature measurements at the end of the experiment. It might also be possible to include data for Sb₁ at 90 kev. I plan to do this experiment in the near future.

There is current interest in the use of clusters containing tens of atoms to obtain high dose low energy implants (Goto et al., 1996). There is likely to be stress build up during the implantation of large molecules or
clusters making this technique potentially useful in understanding the processes involved. This is another area for possible future work.
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APPENDIX I.
Listing of data logging program used to control the data acquisition process and translate ASCII data from the frequency counter into numerical values and store them in a file for later processing.
/** DATALOG.C **/

#include <bios.h>
#include <conio.h>
#include <stdio.h>
#include <stdlib.h>

#define COM1 0
#define DATA_READY 0x100
#define SETTINGS (0x80 | 0x03)
FILE *fptr, *fopen();

void main()
{
    int ch_in, ch_out, status, chan, i, n;
    long int value;
    int getch(void);
    char data[256], str[8], filename[10];
    printf("Enter Filename ");
    scanf("%s", filename);
    printf("Press RESET Button on Frequency Counter then Press RETURN");
    getch();
    fptr=fopen(filename, "w");
    if (fptr == NULL) printf("error in opening file\n");
    bioscom(0, SETTINGS, COM1);
    bioscom(1, 32, COM1);
    chan = 48;
    i = 1;
    while (1)
    {
        status = bioscom(3, 0, COM1);
        if (status & DATA_READY)
        {
            if ((ch_in = bioscom(2, 0, COM1) & 0x7f) != 0)
            {
                data[i] = ch_in;
                i = i + 1;
            }
        }
        if (kbhit())
        {
            if ((ch_out = getch()) == 27) exit(0);
            bioscom(1, ch_out, COM1);
        }
        if (ch_in == 13)
        {
            delay(500);
            printf("CHANNEL %c ", chan);
            chan = chan + 1;
            if (chan == 52) chan = 48;
            {
                (str[0]=data[3];
                for(n=1;n<7;++n)str[n]=data[n+4];
                str[7]=0;
                value=strtol(str);
                fprintf(fptr, "%ld\n", value);
                for(n=0;n<4;++n)putch(str[n]);
            }
            {
                for(n=0;n<4;++n)str[n]=data[n+2];
                str[4]=0;
                value=strtol(str);
                fprintf(fptr, "%ld\n", value);
                for(n=0;n<4;++n)putch(str[n]);
            }
            i = 1;
            if (chan == 49) sleep(25);
            bioscom(1, chan, COM1);
        }
    }
}
APPENDIX II.
Listing of BASIC program which performs the solution algorithm and presents the results graphically and stores data for further processing by a spreadsheet program.
CLOSE
OPEN £10 INPUT "sput92.in"
OPEN £11 OUTPUT "sput92.out"
INPUT £10 f1,f2,f3
a£=1.1e-6
b£=-3e-4
c£=-2.0e-4
d£=0
e£=3.3e-7
f£=-2.8e-5
y£=4.5e-5
INPUT £10 af,bf,af,tf
bf£=bf/1000:af£=af/1000:sf£=sf/1000:t=tf/100
a40£=af£*a£*C C t-40*3-b£*b£*t-40
b40£=bf£*b£*C C t-40*2-d£*d£*t-40
s80£=sf£*f£*C C t-80*3-f£*f£*t-80
s50£=sf£*y£*C (C t-50*2)
ak£=-7.82e+4
bk£=-5.21e+4
sk£=5.12e+4
ap£=5.13e-7
bp£=-2.89e-7
t£=t
ord=50
WHILE NOT(EOF(£10))
INPUT £10,af,bf,af,tf
294 n=0
bf£=bf/1000:af£=af/1000:sf£=sf/1000:t=tf/100
295 IF te>50 THEN 500
nm=(af£*bp£-bf£*ap£-a40£*bp£+b40£*ap£-a£*bp£*(te-40)*3+b£*b£*t-40*3)/C ak£*bp£-bk£*ap£
ns=(bf£*b40£-c£*b£*t-35*2-d£*b£*t-35)/b£
xsq=(sk£*nm+s50£-sf£)/y£
IF xsq<0 THEN 400
x=SQR(xsq)
n=70-x
340 IF ABS(te-nt)<1 THEN 370
te=te+0.3*(nt-te)
n=n+1
IF n=12 THEN 294
GOTO 295
370 PLOT ord;1500+ns/30 MARKER 2
PLOT ord;4000+nm*5e7 MARKER 1
PLOT ord;nt*40 MARKER 1
ord=ord+10
PRINT £11,nn,ns,nt
400 WEND
CLOSE
END
500 nm=(sf£-s80£-e£*f£*(te-90)*3-f£*f£*(te-90))/sk£
ns=(af£-a40£-e£*f£*(te-90)*3-b£*b£*(te-40)-ak£*nm)/ap£
d£=b40£-bf£
zsq=(df/c£)*2-4*(df+bk£*nm+bp£*ns)/c£
IF zsq<0 THEN 400
x=0.5*(df/c£+SQR(zsq))
n=35+x
GOTO 340
APPENDIX III.
Listing of real time data acquisition and calculation program which translates ASCII data from the frequency counter into numerical values, stores them in a file for later processing and performs the solution algorithm presenting the data on the printer in tabular form. In order to be totally reliable, this program requires further error checking to avoid problems when data will not produce a convergent answer.
/* RESULTS.C */

#include <bios.h>
#include <confio.h>
#include <stdlib.h>
#include <stdio.h>

#define COM1 0
#define DATA_READY 0x100
#define SETTINGS (0x30 | 0x03)
FILE *fptr, *open();

void main()
{
    int ch_in, ch_out, slen, status, chan, i, n, m, y, init;
double fa, fb, fs, t, te, nt, nm, ns, a40, b25, s90, s50, a, b, c, d, e,
f, g, x, ak, bk, sk, ap, bp, df, sqrt(double x);
    long int value[4];
    int getch(void);
    char data[25], str[81], filename[103], outbuff[50];
    printf("\nEnter Filename ");
    scanf("%s", filename);
    printf("Press RESET Button on Frequency Counter then Press RETURN");
    getch();
    fptr=open(filename, "w");
    if (fptr == NULL) printf(" error in opening file\n");
    bioscom (0, SETTINGS, COM1);
    chan = 48;
    i = 2;
    init=0;
    a40=5941.987;
    b25=6954.655;
    s90=4969.397;
    s50=4969.414;
    a=8.8e-7;
    b=0;
    c=-4.5e-4;
    d=0;
    e=4.1e-7;
    f=-1.6e-4;
    g=-4.0e-5;
    ap=5.194e-7;
    bp=-2.9e-7;
    ak=-7.82e+4;
    bk=-5.21e+4;
    sk=-5.12e+4;
    te=20;
    y=0;
    bioscom (1, chan, COM1);
    while (1)
    {
        status = bioscom (3, 0, COM1);
        if (status & DATA_READY)
            if ( (ch_in = bioscom (2, 0, COM1) & 0x7f) != 0)
                {
                    data[i] = ch_in;
                    i = i + 1;
                }
        if (kbhit ( ) )
            {
                if ( (ch_out = getch ( ) ) == 27) exit (0);
                bioscom ( 1, ch_out, COM1);
            }
        if (ch_in == 13)
delay (500);
n = chan - 47;
if ((data[2]!=78)&&(data[4]==46))
    
    { str[0]=data[3];
      for(n=1;n<7;n++)str[n]=data[n+4];
      str[7]=0;
      value[m]=atol(str);
      printf(fptr, "%ld\n",value[m]);
    }

  if ((data[2]!=78)&&(data[7]==72))
    
    { for(n=0;n<4;n++)str[n]=data[n+2];
      str[4]=0;
      value[m]=atol(str);
      printf(fptr, "%ld\n",value[m]);
    }

  i = 1;
  while(chan == 51)
  
  if ((fa=value[1];fb=value[2];fs=value[3];t=value[4];
        fa=fa/1000;fb=fb/1000;fs=fs/1000;f=fa/1000;)
    
    printf("\nCH0 %8.3f CH1 %8.3f CH2 %8.3f CH3 %8.3f\n"
        , fa, fb, fs, t);

  if (init == 0)