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AUTHOR

J. G. Perkins

TITLE

ION IMPLANTATION OF THIN AND METAL AND DIELECTRIC FILMS
Preamble

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ION IMPLANTATION OF THIN METAL

AND DIELECTRIC FILMS

J G PERKINS

OCTOBER 1967 - DECEMBER 1970

A Thesis submitted for the degree of
Doctor of Philosophy to the Department of
Electronic and Electrical Engineering,
University of Surrey, Guildford, Surrey.
SUMMARY

The work has been directed towards the investigation of the ion implantation doping effects in thin metal and dielectric films so that knowledge may be gained regarding the feasibility of using ion implantation to produce active and passive thin film devices for microcircuits. Measurements concentrated on the detailed conduction properties, structure and composition of the films at varying stages of the ion implantation doping processes.

Aluminium and titanium thin films are implanted with oxygen atoms to ion doses of about $10^{17}$ ions cm$^{-2}$. During implantation the films' resistivities change from that of metal to that of a dielectric. Electron microscope and electron diffraction observations show that as the oxygen dose is increased then metal-oxide clusters form and grow eventually reaching 200 - 300 Å in diameter. The film then consists of a metal/metal oxide matrix and the process of electronic conduction is an activated one, with activation energies of about 0.30 eV for the aluminium/aluminium oxide system and about 0.25 eV for the titanium/titanium oxide system.

Evaporated silicon oxide films are doped with aluminium and titanium atoms by the process termed 'recoil atom implantation'. This method of doping thin films is shown by use of radioactive measurements to be an effective and efficient method provided the film thickness is less than about 500 Å. As the metal atom concentration in the dielectric is increased the resistivity of the film decreases from that of an insulator to that of a metal showing a positive temperature coefficient of resistance. Electron microscopy and electron diffraction studies show that the metal atoms form clusters within the dielectric matrix producing metal/SiO cermet type structures.
The conduction properties of the implanted films are explained at low electric field strengths on a conduction model incorporating thermionic emission and quantum mechanical tunnelling mechanisms between homogeneous arrays of spherical metal particles in a dielectric matrix. This model yields potential barrier values, \( \phi_0 \), of 0.92 eV and 0.80 eV for the aluminium/aluminium oxide and titanium/titanium oxide material respectively, formed by oxygen ion implantation, and values of 1.00 eV for the dielectric silicon oxide in the case of metal atom implantation. At high electric field strengths the conduction equations are modified by a Poole-Frenkel type emission over a field lowered potential barrier. This manifests itself in
\[ \log I \propto F^{\frac{1}{2}} \] and \[ SE \propto F^{\frac{1}{2}} \] dependences, where I is the current, F the electric field and SE the activation energy for conduction.

It is concluded that ion implantation can change in an accurate and reproducible way the electrical properties of thin metal and dielectric films and is a feasible method for producing thin film devices with a wide range of properties.
ACKNOWLEDGEMENTS

The work presented in this thesis was undertaken while the author was attached for a period of three years to the Ion Effects Group, Superintendency Nuclear Effects, Atomic Weapons Research Establishment, Aldermaston, Reading. The project was part of a collaborative programme between the Department of Electronic and Electrical Engineering, University of Surrey, Guildford and AWRE.

The author would like to thank his industrial supervisor Dr L E Collins and his University supervisor Dr K G Stephens for their many useful discussions and advice. He would also like to acknowledge the useful discussions with colleagues P T Stroud, P A O'Connell, F R Pontet, A W Tinsley and P R C Stevens during the period of the work.

Thanks are also due to the following; Miss Helen Lindsay for her careful electron microscopy and diffraction work; Mr T D J Cameron for his expert electronics assistance; Mr G C Goode and the staff of the Aldermaston 'Herald' reactor for making available their neutron activation facilities; the staff of the Aldermaston 6 MeV Van de Graaff accelerator for the efficient operation of the facility during the helium-3 charged particle activation analysis work; and the Department of Chemical Physics, University of Surrey for making available the Infra Red spectrophotometer and photomicrodensitometer.

The author would also like to convey his gratitude to the management of AWRE, and in particular Dr H R Hulme, Dr R Batchelor and Mr J J McEnhill, for the generous financial support and the use of their facilities during the period of research.

Finally he would like to thank Mrs C A Hicks for her help in preparing the manuscript, Miss Joy Crees and Miss Jackie Bennett for typing the final draft of the text and his wife Jane for her patience and understanding.
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<td>A</td>
<td>a function dependent on the tunnelling barrier width</td>
</tr>
<tr>
<td>Ao</td>
<td>count rate of radioproduct at end of irradiation</td>
</tr>
<tr>
<td>A_r</td>
<td>Richardson constant</td>
</tr>
<tr>
<td>A_t</td>
<td>count rate of radioproduct at a time t after end of irradiation</td>
</tr>
<tr>
<td>a</td>
<td>collision screening length</td>
</tr>
<tr>
<td>a_o</td>
<td>Bohr radius</td>
</tr>
<tr>
<td>B</td>
<td>a function dependent on the barrier width</td>
</tr>
<tr>
<td>C</td>
<td>capacitance</td>
</tr>
<tr>
<td>D</td>
<td>atomic spacing</td>
</tr>
<tr>
<td>D_o</td>
<td>disintegration rate of radioproduct at end of irradiation</td>
</tr>
<tr>
<td>d</td>
<td>dimension of a metal particle</td>
</tr>
<tr>
<td>E_i</td>
<td>energy of incident ions</td>
</tr>
<tr>
<td>E_r</td>
<td>Rydberg constant for hydrogen</td>
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<tr>
<td>E_d</td>
<td>displacement energy</td>
</tr>
<tr>
<td>E_o</td>
<td>threshold energy for a nuclear reaction</td>
</tr>
<tr>
<td>E_r</td>
<td>maximum energy transferrable in a head-on collision</td>
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<tr>
<td>E_{min}</td>
<td>minimum energy needed to escape from a surface or interface</td>
</tr>
<tr>
<td>δE</td>
<td>activation energy of conduction</td>
</tr>
<tr>
<td>δE_c</td>
<td>coulombic potential of a metal particle</td>
</tr>
<tr>
<td>e</td>
<td>charge of an electron</td>
</tr>
<tr>
<td>F</td>
<td>average field (Vcm^{-1}) over the electrodes of the film</td>
</tr>
<tr>
<td>f</td>
<td>frequency</td>
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<tr>
<td>f(E)</td>
<td>Fermi function</td>
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<tr>
<td>r(x/a)</td>
<td>collision screening function</td>
</tr>
<tr>
<td>G</td>
<td>conductance of film</td>
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Planck constant, \( h = h/2\pi \)
current
current density
high frequency dielectric constant
low frequency dielectric constant
Boltzmann constant
electronic stopping coefficient
electron mean free path
atomic mass. \( M_1 \) refers to incident ion and \( M_2 \) refers to target material
mass of an electron
relative mass of a tunnelling electron
atomic density of target material
density of states function
refractive index
collision density
probability of transport of an electron of energy \( E_x \)
total ion range
mean ion range
resistance of film
average projected ion range
radius of metal particles
sputtering coefficient (backward)
sputtering coefficient (forward)
spacing between particles
reduced barrier width \( \Delta s = s - s_1 - s_2 \)
points in the potential barrier at which the barrier potential is equal to the Fermi levels of the particles
absolute temperature
\( T_{1/2} \)  
radioprodut half-life

\( t \)  
film thickness

\( V' \)  
potential between particles

\( V \)  
applied voltage

\( V(x) \)  
potential due to point charge at a distance \( x \)

\( Z \)  
atomic number. \( Z_1 \) refers to incident ion and \( Z_2 \) refers to target material

\( Z_o \)  
\( \frac{Z_1^{2/3} + Z_2^{2/3}}{2} \)

\( \alpha \)  
function given by \( \beta F^2/kT \)

\( \beta \)  
constant expressing field dependency of the activation energy

\( \varepsilon_0 \)  
permittivity of free space

\( \varepsilon_F \)  
energy of the Fermi level

\( \varepsilon' \)  
Lindhard universal range parameter

\( \eta \)  
metal work function

\( \lambda \)  
wavelength

\( \xi \)  
conduction supply function

\( \xi_e \)  
collision function given by \( Z_o^{1/6} \)

\( \rho \)  
resistivity (\( \Omega \)-cm)

\( \rho' \)  
Lindhard universal range parameter

\( \sigma \)  
reaction cross section

\( \bar{\sigma} \)  
mean reaction cross section

\( \tau \)  
irradiation time

\( \Phi \)  
recoil atom flux

\( \Phi_f \)  
incident ion flux

\( \Phi_i \)  
image potential

\( \Phi_o \)  
undistorted barrier height

\( \bar{\Phi} \)  
average barrier height

\( \Phi(x) \)  
height of potential barrier at \( x \)

\( \Delta\Phi \)  
amount barrier lowered by applied field

\( \Psi \)  
electron affinity of the dielectric
CHAPTER I

GENERAL INTRODUCTION

1.1 Ion implantation and its interest

When an energetic ion is incident on a solid surface one or more of several processes can take place:

(a) it can become neutralized by an Auger-like transition a short distance in front of the surface (Hagstrum 1954), giving rise to secondary electron ejection;

(b) the ion can be reflected from the surface without neutralization, that is, ion reflection or scattering can take place;

(c) the ion can cause ionized species of the target atoms to be liberated (Kistemaker and Snoek 1962), or

(d) the ion can penetrate the target lattice transferring momentum to one and successively more lattice atoms in predominantly elastic collisions (Bohr 1948).

In this latter process those lattice atoms which receive sufficient momentum may leave their lattice sites producing disorder, damage and the ejection of atoms from the surface. The incident ion however can either finally come to rest within the solid (i.e. it is trapped), or escape through the surface with reduced kinetic energy. For heavy ions in the 10–200 keV energy region the penetration depth before coming to rest in solids is typically 100–5000 Å (1 Å = 10⁻⁸ cm). For any particular ion-target system the penetration, or range, can be accurately controlled by variation of the ion energy. Thus the method lends itself to the impurity doping of solids to known depths beneath the solid surface. This technique of doping solids has been termed ion implantation.
Taking place together with ion implantation we have associated ion bombardment phenomena, such as surface sputtering and etching. Although studies of these processes have been carried out for over a hundred years, much of the work was of a basic nature and only since 1950 have applications of ion implantation and ion bombardment become of importance. They now play a role in many fields of interest: the deposition of thin layers of metals, semiconductors and insulators, as well as of compounds; wall problems in plasma physics; the cleaning and ionic etching of surfaces; ion-getter and ion sputtering vacuum pumps; solid state atom and ion sources; specimen thinning; micro-machining; glass polishing; the alteration of chemical reaction rates at solid surfaces; analysis of surface conditions and target materials; the doping of semiconductors for production of commercial devices; material and surface problems in real and artificial satellites; and last but not least the understanding of the interaction between atomic particles.

1.2 Aims of the research

The aim of this research is to investigate the electrical conduction properties of thin films that have been doped with impurity atoms by ion implantation and bombardment methods. The electrical properties are correlated with the microstructure and composition of the films. Possible technological applications of ion implantation to thin film microcircuitry are also considered.

The major effort of ion implantation doping was directed in the early 1960's towards the production and understanding of single crystal semi-conducting devices. This was natural as the experimental advances of diffusion techniques together with the detailed knowledge developed from wave mechanisms of the behaviour of electrons in ideal crystals had overshadowed developments in the electrical properties of the amorphous state. Recently however, there has been a great deal of interest attached to dielectric, semiconductor and mixed metal/dielectric, ie cermet, thin films due to the
discovery in such films of memory effects, current controlled negative resistance, fast switching phenomena (Simmons 1970), controlled high resistivity and predictable temperature coefficient of resistance. There is thus currently a considerable research effort being directed towards the eventual understanding and commercial exploitation of amorphous materials. The two main reasons are as follows: firstly, the amorphous devices perform electric functions not found in discrete crystalline devices, and secondly, because of their very nature, amorphous devices can be expected to be much less sensitive to high energy radiation than crystalline devices. Two main problems are at present facing the development of such amorphous passive and active devices. These are the problems of preparation — that the electrical properties are consistent and reproducible — and the fact that the theoretical knowledge of the amorphous state is still relatively in its infancy when compared with the crystalline state.

Ion implantation has been shown to be an accurate and controlled means of introducing impurities into a solid, and in this work we implant thin metal and dielectric films with impurity atoms, with a view to accurately and controllably changing their properties. Ion implantation may offer a better method of controlled doping than evaporation or sputtering techniques.

As well as the effect of doping, phenomena associated with ion implantation such as radiation damage and sputtering cause changes in electrical properties of thin film targets. It is necessary therefore, to understand the relative contributions of such processes and it is to this end that part of the thesis has been orientated.
The first qualitative observations of the effects of ion bombardment of surfaces was reported more than a century ago. In 1851, Plucker observed that in X-ray tubes a continuous removal of gas occurred and the X-rays became 'harder' since increasingly high voltages were required to operate the tubes. In 1852 Grove noted that surfaces struck by energetic ions were slowly eroded away due to the removal of the target material by the impinging ions. Many of the ensuing early experiments, for example those by Blechschmidt (1926), were performed in glow discharges of the Grove type so as to reach a reasonably high ion-current density. However, the high pressures in these systems are a serious disadvantage as there are nearly always complications owing to back diffusion of sputtered particles and contamination of the bombarded surface. When in the discharge a magnetic field is used (Penning and Moubis 1940) or an independent electron emitter (Güntherschulze 1953, Wehner 1955), or both (Koedam 1958, Honig 1958) the 'discharge' can be maintained at a much lower gas pressure with the same high density of ions. Modern experiments of ion bombardment and implantation are now usually undertaken on new types of apparatus, the mercury pool discharge system, in which the target is inserted in the manner of a Langmuir probe into the discharge region, and as in the present investigation the ion beam method. The ion beam method is now more widely used especially in the field of ion implantation. Although the beam intensity is much lower than in the discharge the beam can be analysed magnetically or electrostatically and double charged and neutral species can be eliminated.

The post-1940 development of the increasing size of machines for producing and accelerating nuclear particles and the increasing investigation and use of nuclear reactors led to problems of target reactions which were the forerunners of today's current studies and theories of ion-target interactions. The interest in ion implantation has grown rapidly, after the
discovery that improved semiconductor junctions could be obtained by introducing the impurity atoms into the host lattice by ion implantation (Ohl 1952, Cussins 1955, King and Solomon 1962, Alvager and Hansen 1962, Rourke et al 1961), and also because of the growing importance of both radiation damage (Seitz and Koehler 1956, Holmes 1964) and sputtering processes (Rol et al 1960, Thompson 1959, 1963).

The early 1960's saw the start of investigations into the more fundamental processes associated with ion implantation. Davies et al (1962) investigated the range-energy relations of heavy ions and found that the profiles agreed well with the calculations of Lindhard and colleagues at Aarhus, Denmark (Lindhard and Scharff 1961, Lindhard et al 1963 a). In 1963 computer studies predicted that heavy ions of keV energies would penetrate to anomalously large depths along low index crystallographic directions (Robinson and Oen 1963, Beales and Besoo, 1963). This effect was termed channelling and was subsequently demonstrated by range measurements on monocrystalline targets of aluminium (Piercy et al 1964), copper (Lutz and Sizman 1963) and silicon (Davies et al, 1964).

Since 1964 the ion implantation doping of semiconductors, channelling, radiation damage and sputtering has grown rapidly and the status of the field can be found in excellent reviews (McCaldin 1965, Dearnaley 1969, Mayer and Marsh 1969) and in various conference proceedings (Koch and Nielsen 1965, Elliott 1968, Palmer et al 1970).

Ion implantation and bombardment studies using thin film targets, usually of polycrystalline material, have mainly been associated with radiation damage investigations using predominantly inert gas ions (Teodosio 1966, Navinsek and Carter 1967, 1968, Hughes and Carter 1968, Merkle and Singer 1967, Merkle 1970, Chechetenko et al 1968, Radzabhov and Ivanovskii 1966). Chemical effects have also been reported using active gas ions. For example Wantanabe and Tooi (1966), Pavlov and Shitova (1967) and Freeman (1970, private communication) have shown that surface layer of silicon
can be converted to silicon oxide by oxygen ion bombardment. Meyer et al (1969) have observed oxidation of copper by the same process. Collins and Richmond (1970), O'Connell (1970 private communication) and Perkins and Stroud (1970) have recently shown that a wide range of resistivity material in thin film form can be produced and accurately controlled by ion implantation and bombardment methods.

As with ion implantation interest in the amorphous state has accelerated rapidly in recent years, and a considerable amount of experimental evidence has been published relating to various aspects of electrical properties of amorphous materials. Relatively recent detailed reviews are available (Jonscher 1967, 1969, Hill 1967 a, Mott 1969, Simmons 1970, Owen 1970) and the following discussion will attempt merely a summary of some of the more important prevailing trends.

Types of amorphous glasses exhibiting semiconducting properties are the transition metal oxides and the chalcogenide glasses. These include oxide and boron-based glasses containing various combinations of tellurium, arsenic and other elements. These glasses often show non-ohmic conduction and switching (Drake et al 1969). The type of glasses which can be switched between two conducting states are probably the most well known and are commonly referred to as Ovshinsky or Ovionic diodes after S R Ovshinsky although the phenomena were apparently first reported by Pearson et al (1962). The samples may be prepared by evaporation (Coward 1968, Ovshinsky 1968), sputtering (Ovshinsky 1968) or by hotpressing the glass between the electrodes (Ovshinsky 1968).

Active device behaviour has been observed in anodically - and thermally - grown oxides and in vacuum-deposited insulators. Chopra (1965 a) has observed current controlled negative resistance (CCNR) in 'formed' thin oxide films of niobium, tantalum and titanium, sandwiched between thin film electrodes. Several reports have been made of negative resistance and

The continuing interest in the technological applications of dielectric films is reflected in the large number of papers dealing with the various aspects of the mechanisms of current flow in these structures. Silicon oxide is one of the most frequently studied materials and various mechanisms have been proposed to explain its behaviour, e.g., Hirose and Wada 1965, Johansen 1966, Hartman et al 1966, Servini and Jonscher 1969.

The conduction in dielectric films can be modified with the introduction of metal atoms and we then have mixed metal-dielectric films, the so-called 'cermets'. Cermets promise to provide controllable high resistivity, predictable temperature coefficient of resistance and high stability.

The majority of investigation into cermet structures have considered the Cr-SiO system. Early work on Cr-SiO films indicated that they could be evaporated with resistivities up to $10^4 \Omega \cdot \text{cm}$ and TCR's smaller than -200 ppm °C$^{-1}$. Brown and Lood (1966) show that such films are relatively stable under thermal aging. No clearly defined structure has been shown to exist in such films. They consist very generally of Cr, $\text{Cr}_2\text{Si}$, Si, SiO, and SiO$_2$ in varying amounts and varying degrees of crystallinity. Ostrander and Lewis (1961) proposed that the components of cermet films are distributed at random in a state of dispersion approaching atomic dimensions. Cermets of other systems such as evaporated Cr-MgF$_2$ (Beckerman and Thun 1961), sputtered Au-SiO$_2$ (Miller et al 1970) and Cr-SiO (Frietag and Weiss 1967) as well as sputtered Ta-Al$_2$O$_3$ (Henrickson et al 1969) have exhibited properties very similar to those observed for evaporated Cr-SiO cermets.
1.4 Purposes of measurements and methods used

1.4.1 Survey of measurements

The results of implanting metal and dielectric thin films with gas ion and metal atoms and the information derived from it are described in this thesis.

The metal films, which were polycrystalline aluminium and titanium, were implanted with oxygen and argon ions with energies between 30 and 120 keV. Aluminium and titanium were chosen as both could be easily prepared in thin film form and both have applications in microelectronics; aluminium being used mainly for resistors and interconnections and titanium for thin film resistors, capacitors and rectifiers (Huber 1965, Lloyd 1965, Wasa and Hayakawa 1967). Ion ranges are also much greater in aluminium and titanium than in say tantalum, another material used a great deal in microelectronics thin film technology. The greater range allows a much thicker 'oxide' film to be produced with oxygen ion implantation. The oxide film is then not so susceptible to surface phenomena such as sputtering.

The dielectric films consisted of evaporated silicon oxide (Hass 1950) of predominantly SiO$_{1.5}$ composition. The metal impurity atoms of aluminium and titanium were introduced into the dielectric by recoil atom implantation using argon gas ions of energy of about 50 keV.

The measurements on both the implanted metal and dielectric films concern the variation of metal/metal oxide (dielectric) atomic concentration, the detailed electronic conduction properties and the microstructure of the films. These quantities were measured as a function of ion dose. The direction of incidence of the bombarding ions was always perpendicular to the macroscopic target surface.
Gas ions were produced in a simple RF (radio-frequency) discharge source and could be accelerated up to 150 keV before being mass analysed and directed onto the target films. Oxygen ions were implanted directly and the metal atoms, as stated above, were implanted into the dielectric by recoil atom implantation. In this latter method atoms from a metal layer on the dielectric, which have received energy in collisions with the incident inert gas ions, recoil across the metal-dielectric interface and become implanted into the dielectric. The ratio of the number of implanted atoms to the number of incident inert gas ions can be greater than unity. The feasibility of using recoil atom implantation for doping materials has been shown with independent work by Shimizu et al (1969) in Japan and by the author (see Chapter IV).

The reason for the choice of recoil atom implantation instead of direct ion implantation were two fold. Firstly, a reliable long running high current density metal ion source capable of 10-20 μA of aluminium and/or titanium ions was not available without a great deal of development. Secondly, any technological application of implantation to thin film devices would become more feasible if high energy discharges could be used instead of an ion beam accelerator. The eventual use of a discharge would favour processes concerned with gas ions as opposed to metal ions, therefore in this work we have concentrated on effects that can be produced with primary gas ions.

Metal to metal oxide atomic ratios were measured by determining oxygen and metal atom concentrations. The oxygen content was determined by the technique of charged particle activation analysis using singly charged helium-3 ions accelerated to an energy of 5.5 MeV. The metal atom concentra-
tions were evaluated by using neutron activation analysis with thermal neutrons, having energies of about 0.024 eV and fluxes of about $10^{12}$ n cm$^{-2}$ sec$^{-1}$, obtained from the Aldermaston Herald reactor.

Resistivity changes of the films during implantations were determined by simply interrupting the ion beam at various stages of the bombardment to allow measurements. The detailed conduction properties were obtained after the samples had been completely removed from the ion accelerator target chamber. The methods used to investigate the conduction mechanisms were to measure the dc current-voltage characteristics and their variation with temperature, and ac conductance and capacitance variations with frequency. These measurements were then correlated with the films' microstructure and composition. The microstructure was investigated by use of electron microscopy and electron diffraction using 100 keV electrons and the composition of the implanted films examined by infra red transmission and reflection spectroscopy in the 400-1333 cm$^{-1}$ frequency region.
CHAPTER II

REVIEW OF THEORY

2.1 Heavy ion penetration

2.1.1 Introduction

In work of the nature involved in this thesis where the fate of an injected ion into a material is important, a knowledge of heavy ion ranges is essential. In the energy region of interest there are two main competing energy loss processes;

(i) elastic collisions between incident ion and target nuclei, and

(ii) electronic excitation.

In the former process incident ions may be scattered in the screened Coulomb fields of target nuclei and the momentum imparted to struck atoms is often sufficient to cause lattice atom displacements. The scattering cross section for nuclear collisions is large for low ion velocities and therefore nuclear stopping can be expected to be the dominant stopping process near the end of the incoming ion's range regardless of its initial velocity. The injected ion, however, may also lose energy by ionising or exciting target electrons, i.e. process (ii) above. This is important at the higher energies where incident ion and target electrons have similar velocities. Electronic stopping is most likely to be significant, therefore, for light and hence fast moving ions during the initial slowing down.

In dealing with and understanding the interaction of an ion and a lattice atom it is necessary to deal with the interatomic forces, on which the mechanics of any collision between atoms depend very sensitively. The potential due to a point charge, Ze at a distance x is given by the well known Coulomb law \( V(x) = \frac{Ze}{x} \). However at a point distance x from the nucleus the full potential due to the nucleus can be expected to be reduced by screening effects from orbital electrons. In general form, then, the potential may be expressed as
\[ V(x) = f\left(\frac{x}{a}\right) \frac{Ze}{x} \] ... (2.1)

where \( f(x/a) \) is the screening function and \( a \) is the screening length.

Considering the interaction of two atoms of atomic numbers \( Z_1 \) and \( Z_2 \), we can write

\[ V(x) = f\left(\frac{x}{a}\right) \frac{Z_1 Z_2 e^2}{x} \] ... (2.2)

2.1.2 Heavy Ion Ranges

The Theory of Lindhard et al

An ion moving through a solid suffers a series of collisions with target atoms which results in a series of deviations in the flight path. (Fig 2.1). These collisions may be random in the case of an amorphous target or correlated small angle collisions if the incident ion is fired into an open crystal direction and channelling occurs. The total range, \( R \), is simply defined as the sum of the path lengths between subsequent collisions. Owing to the statistical nature of the collision processes there is a spread in total ranges and an average total range, \( \bar{R} \), may be defined which is an arithmetic average of all total ranges. In experiments where the final position of the implanted ion is important, what is of interest is the depth normal to the surface plane. A mean projected range, \( R_p \), may be defined as the most probable depth of penetration normal to the surface.

The first published estimate for the range of atomic projectiles in the keV energy region was made by Nielsen (1956) using a \( 1/x^2 \) approximation for the Bohr (1948) potential. This was followed by work by Holmes and Liebfried (1960), Lindhard and Scharff (1961) and Powers and Whaling (1962).
FIG. 2.1 ILLUSTRATING RANGE CONCEPTS
The calculations of range profiles that have become widely accepted and used are those of Lindhard, Scharff and Schiött, the so called 'LSS theory' (Lindhard et al, 1963 a, 1963 b) and it is with their theory that we will be concerned in this thesis.

In their treatment of the slowing down process of ions Lindhard et al used the Thomas-Fermi like treatment of the dependence on both \( Z_1 \) and \( Z_2 \), and in equation (2.2) \( f(\frac{X}{a}) = \Phi(\frac{X}{a}) \) the Thomas-Fermi function, where

\[
\Phi(\frac{X}{a}) = \Psi(\frac{X}{a}) - C_2 \frac{a^2}{\sqrt{C}} \tag{2.3}
\]

and \( \Psi(\frac{X}{a}) \) is the solution of

\[
\Psi''(\frac{X}{a}) = \left\{ \Psi(\frac{X}{a}) \right\}^{3/2} \frac{X}{a} \Psi'(\frac{X}{a}) \tag{2.4}
\]

and has been tabulated by Gombas (1956). Considering such a screened potential involving only the one screening parameter \( a' \), LSS express their results in terms of two dimensionless parameters \( \rho' \), \( \varepsilon' \) which are a natural measure of range of energy for an ion colliding with atoms at rest.\(^6\) We have

\[
\rho' = \frac{R N M_2 \sqrt{4 \pi a' M_1}}{(M_1 + M_2)^2} \tag{2.5}
\]

and

\[
\varepsilon' = \frac{a' M_2 E_1}{Z_1 Z_2 e^2 (M_1 + M_2)} \tag{2.6}
\]

\(^6\) LSS actually use the parameters \( \rho \), \( \varepsilon \); they have both been primed in our case to avoid the confusion of \( \rho' \) with resistivity.
where \( a = 0.53 \times 0.8853 \times 10^{-8} \frac{Z_{50}^3}{Z_{10}^3} \)

\( R = \) range

\( E_i = \) incoming ion energy (in ergs)

\( Z_{50} = \frac{Z_1^2}{2} + \frac{Z_2^2}{2} \)

\( N = \) density of scattering centres

\( M_1, M_2 = \) mass of incident ion and target atom respectively

\( e = \) electronic charge

The ranges are then expressed in terms of universal plots. These curves are reproduced from Lindhard's original papers in figures 2.2(a) and 2.2(b).

The straight line \( \rho' = 3.06 \rho \) is equivalent to Nielsen's results. The conversion factor to obtain projected ranges from total ranges given by Lindhard is

\[
\frac{R_p}{R} = \frac{1}{1 + \frac{M_2}{3M_1}} \quad \ldots (2.7)
\]

The effect of electronic stopping is also shown in terms of an electronic stopping constant, \( k_e \), given by

\[
k_e = \frac{Z_{50}^{1/3}}{2^{1/6} (Z_{10}^{2/3} + Z_{20}^{2/3})^{1/4} M_{50}^{1/2} M_{20}^{1/2}} \quad \ldots (2.8)
\]

where the quantity \( Z_{50} = 2^{1/6} \).

The parameter \( k_e \) is normally of the order of 0.1 to 0.2, and only in the exceptional case of \( Z_1 \ll Z_2 \) can \( k_e \) become larger than unity.

Johnson and Gibbons (1969) have performed detailed computer calculations on the LSS theory for a wide range of ion-target systems. Figures 2.3(a) and 2.3(b) show their computed average projected ion ranges, \( R_p \), and electronic and nuclear energy losses with ion energy respectively for the argon-aluminium, and oxygen-aluminium systems. Range-energy curves for argon-titanium and oxygen-titanium systems computed by Stevens and
FIG. 2.2(a) RANGE CURVES FOR VARIOUS ELECTRONIC STOPPING CONSTANTS, $\varepsilon' < 10$

FIG. 2.2(b) RANGE CURVES FOR VARIOUS ELECTRONIC STOPPING CONSTANTS, $\varepsilon' > 1.0$
FIG. 2.3(a) Projected Ranges in Aluminium and Titanium

FIG. 2.3(b) Energy Loss in Aluminium, $\tau$, Nuclear Stopping; $\sigma$, Electronic Stopping.
Wankling (1968, private communication) are also shown. In figure 2.3(a) the experimentally determined data for argon ions in aluminium found by Davies et al (1963 a) shows how close are the theoretical predictions.

Due to the random nature of the collision processes there will be a spread in range about the mean approximating to a Gaussian distribution. Lindhard gives the expression for the spread where nuclear stopping dominates as:

\[
\langle \Delta R^2 \rangle_{av} = \frac{2M_1 M_2 R_p^2}{3(M_1 + M_2)^2}
\]

If electronic stopping is significant over the first part of the range, the above equations for straggling must be modified.

2.1.3 Penetration and density of recoil atoms

As well as causing lattice displacements which manifest themselves as 'radiation damage', recoil atoms through collision sequences can cause ejection of surface atoms from the front face (ie backspattering) and from the back face (ie forward sputtering) of a thin film. If the thin film is now placed on a substrate it is reasonable to assume that the forward directed recoils that have sufficient energy will cross the thin film-substrate interface and become implanted into the substrate material. The ranges of such atoms are not so easily determined as in the case of directly implanted atoms where the straightforward LSS theory applies.

Robinson (1965) considers an infinite, homogeneous, structureless medium (that is, a gas), containing a uniformly distributed isotropic source of mono-energetic particles of the same mass as those of the medium. The source particles are slowed down by elastic collisions with the atoms of the medium, displacing these from their original positions to slow down in turn by further elastic collisions.

\* \[\langle \Delta R^2 \rangle_{av} = \frac{1}{\hbar^2}; \text{ half width } \omega_1 = 2.35\sigma = 1.67/\hbar\]
For hard-core scattering which is isotropic in the centre-of-mass system, the atomic collision density \( n(E) \) may be described by the equation

\[
n(E) = \frac{2E}{E^2} \quad \ldots (2.10)
\]

where \( E \) is the energy of a mono-energetic source of unit strength.

Equation (2.10) can be rewritten generally as

\[
n(E) = \frac{kE^{k-1}}{E^k} \quad \ldots (2.11)
\]

which includes as special cases the familiar result for neutrons slowing down in hydrogen \((k = 1)\) and the atomic slowing down case discussed by Robinson \((k = 2)\).

The hard-core approximation represents the scattering of energetic atoms only rather poorly, however Robinson using more realistic interatomic potentials finds that the collision density \( n(E) \) is relatively insensitive to much of the difference between the hard-core approximation and the correct differential scattering cross section. A similar insensitivity occurs in the number of displaced atoms produced in a cascade (Lehmann 1961, Cen and Robinson 1964). The calculation above is of the collision density, whereas experimental observations are essentially of the flux density. However, in the atomic case, unlike the neutron case, the (microscopic total) scattering cross section is large enough such that the moving particle interacts at (essentially) every interatomic distance and may, therefore, be regarded as practically energy independent since its magnitude depends primarily upon crystallographic parameters. Thus the flux and collision densities will differ only by a constant.
Thompson (1968) using a simpler approach also finds a $1/E^2$ spectrum away from the source energy, and also shows the relationship experimentally with $\text{Ar}^+$ and $\text{Xe}^+$ ion bombardment of gold. Nelson (1969), using Robinson's and Thompson's theories, investigates the feasibility of using recoil atoms as a method of implantation of semiconductors. The flux of atoms crossing a plane can be written (following Thompson) as

$$d\Phi(E, E_i) = \frac{D}{E^2} \int_{E}^{E_r} S(E_r) E_r dE_r \quad \ldots (2.12)$$

where $D$ is the atomic spacing,

$E_r$ the maximum energy transferred in a head-on-collision and is equal to $4 \frac{M_1 M_2}{(M_1 + M_2)^2}$

$E_i$ the incident ion energy, and

$S(E_r)$ is given by

$$S(E_r) dE_r = N \phi_I d\sigma(E_r, E_i) \quad \ldots (2.13)$$

where $\phi_I$ is the incident flux,

$N$ the target density, and

$d\sigma$ is

$$d\sigma(E_r, E_i) = \frac{\sigma(E_i) dE_r}{E_r}$$

using an increase square potential, where

$$\sigma(E_i) = \frac{2 \pi \rho_0^2 E_r Z_1 Z_2 (M_1 + M_2)}{2.72 M_2 (Z_1^{2/3} + Z_2^{2/3})^{1/2} E_i}$$
So substituting into equation (2.12) we get

\[
\frac{d^3 \Phi(E,E)}{dE_1 dE_2 dE_3} = \frac{4\pi \alpha^2}{2.72 \left( M_1 + M_2 \right)} \left( 2^{2/3} \frac{Z_1 Z_2}{2^{1/3}} \right)^{1/2} \left( \frac{1}{E_1^2} - \frac{1}{E_r^2} \right) \quad \ldots (2.14)
\]

where \( E_r \) is the Rydberg constant for hydrogen (13.6 eV), with all other parameters having been defined previously.

The total number of atoms can be determined by integration of (2.14) from some minimum energy \( E_{\text{min}} \) to \( E_r \). For \( E_r \gg E \), the concentration is independent of \( E \) and proportional to \( \frac{1}{E} \) as expected.

If we take \( E_{\text{min}} \) as being equal to 25 eV, typical of displacement energies for most metals, then integration of equation (2.14) gives the ratio of the number of aluminium atoms recoiling across an interface to the number of incident gas ions, as being about 4 for the argon-aluminium system. Sputtering values near this figure have been found by the author (see Chap IV) showing that recoil atom implantation can be very efficient as far as the number concentration is concerned. The \( \frac{1}{E^2} \) dependence, however, of concentration upon energy makes the process inefficient for deep implantations, that is, for a penetration greater than about 500 \( \bar{R} \), (see chap IV, sect 5.2.3.2).

2.2 Electronic conduction phenomena in thin films

2.2.1 Introduction

Electron microscopy and electron diffraction investigations (see Chapter V) show that the implanted films consist of metal/metal oxide mixtures, the metal existing as islands in a dielectric medium, and that conduction is electronic not ionic in nature. The dielectric medium is either amorphous or consists of crystallites of up to 300 - 400 \( \bar{R} \) in diameter. In this section we therefore review the relevant electronic conduction mechanisms.
Firstly the salient features of the theory of amorphous conductors especially as it applies to dielectric films are recalled. The general consensus of opinion here is that the basic features of the band structure, such as the width of the forbidden gap, are determined primarily by the short range order, i.e. by the relative disposition of nearest neighbours in the solid. We then consider electronic conduction in dielectrics which may be due to the motion of 'free' carriers - electrons in the conduction band or holes in the valence band - or alternatively to the motion of quasi-localized carriers which is otherwise described as hopping of band carriers between localized sites in the dielectric. The former process requires an activation energy in order to excite a carrier into the relevant band, and this energy can normally be supplied thermally, or by other free carriers which have acquired a high energy in an electric field, leading to an avalanche process. The hopping process requires less energy than the activation into the free band and this energy may, in the event of very high density of localized centres, tend to zero as in the case of impurity band conduction in semiconductors.

Finally we discuss the conduction in thin discontinuous films. There is a striking change in the conduction behaviour of a film as its thickness is reduced to the stage when it becomes an island structure. For a metal film this change is generally from a low to a very high sheet resistance. A similar change is observed when a second, non-conducting phase is introduced to separate the metal grains from each other, i.e. as in mixed metal-metal oxide films where the metal exists in island structures.

**2.2.2 Conduction in amorphous materials**

In crystalline materials the band structure of the material is expressed through the density of states $N(E)$, the quantity $N(E)dE$ representing the number of electron states with energy between $E$ and $E + dE$. The form of $N(E)$ is shown for a metal and for a semiconductor or insulator in
The Bloch–Floquet theorem states that the one-electron wave functions must be of the form

$$\psi(x) = \psi_{kn}(x) = \exp(i k x) U_{kn}(x) \quad \ldots \quad (2.15)$$

where the wave vector $k$ is in the first Brillouin zone, $U_{kn}(x)$ has the periodicity of the crystal structure, and $n$ is the band index. Thus all wave functions in the crystal are extended; the magnitude of $\psi$ is of the same order everywhere in the crystal. Moreover all states $\psi$ possess perfect phase coherence, i.e., long-range order in the phase. Given the phase at one point, we can determine the phase at any other point in the crystal provided only that we know the wave vector $k$. The corresponding one electron energies for semiconductors

$$E = E_n(k) \quad \ldots \quad (2.16)$$

fall into continuous bands of allowed levels separated by forbidden gaps.

Mathematical treatment of the density of states in amorphous materials has proved extremely difficult (see Mott 1967, Halperin 1968, Gubanov 1965). However, it has been shown that with the disappearance of long-range order and with small departures from the short-range order, as found in amorphous materials, the energy spectrum retains its band structure. One does, however, obtain a broadening of the allowed bands and a spreading of their edges. In many materials the gap either persists, as in glass (fig 2.4 (d)) or is replaced by a minimum (fig 2.4 (c)) usually termed a 'pseudogap'. Near the extremities of the gap, or in the 'pseudogap', the wave functions are strongly perturbed by the irregular arrangements of the atoms, and the electrons will move by a sort of Brownian movement through the lattice.
F. 2. 4

**Density of States in a Monovalent Metal.** $E_F$ is the Fermi energy.

**Density of States in an Intrinsic Semiconductor.** The occupied valence band is shaded. AB is the 'band gap.'

**Suggested Form of the Density of States in Non-crystalline Insulators and Semiconductors.**

In (d) the gap remains as in glass; in (c) the gap has disappeared. Localized states are shown shaded.
Mott et al (1967) obtained a criterion for the localisation of states by calculating the ratio of the density of states \(N(E)\) under the perturbation of the random scattering centres to the density of states \(N(E)\) obtained for a free electron gas. Using the condition that \(L = \lambda\), where \(L\) is the mean free path over which the wave function defined in equation (2.15) is valid and \(\lambda = \frac{2\pi}{k}\) is the wavelength, they showed that for a state to be localized in space

\[
\frac{N(E)}{N(E)_{\text{free}}} < \frac{1}{2} \quad \ldots (2.17)
\]

For energies in the pseudogap, or very near the extremities of the conduction and valence bands the electrons in a localized state can be described as trapped, so this means that the absence of crystalline order produces a high density of traps. The range of energies in which states are localized is shown shaded in figs 2.4 (c) and 2.4 (d). It is obvious that one can have a continuum of energy levels, as shown by the shaded areas, and in each of these energy levels the electron is trapped and unable to move. Tunnelling between states cannot occur because if two states are close enough together for tunnelling they split into two states which do not have the same energy (Mott 1968).

2.2.3 Conduction in dielectric thin films

Conduction in films that consist of mixed phases of metal and the dielectric may possibly take place by conduction in the dielectric conduction 'band' of localized or non localized states. It is therefore important to mention the mechanism prevalent in the conduction of dielectrics. The majority of detailed investigations have been carried out on the evaporated silicon oxide films due to the extensive use of these films for insulation (Lessor et al, 1964), capacitors (Siddall 1959) and hermetic encapsulation (Hartman and Chivian 1964).
It is a well established fact that at electric fields, $F$ in excess of some $10^4$ V cm$^{-1}$ many dielectric films exhibit conductivity characteristics of the form

$$I \propto \exp \left( \frac{\beta F^{1/2}}{kT} \right) \quad \ldots (2.18)$$

where $T$ is the absolute temperature


This has been taken as evidence of either Schottky or Poole-Frenkel emission. The Schottky effect is thermionic emission from a plane electrode over a field-lowered barrier, and the Poole-Frenkel effect (Frenkel 1938) is thermionic emission from a point defect, surrounded by a Coulombic potential, over a field-lowered barrier. We can write the potential barriers in each case,

$$\Delta \phi_{PF} = \left( \frac{e^3}{4\pi \varepsilon_0 K} \right)^{1/2} F^{1/2} = \beta_{PF} F^{1/2} \quad \ldots (2.19)$$

$$\Delta \phi_{S} = \left( \frac{e^3}{4\pi \varepsilon_0 K} \right)^{1/2} F^{1/2} = \beta_{S} F^{1/2} \quad \ldots (2.20)$$

where $K$ is the high frequency dielectric constant equal to the square of the refractive index $n$

$\varepsilon_0$ the permittivity of free space.
These effects are governed by equations of the form (Poole-Frenkel)

\[ I = I_o \exp \left[ -\left( \Phi_{PF} - \Delta \Phi_{PF} \right) / kT \right] \quad \ldots (2.21) \]

(Schottky)

\[ I = I_o' \exp \left[ -\left( \Phi_S - \Delta \Phi_S \right) / kT \right] \quad \ldots (2.22) \]

Thus theoretically by numerical calculation of \( \beta \) it should be possible to decide between the two effects. However, it is not always possible to obtain a satisfactory agreement with either theory. Experimental values of what should be the Poole-Frenkel bulk limited process tend to agree with the Schottky electrode limited mechanism.

O'Dwyer (1966) considered an electronic model of a dielectric with traps, together with Schottky emission from an injecting electrode and with Fowler-Nordheim correction for tunnelling through the top of the barrier at high fields, but his values of \( \Phi (\sim 0.9 \text{ eV}) \) seem to be rather high to be compatible with the experimentally determined values for silicon oxide (0.43 - 0.56 eV). Hirose and Wada found it necessary to assume a value of \( \kappa = 12 \) to obtain agreement with the Poole-Frenkel formula. This is certainly unrealistically high for what must be taken as the high frequency dielectric constant, with \( n = 1.5 - 2.0 \) for SiO, (Heavens 1960). Johansen sought to reconcile his coefficient favouring the Schottky mechanism with the fact that his currents were bulk-dominated by postulating emission from small silicon islands uniformly distributed in the matrix of silicon oxide.

Simmons (1967) has proposed a model of \( N(E) \) to explain data favouring the Schottky mechanism with the Poole-Frenkel mechanism. In his model the Fermi level in the silicon oxide was in the pseudogap between a
deep-lying donor level (filled) and a shallow neutrally charged (unfilled) acceptor level near the non-localized conduction band. The possibility of donor levels, which were charged when unfilled, lying below shallow acceptor levels was suggested on theoretical grounds by Gubanov for disordered materials in general. The resulting 'bulk' conduction is field dependent in a manner usually associated with Schottky emission although the Poole-Frenkel effect is the true operating mechanism. Simmons further shows that this model is the only simple system of a single trap and donor level that will exhibit an anomalous Poole-Frenkel effect.

Yeargan and Taylor extend Simmons' Poole-Frenkel model to include the effect of compensation. The relative densities of donor and acceptor sites control the slope of the log $J$ vs $F^{1/2}$ plots. With only one type of site present, the slope equals that expected for Schottky emission, and when sites of the opposite type compensate the slope doubles. The degree of compensation must be known to determine the barrier heights separating the emission site from the band edge.

Optical absorption measurements on silicon oxide yields an energy gap of 4 eV in width. Diffuse absorption edges can be explained as being due to the transition to and from localized states near the edges of the pseudogap, (Rawlings, 1968).

The variations in $\Phi$ found experimentally, values lying between 0.43 eV and 0.56 eV, are probably due to deposition conditions. It seems the degree of oxidation of silicon oxide determines electrical properties rather than the presence of impurities (Allam and Pitt 1967, York 1963, Hass 1950, Pliskin and Lehmann 1965).

2.2.4 Conduction by impurity centres

Because of the low mobility of an electron in an impurity level at normal temperatures, impurity conduction will be masked if there are many electrons in the conduction band. In an insulator, however, there is a very
low density of thermally generated free carriers in the conduction band and thus impurity conduction is more likely to be observed in these types of materials than in semiconductors.

At low concentrations the overlap between the wave functions of neighbouring impurity sites is small and the banding between the sites is smaller than the energy difference between the sites due to the variations of local electric fields. The local fields are produced by nearby ionized acceptors and donors. The electrons are then localized; their wave functions decay exponentially with distance to infinity, and neighbouring impurity states are non-degenerate. If one of the donor electrons is close enough to one of the vacant donor sites it can hop to the site. The transfer is accompanied by the emission or absorption of a phonon so that energy is conserved, and the charge transfer will be random in the absence of an electric field and there will be no net current. An electric field produces an average gradient of donor state energy in the field direction which will cause an increase in the transfer rate to sites of lower field energy. Hence a current will flow in the field direction. Two possible mechanisms have been proposed for actual electron transfer. These are

(i) that the electrons tunnel through the potential barrier from the occupied impurity centre to the unoccupied one (Miller and Abrahams 1960) and

(ii) that the electrons jump over the potential barrier from the occupied to the unoccupied sites (Mycielski 1961, 1962).

Wei (1963) has used an impurity conducting model to analyse conduction in thin discontinuous metal films (see next section). He believes that the metallic microparticle acts as donor impurities (i.e., majority carriers) and the substrate (ionic in Wei's cases) contributes acceptor impurities (i.e., minority carriers) in the form of colour centres. The activation energy is then related to the density of impurities. Wei does not make
clear, however, how the metal particles act as donors, nor why the colour centres act as acceptors.

2.2.5 Conduction in discontinuous thin metal films

Very thin metal films evaporated or sputtered on insulating substrates have a much higher resistivity than bulk metals and often show a negative temperature coefficient of resistance (TCR), unlike the bulk metals from which they are prepared (Mostovetch and Vodar 1951). There is ample evidence that metal films with a negative TCR are not continuous, but have an island structure consisting of aggregates of microparticles (for a survey, see Neugebauer 1964).

The temperature dependence of the electrical conductance of such an island-structure film is observed to obey

\[ I = \text{const} \cdot \exp \left\{ - \frac{\delta E}{kT} \right\} \]  \tag{2.23}

where \( k \) is Boltzmann's constant, and \( T \) is the absolute temperature. The value of \( \delta E \) depends on the thickness of the film and tends to decrease for thicker films. The values measured for \( \delta E \) are of the order of \( 10^{-1} \) eV or smaller. In thicker films, where the islands have grown together, the TCR is positive, as in the bulk metal. At low electric fields, films having an island structure show an ohmic behaviour; however, at higher field strengths the conductance increases with increasing field strength over the film.

Neugebauer and Webb (1962) suggest that the conduction mechanism is tunnelling of electrons between the islands through the separating vacuum. They suppose that tunnelling of an electron between two particles is possible only if one of the particles has a charge \( e \) or \(-e\) (\( e \) is the electronic charge) before the electron transfer takes place. Their point is that after
tunnelling of an electron between two neighbouring and initially neutral islands, the resulting two charged islands represent a higher energetic situation than before, where tunnelling of an electron between a charged and a neutral particle does not change the energy of the system. Therefore only tunnelling between an initially charged and a neutral island would be possible.

If the electric field is taken into account, Neugebauer and Webb find for the potential energy of the system $W$,

$$ W \sim \frac{e^2}{4\pi\varepsilon_0 Kd} - \frac{e^2}{4\pi\varepsilon_0 K(d+x)} - xeF_s \quad \ldots (2.24) $$

where $x$ is the distance from a positively charged island, $r$ the particle radius, and $d=2r$, $F_s$ the electric field between the islands.

The activation energy is then given as the maximum in the energy curve as the electron travels along the direction of the applied field away from the remaining positively charged islands. Then

$$ \delta E \sim W_{\text{MAX}} = \frac{e^2}{4\pi\varepsilon_0 Kd} - 2 \left( \frac{e^2F_s}{4\pi\varepsilon_0 K} \right)^{1/2} + xeF_s \quad \ldots (2.25) $$

As well as the temperature dependent deviations from Ohm's law at high fields this equation also predicts that at any one temperature the conductance of thick films should change more rapidly with applied voltage than with thinner ones. This is because $F_s$ changes more rapidly with voltage, as with thicker films there are fewer particles and therefore a much greater voltage drop across each gap.

Weitzenkamp and Bashara (1966) use the same model as Neugebauer and Webb with one slight modification. They consider a model based upon a
single transition to the adjacent particle, which does not involve maximizing equation (2.24). The activation energy then becomes simply

\[ \delta E = W \sim \frac{e^2}{4\pi\varepsilon_0 kd} - \frac{e^2}{4\pi\varepsilon_0 k(d+s)} - se_{FS} \quad \ldots (2.26) \]

which unlike \( \delta E \) from equation (2.25), includes the particle spacing, \( s \).

If the two islands have unequal charges before the transition, then

\[ \delta E = \Delta n_1 \left\{ \frac{e^2}{4\pi\varepsilon_0 kd} - \frac{e^2}{4\pi\varepsilon_0 k(d+s)} - 4\pi\varepsilon_0 s e_{FS} \right\} \quad \ldots (2.27) \]

where \( n = (n_1 - n_2) \)

\( n_1 \) = number of positive charges initially on first island

\( n_2 \) = number of positive charges initially on second island

Herman and Rhodin (1966) suggest that the conduction occurs through the substrate, by tunnelling between regions in the substrate surface immediately below the microparticles. The charge carriers are contributed to the insulator surface by two metallic microparticles. These authors also assume the activation energy to be electrostatic in nature, and to have a size dependence that resembles the one predicted by Neugebauer and Webb:

\[ \delta E = \frac{e^2}{4\pi\varepsilon_0 k} \left\{ \frac{1}{d} - \frac{1}{d+s} \right\} \quad \ldots (2.28) \]

An expression for the field dependence is not given in their paper.
Another possible origin of an activation energy has been given by Hartman (1963) who believed that electron tunnelling occurs between the neutral particles. He considers the band structure of the individual microparticles to be discrete because of the small size of the particles. Hartman suggests that the nth levels (the highest occupied levels at absolute zero), but not the (n + 1)th levels, of neighbouring particles become uncrossed when a small electric field is applied along the film (or between particles). Therefore, the activation energy would correspond to the difference in energy between the nth and (n + 1)th levels, ie,

\[ SE = \frac{h \pi^2}{2 m d D} \quad \ldots (2.29) \]

where \( h \) is Planck's constant divided by \( 2\pi \),

\( m \) is the electron mass, and

\( D \) is the atomic spacing.

Hartman predicts a decrease in conductance at high field strengths, because of the increasing of the (n + 1)th levels. For particle dimensions of 100 Å this should occur at a field strength of about \( 10^3 \) V cm\(^{-1}\).

Thermionic emission, suggested among other by Nifontoff (1953), Minn (1960) to be the conduction mechanism, has usually been rejected because of the low activation energies found by measurement. Van Steensel (1967), however, adopts a thermionic emission model with the condition that the rather low activation energies are accepted as representing the barrier heights. He explains the low barrier height as being due to a reduction owing to the image-force effect, if the metal-insulator work function is supposed to be of the order of 0.5 - 1 eV. Van Steensel also established that the low frequency value of the dielectric constant does not play a role in the conduction process, and that conduction through the substrate is likely.
In a recent series of papers Hill (1964, 1967 b, 1969 a, b, 1970 a) has developed a conduction theory based upon that of Neugebauer and Webb. It has been modified to take into account the interaction of neighbouring particles, the effect of mobile ions in the substrate, and the quantization of potential in a small particle. The barrier to tunnelling is the energy difference between the Fermi level of a particle and the lower edge of the conduction band in the substrate, modified by the effects of the charge exchange process, image forces, the applied field, and in the case of substrates containing free alkali ions, the local potential well around each ion. Four types of film structures are analysed, depending on whether the particles and the gaps between them are large or small. For small particles and small gaps the basic mechanism of conduction is one of activated quantum-mechanical tunnelling with for low fields an activation energy given by

$$\delta E = \frac{e^2}{4\pi\varepsilon_0 kr} \left\{ \frac{r + 2s}{r + s} \right\}$$

... \((2.30)\)

and a \(\log J \propto \frac{1}{E}\) high field dependence; for large gaps conduction in the substrate, i.e. thermionic emission or bulk conduction, dominates, whereas for large particles with small gaps a simple unactivated tunnelling process is dominant.

Kiernan and Stops (1969), adopting the Hill model, have modified the distribution functions of electrons associated with the islands to allow for charge transfer. They find expressions for the current \(J\) that are consistent with the Hill model for the case when \(\delta E > kT\).
CHAPTER III
APPARATUS

3.1 Introduction

The apparatus used in the deposition and the ion implantation and bombardment of the thin films will be described in the following pages. The apparatus that was used in the vacuum evaporation of the films was of a conventional design and as a detailed description can be found in Holland (1956) the corresponding sections in this thesis will therefore be short. Sections 3.5 and 3.6 describe the experimental arrangements of the ion accelerator and the target chamber respectively.

The experimental technique employed in making radioactive measurements, electrical measurements, and microstructure studies on the thin films after ion implantation are dealt with in the relevant separate chapters.

3.2 Vacuum Evaporation

The deposition of the thin film targets was performed in a conventional twelve-inch diameter bell-jar coating plant (Holland 1956, Spinks 1966). The bell-jar chamber was pumped by a 6-inch diameter liquid nitrogen trapped oil diffusion pump with a pumping speed of about 500 litres per second. The pump was separated from the chamber by a combined oil baffle and isolation valve. This permitted the diffusion pump to be kept under vacuum and at operating temperatures when the coating chamber was at atmospheric pressure. The diffusion pump was backed by a 50 litres per minute rotary pump which did not incorporate gas-ballasting. 'Neoprene' rubber rings - 'O' rings - were used as the sealing medium for the vacuum flanges. Typical pressures at which evaporations took place were $1.10^{-6}$ torr to $5.10^{-6}$ torr and this was maintained by use of a hot filament ionization gauge in the chamber. 'Back' pressures and 'roughing' pressures were measured using a Pirani gauge.

-45-
Heavy duty electrodes conducted into the chamber through vacuum 'lead-in's' were the electrical power used for heating the sources. A shutter operated externally through a Wilson rotary shaft seal shielded the substrates from the source until evaporation commenced. The substrates were always kept at room temperature before films were condensed upon them. Evaporation rates were in the $10 - 40 \text{ A sec}^{-1}$ region as measured by the rate monitor (see sect. 3.4). The source to substrate distance was kept large so as to prevent the growth of granular film deposits.

**TABLE I**

<table>
<thead>
<tr>
<th>Material</th>
<th>MP (°C)</th>
<th>Evap, Temp (°C)</th>
<th>Evap Technique Used</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium (99.99)*</td>
<td>660</td>
<td>996(?) 1148(?)</td>
<td>W, helical coil</td>
</tr>
<tr>
<td>Chromium (99.98)</td>
<td>1900</td>
<td>1205</td>
<td>W, conical basket</td>
</tr>
<tr>
<td>Copper (99.9)</td>
<td>1083</td>
<td>1273</td>
<td>Mo boat</td>
</tr>
<tr>
<td>Gold (99.99)</td>
<td>1063</td>
<td>1465</td>
<td>Mo boat</td>
</tr>
<tr>
<td>Titanium (99.9)</td>
<td>1727</td>
<td>1546</td>
<td>W, helical coil</td>
</tr>
<tr>
<td>Silicon Monoxide (99.9)</td>
<td>1100-1400</td>
<td>Ta boat</td>
<td></td>
</tr>
</tbody>
</table>

+ All materials of high purity obtained from Koch-Light laboratories, Colnbrook, Bucks.

* Figures under the name of the material indicate the purity.
Table I summarises some properties of the materials used in evaporations and the type of filament used in each case. For aluminium and titanium a tungsten multi-strand helical filament was used, care being taken in the case of titanium to make sure that the evaporant did not exceed approximately thirty per cent of the weight of the tungsten filament. Chromium, in pellet form was evaporated from a tungsten conical basket filament, while gold and copper were evaporated from a molybdenum boat. The dielectric silicon monoxide was evaporated from a tantalum tube source, the silicon monoxide vapour escaping through a narrow rectangular slit. Although the pure compound silicon monoxide, with a density of $2.15 \text{ gm cm}^{-3}$ was used as starting material, the composition of the final evaporated film is extremely sensitive to evaporation temperature (Hass 1950), and densities of the films can vary between 2.0 and $2.3 \text{ gm cm}^{-3}$. Because of this the boat temperature was carefully measured by a pyrometer at all evaporations of silicon monoxide. The evaporations were carried out at $1250^\circ C$ as measured by the pyrometer, which should yield, according to Hass, a film of density of $\approx 2.2 \text{ gm cm}^{-3}$. The pyrometer had previously been calibrated to $\pm 1\%$ by monitoring the boat temperatures with a Pt-Pt-Rh thermocouple. Contamination of films by the source material due to dissolved heater material in the evaporant can be a problem if it is large. O'Connell (private communication) has measured a value of tungsten of 1 part in $10^6$ in aluminium films evaporated from the above systems.

The different sample geometries that were used were obtained by use of simple masking techniques using thin wires and specially fabricated aluminium sheet masks. So as to enable good electrical contact to the samples to be made for electrical measurements, contact lands were deposited before the evaporation of the target films. These contact lands consisted of a thin layer, about $100 \AA$, of titanium or chromium beneath a thick layer of about $\ldots$
5000 Å of gold. Contact wires could then be soldered onto the gold. It was essential that these layers were deposited in the same vacuum pump-down cycle, otherwise the gold adhesion to the titanium first layer was very weak, and the fine gold wires could not be soldered onto the contact lands.

3.3 Substrate Cleaning

All metal and dielectric films were evaporated onto either Corning 7059 or fused silica (SiO₂) glass substrates. To obtain the most durable and adherent coatings on glass substrates the support surface must be free from contaminant films such as grease, adsorbed water etc. Various chemical methods have been devised for the cleaning of materials, and of the few tried the following procedure was found to be the most effective in keeping pinholes, as observed in an optical microscope, to a minimum. The glass substrates are first washed in 'teepol' detergent solution and then mounted in racks whilst immersed in water. When loaded, the rack was immersed in clean isopropyl alcohol which was held in a container in an ultrasonic bath. After ultrasonic cleaning for a few minutes the rack was removed from the alcohol and the residual alcohol on the surface of the slides allowed to evaporate. The slides were then ready for loading on to the coating jigs. Other procedures where polishing of the glass surface with various cloths or cotton wool took place, resulted in the formation of many pinholes in the condensed films. This was probably due to the development of electrostatic charges during polishing, which firmly holds minute dust particles on to the cleaned surface.

3.4 Thickness Monitoring

Film thicknesses were controlled during the evaporations by the monitoring of the evaporation rate and the mass of material deposited. This was achieved by using a quartz crystal oscillator film thickness monitor in the evaporation chamber. The principle of this is that increasing the mass of a vibrating piezo-electric crystal by depositing a thin layer of foreign matter upon one of its faces alters its resonant frequency (Sauerbrey 1959).
The sensitivity, \( S_c \), (frequency of change per unit weight of deposit) is given by Cady (1964) as

\[
S_c = \frac{\rho_d f^2}{\rho_c H}
\]

where \( f \) is frequency, \( \rho_c \) the density of the crystal (quartz), \( \rho_d \) the density of the film on its surface, \( t_c \) the thickness of the crystal, and \( H \) a characteristic wave constant. So we see that for high sensitivity we need a high characteristic frequency, \( f \), and a low \( H \), i.e., small \( t_c \), and also a low temperature coefficient (Bechmann 1955).

The monitor used was that described by Lawson (1967) incorporating AT-cut crystals with a resonant frequency of 4.15 MHz, with \( H = 1662 \) kHz and a stationary point on the temperature coefficient curve at 28°C. The method was to beat the monitor frequency with another frequency from an identical crystal, i.e., a matched pair was used, and measure the difference in frequency between the two as the material was deposited onto the monitor. The advantages of this method over a straightforward measurement of frequency shift was that the frequency difference can be measured with an electronic digital counter of relatively poor stability and also the fact that measurements could be made at a faster rate. The evaporating area in the crystal was well defined as of 0.6 cm diameter by one aperture. The monitor was calibrated by independent thickness determination of films condensed on glass slides situated adjacent to the monitor, using both optical transmission (Heavens 1955) and interference fringe methods (Wiener 1887, Tolansky 1948, 1960). The former method checked calibration and sensitivity in the 0-150 \( \xi \) film thickness region using the transmission data for aluminium films at a wavelength of 5000 \( \lambda \), see figure 3.1 (Walkenhorst 1941). For determination of thicknesses greater than 1000 \( \xi \), Fizeau fringes of equal thickness were used. These
were obtained in an optical apparatus of the type shown in figure 3.2. The interferometer consists of two slightly inclined optical flats, one of them supporting the film, which forms a step on the substrate. When the second flat is brought in contact with the film surface and the interferometer is illuminated with a parallel monochromatic beam at normal incidence and viewed with a low-power microscope, dark fringes can be observed which trace out the points of equal air-gap thickness. The two adjacent fringes are separated by $\frac{\lambda}{2}$, where $\lambda$ is the wavelength of the source, in this case 5461 Å, the green mercury line. The surface of the optical flats were highly reflecting (the upper flat, must however possess an observable transmission) and were very close together, and the reflected fringe system consisted of very fine dark lines against a white background with a fringe width of about $\frac{\lambda}{50}$. By adjusting the relative position of the flats to form a wedge-shaped air gap the fringes were made to run in straight lines perpendicular to the steps on the opaque film. The fringes showed a displacement as they passed over the film step edge. This displacement expressed as a fraction of the $\frac{\lambda}{2}$ fringe spacing gives the film thickness, which could be measured to an accuracy of about one tenth of a fringe spacing, ie about 250 Å. It is necessary to coat the film as well as the exposed glass surface with the same reflecting layer in order that phase changes on reflection from the two sides of the step are the same.

Calibrations gave a frequency difference of 1 Hz equivalent to 1 Å of aluminium film deposited. The change in frequency with deposited mass was found to be linear for films up to 0.5 mg cm$^{-2}$. As the frequency change is directly proportional to mass it is necessary to calibrate the instrument for one material only.
**FIG. 3.1** Optical transmission versus aluminium film thickness.

**FIG. 3.2** Film thickness determination using Fizeau fringes.
Measurements with the thickness monitor across the length of the substrate holders showed that for all the source-substrate geometries used the variation in film thickness from one end of the holder to the centre, where the monitor was placed, was never more than 10%. This figure agrees with the theoretical calculations assuming that the source helix can be represented as an ideal cylindrical source (Holland 1956). If $h$ is the source to substrate distance, $l$ the filament length and $d$ the film distance from the monitor then for a typical evaporation $h/l = 5.0$ cms, $l = 5.0$ cms and $d/l = 0.8$. Then theoretically from Holland $t/t_o = 0.9$, where $t_o$ is the film thickness immediately above the centre of the evaporation boat.

3.5 Ion Accelerator

The accelerator used for the irradiations is shown schematically in figure 3.3. A photograph of the beam lines and associated equipment is shown in figure 3.4. The beam line on the right hand side is the UHV (ultra-high vacuum) beam line. The ion source used for the gas ion generation was of the conventional rf type (Septier 1967). The plasma was formed by a high frequency discharge within a quartz envelope containing the gas by means of a 16 MHz frequency generator. The generator is coupled to the discharge by a coil, i.e., we had inductive coupling. The source is similar in construction to the source described by Collins et al (1966), the canal length being kept short in order to reduce the positive ion losses, due to charge exchanges. The ions were extracted from the source by applying up to +5 kV to the probe electrode and the beam was focused and accelerated by a three gap accelerator tube, when up to 150 keV was applied across the system. The accelerating voltages were supplied by an 150 keV SAMES electrostatic voltage generator. The beam was mass analysed using $60^\circ$ magnetic deflection utilising a water cooled electromagnet capable of giving 15 kG. After analysis the beam was
FIG. 3.3 Ion Accelerator - Schematic.
FIG. 3.4 Ion Accelerator as viewed from Target Chamber End.
passed through two sets of deflector plates set at 90° so that the beam was carried across the specimen by the output from two independent free running triangular waveform oscillators of frequency about 1 and 100 Hz, thus giving a uniformly irradiated area at the target.

The source and magnet box were pumped by a 6-in diameter liquid nitrogen-trapped oil diffusion pump. After the magnet there were two separate beam lines, one capable of high vacuum, ~10⁻⁶ torr, and the other capable of ultra-high vacuum, ~10⁻⁹ torr. The latter system was not used very often as results (see Chap V) showed that electrical properties were independent of background flux during the ion implantations and bombardments. The high vacuum beam line and target chamber were pumped by 2 2-in. oil diffusion pumps. The target chamber could be isolated from the rest of the accelerator by a vacuum gate valve. Both of these pumps were again liquid nitrogen trapped. The pumping system enabled a base pressure of about 2·5 ·10⁻⁶ torr as measured on an ionization gauge to be maintained in the target chamber. The ultra-high vacuum had a 6-in oil diffusion pump, liquid nitrogen trapped, following the deflector plates. This was followed by a differential pumping unit connecting the oil pump to a stainless steel chamber pumped by both an argon ion getter pump and titanium sublimation filaments. The target chamber had a small 1-inch diameter mercury diffusion pump attached to it, to enable a pressure of about 10⁻⁵ torr to be reached in the chamber before it was opened up via a gate valve to the main UHV pumping chamber. Base pressures of about 2·10⁻⁹ torr as measured by Bayard-Alpert gauges were obtained. All rotary pumps on the system utilized 'gas-ballasting' to prevent condensation of vapour in the pump (Caede 1950). Flanges in the ultra-high vacuum system utilized 'Viton' 'O'-Rings and indium for the sealing media. All pumps in the system had automatic cut-outs in case of emergencies from power failures and cessation of water flow. The system was then continuously pumped.
Two ion beams have been used for most of the work, the $\text{Ar}^+$ and $\text{O}_2^+$ beams. The $\text{O}_2^+$ beam was selected in preference to the $\text{O}_1^+$ beam for oxygen implantations as the former was approximately of twice the intensity (i.e., four times atomic intensity) of the latter. Since molecular ions dissociate into two particles on striking the target surface, the effective ion energy of $\text{O}_2^+$ ions will be half the accelerating energy. A reasonable working current, i.e., greater than $0.5 \mu\text{Acm}^{-2}$, was obtained with energies greater than 30 keV for $\text{O}_2^+$ ions and greater than 20 keV for $\text{Ar}^+$ ions. Typically, at operating energies of about 80 keV the current was of the order of $10^{-20} \mu\text{Acm}^{-2}$.

3.6 Target Chamber

The complete chamber consists of two main parts, a stainless steel chamber incorporating a cylindrical guard ring, an ion admittance valve and beam aperture, and a stainless steel target chamber flange holding the sample. The flange is shown schematically in figure 3.5. Both parts could be transferred to different beam lines relatively quickly. During experiments on any one particular beam line the main chamber was permanently fastened to the main beam line and the base plate could be easily removed to facilitate the changing of the sample.

The target films and substrates were supported on a copper block which was in turn supported by four stainless steel BA threads, about 7 cm long, fastened to the 10 cm diameter target base flange. These threads also supported an aluminium beam defining aperture, an aluminium current monitor, and a tungsten wire filament loop (about 3 cm in diameter) which was placed in front of the target. During bombardments a current was passed through the tungsten loop until it began to emit electrons. This cloud of electrons neutralised any positive surface charge on the target film and made sure that no charging up of the surface took place leading to breakdown and erroneous results. Leads to connect the sample, the neutralising filament, and the
TARGET CHAMBER BASE PLATE

TARGET SUPPORT [Cu]

DEFINING APERTURE (Al)

A1 CLAMPS

CURRENT MONITOR (Al)

TARGET

MICA INSULATORS

Ar^+ BEAM

SAMPLE CONTACTS

CI 12V 2.5A

NEUTRALISING FILAMENT (W LOOP)

FIG. 3.5 TARGET CHAMBER BASE FLANGE - SCHEMATIC
current monitor with external circuits were brought through the base plate via a multi-way vacuum lead through. Within the larger chamber the cylindrical guard ring was at a negative potential of about 300 volts to suppress the current of secondary electrons generated at the target and at the current measuring sensor. The guard cylinder was also cooled to just above liquid nitrogen temperatures by means of a cold finger immersed in liquid nitrogen. This was essential in order to decrease the contamination of the target surface due to hydrocarbon vapours which are decomposed by the ion beam and which, if not checked, can build up to form tens of monolayers of carbon on the surface.

In all cases the beam fell at virtually normal incidence onto the surface of the target within a deflection angle of $\pm 0.15^\circ$. 
In order to be able to relate the detailed electrical properties of the implanted film to their thin film compositions it is necessary to have a measure of the level of metal and oxygen impurity doping at any particular stage of the bombardment. For implantations of ions into thick films, that is where the film thickness is much greater than the ion range, this calculation is relatively simple provided the ion energy is greater than about 5-10 keV. Above this energy the trapping or 'sticking' coefficient is unity (Brown and Davies, 1963) and so the number of impurities can be considered as being equal to the ion dose. This number can and does become modified with the sputtering of the surface during the bombardment process.

When the ion range is greater than or about equal to the thin film thickness, as in recoil atom implantation, then atoms from both the film and substrate can recoil forward and backward across the thin film substrate interface. In order to determine the processes involved and to obtain a measure of the number of recoiling atoms across such an interface we have used radioactive tracer and activation analysis techniques. Such methods have been used quite extensively in investigating atomic collision phenomena such as ion ranges (Davies et al 1960, 1961, 1963(a), (b), Dearnaley et al 1970, Whitton and Carter 1970) and sputtering (Nelson and Thompson 1961, Musket and Smith 1968, Colligon and Bramham 1970, Robison 1968).

The concentration of backward recoiling oxygen atoms from a silica substrate into a metal film during argon ion bombardment has been measured by using helium-3 charged particle activation analysis (Markowitz and Mahoney 1962). The number of forward recoils from the metal film into silica and polythene substrates was measured using thermal neutron activation.
analysis. This chapter describes the theory and experimental techniques used and the measurements obtained in the investigations of the above processes.

The most widely used method of analysis has been thermal neutron activation analysis using neutrons of energies of about 0.02 eV. This method possesses high sensitivity for a wide variety of materials, but the induced radioactivity due to other elements present in the sample can cause interferences unless some form of radiochemical separation procedures is used. Although convenient for determination of metal concentrations thermal neutron activation analysis is not sensitive enough for oxygen determinations.

Alternatives for oxygen evaluation are fast neutron activation analysis using 14 MeV neutrons (Persiani and Cosgrove 1968(a),(b), Vogt and Ehmann 1965), and charged particle activation analysis using protons and deuterons (Amsel 1963, Thompson 1961, Amsel and Samuel 1962, 1967, Kover and Musselin 1968), helium-3 ions (Markowitz and Mahoney 1962, Demildt 1963, Holm 1962, Holm et al 1967), and $\alpha$-particles (Engelmann 1965, Saito et al 1963). The low depth of penetration into matter of charged particles, especially helium ions, and the high heat dissipation that can occur if large beam currents are used have limited the applications of charged particle activation analysis. The method however is more suitable to analysis of oxygen in thin films than fast neutron activation.

For a more detailed review of activation analysis techniques the reader is referred to Coleman and Pierce (1967).

4.2 Oxygen Atom Determination using helium-3 charged particles

4.2.1 Theory

The advantage of the use of helium-3 ions in activation analysis for low Z-elements has been shown by Markowitz and Mahoney (1962). Because many reactions of helium-3 particles with low Z-elements are exo-ergic and because the Coulomb barriers of these elements are relatively low, the
energy of the helium-3 ions does not need to be high. Conversely, if the atomic number of the matrix is large enough, the matrix interference becomes negligible because the low energy helium-3 ions cannot overcome the Coulomb barriers of the matrix nuclei.

The reactions used are

$$^{16}O + ^{3}He \rightarrow ^{19}Ne \rightarrow ^{18}F + ^{1}H + 2.0 \text{ MeV}$$

and

$$^{18}Ne \rightarrow ^{18}F + ^{1}H + ^{0}n - 3.0 \text{ MeV}$$

A count of the $^{18}F$ can be made either by $\beta^+$ counting or by gamma ray detection of the annihilation radiation. Interferences by activation of other elements can be largely eliminated by control of the bombarding energy of the helium-3 particles (Ricci and Hahn 1968). The disintegration rate $D_0(t)$ of a radio-product immediately after irradiation for a time $t$ is given by (Friedlander et al 1964),

$$D_0(t) = \phi_r \sigma N \left( 1 - e^{-\frac{0.693 t}{T_2}} \right)$$

... (4.1)

where $\phi_r$ is the particle flux, $\sigma$ the reaction cross-section, $N$ the number of target atoms per cm$^2$, and $T_2$ the half life of the radionuclide. For charged particle activation analysis, however, as opposed to neutron activation analysis, the energy loss in the target of the incident beam can be appreciable and so the variation of $\sigma$ with thickness must be taken into account. Ricci and Hahn (1965, 1967(a)) define an average cross section $\bar{\sigma}$, where

$$\bar{\sigma} = \frac{\int_{E}^{\infty} \sigma E dE}{\int_{E}^{\infty} E dE}$$

... (4.2)
where $\sigma_E$ represents the variation of cross section with particle energy (the excitation function), and the interval $E$ to 0 accounts for the energy lost by particles in travelling a distance $R$, where $R$ is the range of the incident particles. Ricci and Hahn have shown that $\sigma_E$ does not change by more than 8% from $Z = 4$ to $Z = 95$. Thus equation (4.2) becomes easily integrable if a simple expression of $\sigma_E$ versus $E$ can be found. To achieve this they fitted straight lines to the He$^3$ excitation functions and from the linear equations and their intervals of validity, integration led to the simple expressions for $\sigma_E$,

\[
\sigma = \frac{2}{3} m_1 E - a_1 + b_1/E^2 \quad E_0 \leq E \leq E_M \quad \ldots (4.3)
\]

\[
\sigma = \frac{2}{3} m_2 E - a_2 + b_2/E^2 \quad E_M \leq E \leq E_F \quad \ldots (4.4)
\]

where

\[
a_1 = m_1 E_0 \quad b_1 = m_1 E_0^3/3
\]

\[
a_2 = m_2 E_M - \sigma_M
\]

and

\[
b_2 = m_1 \left( \frac{2E_M^3}{3} - E_0 E_M^2 + \frac{E_0^3}{3} \right) + m_2 \left( \frac{E_M^3}{3} - \sigma_M E_M^2 \right)
\]

\[
m_1 = \sigma_M / (E_M - E_0) \quad \text{and} \quad m_2 = (\sigma_F - \sigma_M) / (E_F - E_M)
\]

The symbols $E_0$, $E_M$, $E_F$, $\sigma_M$, $\sigma_F$ are all graphically defined in figure 4.1, which shows the straight line fitting of the excitation function for the reaction $^{16}\text{He}(^3\text{He},p)^{18}$. Thus, once the constants involved are computed these simple equations lead easily to values of $\sigma$ in terms of bombarding energy $E$. Ricci and Hahn (1968) state that this method of calculating $\sigma$ is accurate to within 10% for He$^3$ irradiation of the light elements.
FIG. 4.1 STRAIGHT LINE CURVE FITTING OF EXCITATION FUNCTION.
4.2.2 Experimental

The overall experiment procedure was to initially activate the oxygen atoms in the fused silica (SiO$_2$) substrates by helium-3 irradiation. Then after the substrates had been cleaned the aluminium films, approximately 300 Å thick were condensed on their surfaces. These samples were then placed into the target chamber of the low energy ion accelerator and bombarded with argon ions of such an energy that the ions penetrated the metal film causing some substrate oxygen atoms to recoil back into the film. The absolute number of these recoil oxygen atoms was determined as a function of incident ion dose by measuring the amount of activity in the metal films after they had been removed from the substrates.

The helium-3 irradiations were carried out at an ion energy of 5.5 MeV using the singly charged beam from the Aldermaston Van de Graaf accelerator. Beam currents were limited to below 0.5$\mu$A cm$^{-2}$ at the target to minimise the likelihood of excessive target sample heating. The bombardment times varied from ten to thirty minutes.

For analysis after argon ion bombardment aluminium films were removed from the activated substrates by etching for a few seconds in a solution of sodium hydroxide which was present in small 1.8 cm dia x 50 cm length polythene bottles. This solution was then counted for F$^{18}$ activity measurement. A further two etches were undertaken in similar polythene bottles, to make certain that any activity which might have become attached to the slides as they were withdrawn from the solution during the previous etch was counted. The final etch was accompanied by a distilled water rinse of the glass surface. To investigate whether or not the etch solution attacked the silica slides some of the slides were activated by helium-3 irradiation and then immersed in a portion of etch solution. Even after being immersed for a time of two hours no dissolved activity could be detected in the solution after removal of the silica substrates.
Activation analysis techniques are not usually absolute methods, although Girardi et al (1964) have shown that the nuclear constants involved are usually sufficiently well known to allow many elements to be determined absolutely with an accuracy of better than ten per cent. However, the more usual method is to irradiate the sample simultaneously with known amounts of a standard material. The sample and standard are then counted under similar conditions and the unknown quantity of the element in the sample is readily calculated. This eliminates the need for accurate measurement of the beam current (ie flux $\Phi$), and bombardment time $\tau$. Therefore using equation $(4.1)$ we can write for the sample and the standard

$$\frac{D_{ox}}{D_{os}} = \frac{\sigma_x N_x}{\sigma_s N_s} \quad \ldots (4.5)$$

where the subscript $x$ refers to the unknown sample and the subscript $s$ to the standard. In both equations $(4.1)$ and $(4.5)$ the parameter $D_o$ can be equated to $A_o = (ODC)D_0$, the product activity in counts per minute at the end of the irradiation (ie time $t = 0$). The ODC is the over-all detection coefficient which includes counter efficiency, geometry, decay scheme, absorption, scattering and any other counter factors. The ODC is therefore a constant for a given counting system. Thus

$$\frac{D_{ox}}{D_{os}} = \frac{A_{ox}}{A_{os}} = \frac{A_{tx}}{A_{ts}} = \frac{\sigma_x N_x}{\sigma_s N_s} \quad \ldots (4.6)$$

where now the ratio $A_{tx}/A_{ts}$ refers to the product activity in counts per minute of the unknown and the standard samples a time $t$ after the end of the irradiations.

Figure 4.2 shows the rotating target holder that was inserted into the helium-3 beam to allow three samples and a standard to be simultaneously irradiated under identical conditions. The targets were mounted onto a
FIG. 4.2 ROTATING SAMPLE HOLDER FOR HELIUM-3 IRRADIATIONS.
copper block which was in turn connected to a rotating shaft driven outside the vacuum by a small electric motor at approximately 1 rev sec⁻¹. The target holder was enclosed by a cylindrical copper shield with a small aperture in it to allow the beam to reach the samples. This shield served as a heat sink as well as an aperture. The samples and rotating shaft were insulated from the shield and the supporting structure of the system. When contact between the samples and copper block was made by conducting silver paint, the current falling on the samples could be measured on a current integrator connected to that part of the shaft outside the vacuum system.

Two standards were used in the experiments, they were 0.0087 cm thick melinex \((\text{C}_{12}\text{H}_{12}\text{O})\) sheet and 0.2 cm thick fused aluminium oxide slides. Both were effectively thick targets, and values of \(\bar{\sigma}\) had to be computed from the excitation function of the oxygen reaction \(^{16}\text{O}^+\text{(He}^3,\text{p})^{18}\text{F}\) (Figure 4.1) using equations (4.3) and (4.5). From equation (4.3) using \(E = 5.5\) MeV, \(m_1 = 116\) mb/MeV, \(a_1 = 364\) mb, \(b_1 = 1,204\) mb/(MeV)², then \(\bar{\sigma}_S = \bar{\sigma} = 101\) mb, so \(\bar{\sigma}_X/\bar{\sigma}_S = 2.72\). For the computation of \(N_S\), the range, \(R\), of the helium ions into the standards was estimated by using the range data of Whaling (1958). Thus as \(\bar{\sigma}_X/\bar{\sigma}_S\) and \(N_S\) can be found then \(N_X\) can be determined.

The 0.511 MeV photopeak resulting from the \(\beta^+\) annihilation radiation of the \(^{18}\text{F}\) was used as a measure of the amount of oxygen present. The gamma rays were counted using either a fixed geometry 3" x 3" NaI(Tl) well-crystal, with a resolution of about 75 keV at 0.511 MeV, or a liquid nitrogen cooled 20 cc lithium drifted germanium counter, with a resolution of 6 keV at 0.511 MeV. Both counting systems were coupled through separate amplifiers to a RIDL Model 400 channel analyzer. The spectrum information was then fed from the multichannel analyzer into a PDP7 computer and the number of counts in the photopeak determined. Counts per minute in the
0.511 MeV photopeak were then plotted against time to obtain the decay curves. During the counting the samples were always surrounded by aluminium sheet of sufficient thickness to ensure complete positron, $\beta^+$, annihilation.

<table>
<thead>
<tr>
<th>Target Nuclide</th>
<th>Radio Nuclide</th>
<th>Half Life</th>
<th>Detection Energy MeV</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{12}\text{C}$</td>
<td>$^{11}\text{C}$</td>
<td>20.5 m</td>
<td>0.511</td>
</tr>
<tr>
<td>$^{12}\text{C}$, $^{14}\text{N}$</td>
<td>$^{13}\text{N}$</td>
<td>10.0 m</td>
<td>0.511</td>
</tr>
<tr>
<td>$^{12}\text{C}$</td>
<td>$^{14}\text{O}$</td>
<td>72 s</td>
<td>0.511, 2.31</td>
</tr>
<tr>
<td>$^{14}\text{N}$, $^{16}\text{O}$</td>
<td>$^{15}\text{O}$</td>
<td>124 s</td>
<td>0.511</td>
</tr>
<tr>
<td>$^{16}\text{O}$</td>
<td>$^{18}\text{F}$</td>
<td>110.0 m</td>
<td>0.511</td>
</tr>
<tr>
<td>$^{28}\text{Si}$</td>
<td>$^{30}\text{P}$</td>
<td>2.6 m</td>
<td>0.511</td>
</tr>
<tr>
<td>$^{23}\text{Na}$</td>
<td>$^{24}\text{Na}$</td>
<td>15.0 h</td>
<td>1.37, 2.75</td>
</tr>
</tbody>
</table>

$m = \text{minutes}, \ s = \text{seconds}, \ h = \text{hours}$

From Table II we see that any interferences with the oxygen detection that might be relevant can easily be avoided. Any nitrogen, carbon or silicon will not produce a radio nuclide of half-life longer than 20.5 mins, and count rates for oxygen measurement were taken four hours after the end of the helium-3 irradiations when only the oxygen decay scheme could be considered as being present. Any sodium interference could be measured by the gamma peaks at 1.37 and 2.75 MeV. The sensitivity of the method for Na and Si detection is anyway a factor of 50-200 down on that of oxygen (Ricci and Hahn 1967(b)).

4.2.3 Results

This section presents the results concerning the number of oxygen atoms that recoil back from a silica ($\text{SiO}_2$) substrate as a function of incident argon ion dose.
FIG. 4.3 **TYPICAL GAMMA SPECTRUM FOLLOWING IRRADIATION.**

FIG. 4.4 **DECAY SCHEME OF STANDARD MEUNEX (C₂H₂O₅) SAMPLE.**
The helium-3 irradiations times were long enough to achieve a count rate in the 0.511 MeV channel of $10^3$–$10^5$ counts per minute. With the irradiations in every case the gamma spectrum from the activated samples showed only the 0.511 MeV peak with no extraneous gamma peaks from other nuclides. Figure 4.3 shows a typical spectrum of a sample of an aluminium film with recoiled activated oxygen atoms present. The annihilation gamma peak is clearly observable as also is the backscatter peak and the Compton edge. The decay of the 0.511 MeV photopeak with time for a melinex standard sample showing the analysis of the various components is shown in figure 4.4. The radioproducts occur from the reactions shown in Table II, in section 4.2.2. We can see that after approximately three to four hours from the end of the helium-3 irradiation the counts per minute in the photopeak correspond to the F$^{18}$ radioproduct exclusively.

Figure 4.5 shows the decay of activity with time of a number of aluminium films containing active atoms sputtered back during low energy oxygen ion bombardment. For these samples the film thicknesses were 300 Å and the argon ion energy was 80 keV. The time of day axis corresponds to a period of time such that the 20 min carbon radioproduct and the shorter lived radioproducts had decayed to a very low count rate. All samples show the decay rate with a half life of about 110 mins, typical of the F$^{18}$ radioproduct produced from the $^1^6$(He, np)F$^{18}$ reactions. By comparing the count rates, at 4 hours from the end of the irradiations, of samples and standards which had been simultaneously irradiated, the ratio $A_t/A_{bs}$ in equation (4.5) could be determined. As then $\sigma_x, \sigma_s$ and $N_s$ could all be calculated $N_x$ the unknown quantity of oxygen atoms cm$^{-2}$ in each sample under investigation could be found. Figure 4.6 shows the variation of $N_x$ the number of recoiling oxygen atoms cm$^{-2}$ from a substrate as a function of argon ion dose (ions cm$^{-2}$).
FIG. 4.5 DECAY OF ALUMINIUM FILMS AFTER HELIUM-3 IRRADIATIONS.
An 80 keV argon ion will emerge from the downstream face of an aluminium film, 300 Å thick, with an average energy of about 50 keV. That is it will lose approximately 30 keV from electronic and nuclear stopping processes in the film (see figure 2.3(b)). A 50 keV argon ion will penetrate into SiO₂ with an average projected range, Rₚ, of 400 Ǻ (Johnson and Gibbons 1969). Thus collision processes will cause oxygen and silicon atoms to be sputtered back across the thin film-silica substrate interface. As the argon ion dose is increased, we see from figure 4.6 that the concentration of such oxygen recoil atoms in the thin films rises initially linearly before reaching a 'saturation' level at an oxygen concentration of near 3 \times 10^{16} atoms cm⁻² and an ion dose of about 2 \times 10^{16} cm⁻². This saturation level is probably due to the fact that after a certain length of bombardment, as many oxygen substrate atoms are being knocked forward across the interface as are being sputtered backwards, thereby causing an 'equilibrium' situation to be built up. This is considered further in section 4.4.

Calculation of the recoil sputtering ratio, S', in the linear region gives a value for S' ≈ 2.6 ± 0.6 atoms of oxygen per incident argon ion. Assuming that the substrate is sputtered as SiO₂, the molecular sputtering ratio would be equal to 1.3 ± 0.3 molecules of SiO₂ per incident argon ion. This compares with a value of 0.4 mol/s/ion found for argon ions of 35 keV energy incident on silica (Hines 1957) and 2.0 mol/s/ion for krypton ions of 30 keV energy incident on quartz (Akishin et al 1963).

4.3 Metal Recoil Atom Determination Using Thermal Neutron Activation Analysis

4.3.1 Theory

In activation analysis using neutrons there is not the distinction between ranges in thin and thick targets that there is with charged particle activation analysis. Our targets are of equal thickness as far as neutrons
FIG. 4.6 OXYGEN ATOMS RECOILING FROM SiO₂ SUBSTRATE.

FIG. 4.7 RECOIL ATOM IMPLANTATION - SCHEMATIC
are concerned due to their large ranges in matter. Therefore using a comparator method with a standard sample, as for the helium-3 activation analysis, the number of atoms of the unknown metal can be determined using equation (4.6) now written in the form

$$\frac{A_{LX}}{A_{LS}} = \frac{N_X}{N_S} \quad \ldots (4.7)$$

as $$\sigma_x = \sigma_s$$

4.3.2 Experimental

Whereas in the previous section we used charged particle activation analysis to measure the number of oxygen atoms that recoil backwards from a substrate into a metal film, in this section we use neutron activation analysis to measure the number of metal atoms that recoil forwards from the film into the substrate (see figure 4.7). We also investigated the number of forward recoils that cross a metal film-vacuum interface (i.e., transmission sputtering).

Aluminium, gold, and copper films are used for the metal films and Table III shows the nuclear reactions used in determining the various metal concentrations.

**TABLE III**

<table>
<thead>
<tr>
<th>Target</th>
<th>Reaction</th>
<th>Radioproduct</th>
<th>Detection Energy (MeV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>$^{27}\text{Al}(n,\gamma)^{28}\text{Al}$</td>
<td>2.27 min</td>
<td>1.78</td>
</tr>
<tr>
<td>Au</td>
<td>$^{197}\text{Au}(n,\gamma)^{198}\text{Au}$</td>
<td>2.69 d</td>
<td>0.411</td>
</tr>
<tr>
<td>Cu</td>
<td>$^{63}\text{Cu}(n,\gamma)^{64}\text{Cu}$</td>
<td>12.8 h</td>
<td>1.34</td>
</tr>
<tr>
<td>Na</td>
<td>$^{23}\text{Na}(n,\gamma)^{24}\text{Na}$</td>
<td>15.6 h</td>
<td>1.37, 2.76</td>
</tr>
</tbody>
</table>

Aluminium films 500 Å thick, were evaporated onto pure fused silica ('Spectrosil') and polythene substrates. The films were then bombarded
with argon ions of energy about 50 keV, such that the average projected
range of the ions was approximately equal to the film thickness ($R_p = 450 \, \AA$, 
for $\text{Ar}^+$ at 50 keV in aluminium, see figure 2.3(a)). During the bombardment 
recoil aluminium atoms obtain enough energy to cross the interface and 
become embedded in the silica and polythene. The surface film was removed 
from the silica by dissolving in NaOH, and the recoil atom concentration 
measured by etching the silica to a depth of about 1$\mu$m in dilute HF acid 
and irradiating the solution in the Aldermaston 'Herald' reactor after 
which the number of aluminium atoms in the etchant were determined from its 
activity. The polythene substrates could be put into the reactor directly 
after removal of the aluminium surface film.

For the experiments with copper recoils a different approach 
was used. Small granules of copper were at first irradiated with neutrons 
in the reactor to produce the radioproduct $\text{Cu}^{64}$ with a half-life, $T_1/2$, of 
12.8 hours. The activity of the granules after irradiation was low enough 
to allow them to be handled with tongs without endangering health. The 
active copper was then loaded into an evaporating boat in the vacuum coating 
chamber. Copper films, 400 $\AA$ thick were then condensed onto fused silica 
substrates. The films were then bombarded in the low energy accelerator 
by 80 keV argon ions. After this bombardment the remaining copper films were 
dissolved off the substrate using dilute hydrochloric acid. The number of 
active copper atoms that had recoiled forwards into the substrate could then 
be determined by comparing the level of activity to that of a standard 
evaporated film of known thickness.

To determine the forward sputtering (ie transmission sputtering) 
yield across a film-vacuum interface a different experimental procedure 
was adopted. Aluminium and gold films, about 2 cms square, were evaporated 
onto a previously deposited sodium chloride film on a glass substrate.

* Measurement of the amount of copper that had diffused from the thin film 
into the substrates without any ion bombardment showed that this could be 
neglected in determinations of the recoil concentration.
Following condensation, the substrate slides were gradually immersed in distilled water. As the sodium chloride dissolved the metal films floated free on the surface where they were subsequently picked up on nickel mesh. The nickel mesh used to support the film had 500 lines per inch, and the wire size was such that it had 65 ± 5% free area. Without the nickel mesh as a backing for the films they presented a handling problem in that the slightest air movement caused them to tear. The nickel mesh supporting the films were mounted on the target chamber base flange and a polythene cylinder, 1.8 cm in diameter and 1.1 cm in length, was mounted behind the films to collect the transmission sputtered atoms. Commercial-grade polythene was chosen as a sputtered atom collector because it contained no heavy metal impurities with large thermal neutron cross sections. Care was taken in handling the collectors, and to this end they were handled throughout with cotton gloves and tongs. It was especially important that no sodium (whose main source was from perspiration) came into contact with the collector. This is because sodium produces a radionuclide Na$^{24}$, with half-life of 15.0 hrs at energies of 1.37 and 2.76 MeV, during neutron activation. The cross section is relatively large and so the sodium peak may tend to obscure other metal peaks in the subsequent analysis. For activation analysis the collectors were sealed in polythene bottles and irradiated in the 'Herald' reactor.

All samples irradiated in the reactor were transported to and from the neutron source by a pneumatic transfer system utilising compressed air. Irradiation, transfer and delay times were automatically controlled by a series of relays. Counting times were also regulated by automatic timers. After irradiation the samples were returned to the counting station which consisted of dual 3" x 3" sodium iodide (thallium) crystals. The output of the detectors was fed into a multichannel analyzer where the gamma ray spectrum was recorded. The reactor produced a thermal flux of approximately $10^{12}$ neutrons cm$^{-2}$ sec$^{-1}$. 
In the experiments using polythene substrates for the aluminium films the argon ion dose was limited to less than $6 \times 10^{15}$ ions cm$^{-2}$. For ion doses greater than this value the polythene was seen to char badly and blister due to radiation damage.

Figure 4.8 shows the number of recoil aluminium atoms versus varying argon ion dose. The curve initially rises steeply and then tends to 'saturate' at about an ion dose of $2 \times 10^{16}$ ions cm$^{-2}$. The saturation, although similar, is not so pronounced as in the oxygen atom recoil experiments. Measurements in the linear part of the curve give an effective sputtering coefficient of aluminium recoils to argon incident ions of about 3.0. Also shown are the number of gold recoils into silica at an ion dose of $3 \times 10^{16}$ cm$^{-2}$. The gold value is close to the aluminium results. Measurements on the transmission sputtering into vacuum of aluminium atoms yielded a result that was a factor of 3-5 times the value of the number of recoils across a film-substrate interface.

The results for copper were doubtful as regards the absolute determination of atom concentration due to a systematic error in calibration. However, figure 4.9 shows the results in terms of arbitrary units against ion dose. The results show the saturation effect quite markedly.

### 4.4 Backsputtering of Aluminium

Neutron activation analysis was used to obtain estimates of the sputtering coefficient of aluminium with high energy argon and oxygen ions. The argon ion energy used was 80 keV, and the oxygen ion energy was 100 keV (ie 50 keV atomic oxygen).

Aluminium films, approximately 1000 Å thick were evaporated onto 99.998% pure iron foil, 0.01 cm thick *. The exact aluminium content of each film was then determined by neutron activation analysis. After the samples

* Made available from Koch-Light laboratories
FIG. 4.8 METAL ATOM RECOIL CONCENTRATION WITH ION DOSE.

FIG. 4.9 COPPER RECOIL CONCENTRATION WITH ION DOSE.
had decayed in activity they were bombarded in the positive ion accelerator by argon and oxygen ions, then removed, and analysed further again by neutron activation. The difference in aluminium content of pre- and post-bombardment measurements was then correlated with the incident ion dose to give a value for the sputtering coefficient in terms of the ratio of the number of sputtered aluminium atoms to the number of incident ions.

Results for the sputtering coefficients, $S$, were

(a) $\text{Ar}^+ - \text{Al} \quad E \approx 80 \text{ keV} \quad S = 0.7 \pm 0.1$

(b) $\text{O}^+ - \text{Al} \quad E \approx 50 \text{ keV} \quad S = 0.5 \pm 0.1$

Figure 4.10 shows these experimental points together with other available sputtering data for argon and oxygen on aluminium and titanium over the energy range 1-100 keV. Taken together the points allow a reasonably accurate assessment of sputtering ratios over the energy range of interest.

4.5 Influence of secondary parameters

Our measurements of recoil and sputtered atoms may be affected by the presence of doubly charged ions, preferential orientations of the target surface, the background gas, and by impurities in the background gas, among the bombarding ions or in the target material.

Weijsenfeld (1967) has found that in his plasma-type sputtering experiments it is not the background gas itself, but the impurity ions created from the background gas that may interfere with the sputtering process. However with our beam-type experiments, using a mass-analysed beam with practically no impurities then only the background gas can interfere with the sputtering process. Snouse and Bader (1962) state that in an oil-free contaminated background the ratio of neutral-background flux to ion flux must be greater than 100 to influence the sputtering process. In our case this ratio is about 25. Such interference with the sputtering process due to background gas would, if present, only affect the back- and transmission-
**FIG. 4.10** SPUTTERING YIELDS VERSUS ION ENERGY FOR ALUMINIUM AND TITANIUM.

**FIG. 4.11** INCREASE IN ADHESION OF ALUMINIUM FILMS ON GLASS AFTER $\text{Ar}^+$ ION BOMBARDMENT.
sputtering data anyway. Most work has been concerned with the sputtering or recoiling of atoms across a film-substrate interface which was prepared in a vacuum of about $10^{-6}$ torr. This interface would not be affected by residual gas in the accelerator. Weijsenfeld also states that from experiments the presence in the high purity target materials of impurities is of no importance.

Preferential orientation in polycrystalline surfaces can effect sputtering yields in the order of 15-30 per cent (Southern et al 1963). To keep this to a minimum in our case films were always evaporated under as identical deposition conditions as possible.

A consequence of the relatively high background gas pressure is that during bombardment oxygen atoms in the metal surface oxide may be 'knocked-in' to the metal films in the same way as metal atoms can be knocked from a metal film into the substrate. This might therefore lead to oxidation and thus changes in resistivity as observed in Chapter V. Whether this mechanism can be significant or not will depend upon whether or not the surface oxide layer can be replenished during bombardment. The number of oxygen atoms impinging on the surface due to the background flux is greater than the number of oxygen atoms that will be sputtered. The oxide layer should therefore be replenished if the aluminium surface does not become passivated to chemisorption due to the bombardment, as in the case of helium ion bombardment of aluminium (Moore et al 1962), argon ion bombardment of uranium (Haymann 1959) and copper (Hondros and Benard 1962). Occluded inert gas has been considered as the explanation of surface passivation, the inert gas atoms impeding migration into the crystal surface. If this is so one would not expect any passivation to occur in our case as the energy of the argon ions was much greater than the order of the film thickness and thus the number of inert gas ions near the surface would be negligible.

The recoiling of surface oxide atoms could therefore quite possibly contribute to oxidation during the oxygen implantations. This is considered further in chapter V, section (5.2.2.7).
4.6 Discussion

In both the case of oxygen atom recoils from the substrate and that of metal atom recoils into the substrate (figures 4.6, 4.8, and 4.9) the density of recoil atoms rises fairly steeply to a saturation value for incident Ar\(^+\) doses in excess of \(3 \times 10^{16}\) ions cm\(^{-2}\). A similar saturation phenomena (see figure 4.11) has been found for the increase in adhesion of aluminium films on glass under argon ion bombardment (Collins et al 1969). The authors suggested that the increase in adhesion was due to the formation of an 'aluminium-oxide' type structure between the thin film and glass substrate, by the recoiling atoms. If the adhesion depended upon the number of aluminium-oxygen type bonds then it seems reasonable to suppose that if the density of recoils saturates then so too will the adhesion.

Since the scattering can be assumed to be nearly isotropic and the range of ions is greater than the film thickness then an equilibrium density of foreign atoms either side of the film substrate interface is to be expected for large Ar\(^+\) doses. On this basis we have considered a simple model for the transfer rate of atoms between film and substrate. If it is assumed that only lamina of thickness \(L_1\) in the film and \(L_2\) in the substrate contribute to the process of atom transfer between film and substrate, (see figure 4.7), then for forward scattering, the number of film atoms \(n_f\) per cm\(^2\) transferred into the substrate will be given by

\[
\frac{dn_f}{d\phi_f} = \left( \sigma_f L_1 N_f - k_2 n_f \sigma_b \right)
\]

where \(\phi_f\) is the projectile flux incident on the film; \(\sigma_f\) and \(\sigma_b\) the total forward and backscattering cross sections, \(N_f\) is the atomic density of the film and \(k_2\) is the fraction of \(\phi_f\) passing into the substrate. Integration between 0 and \(\phi_f\) leads to the relationship

\[
n_f = \frac{\sigma_f L_1 N_f}{\sigma_b k_2} \left( e^{-\phi_f k_2 \sigma_b} - 1 \right)
\]

\[\text{(4.9)}\]
similarly the relationship for substrate atoms backscattered into the film will be (Stroud 1970, private communication)

\[ n_s = \frac{k_2 \sigma_f' L_2' N_s}{\sigma_b' L_1'} \left\{ 1 - \exp \left[ -\left( \frac{\phi_f' L_1'}{\sigma_b' L_1'} \right) \right] \right\} \quad (4.10) \]

where \( N_s \) is the atomic density of the substrate and \( t \) is the thickness of the film. The fraction \( k_2 \) is easily calculated from theoretical range parameters and for 80 keV \( \text{Ar}^+ \) in 500 \( \AA \) aluminium is 0.76. Estimates of \( L_1 \) and \( L_2 \) are not simple but for the present studies values have been estimated by assuming \( L \) equal to the range of a struck atom possessing the maximum obtainable recoil energy. For both aluminium and oxygen atoms struck by \( \text{Ar}^+ \) at 80 keV \( L_1 \) and \( L_2 \) are greater than 500 \( \AA \), the film thickness adopted in the experiments. \( \sigma_f' \) and \( \sigma_b' \) for backscattered oxygen have been obtained by fitting equation (4.10) to the extreme points on the curve in figure 4.7. We find \( \sigma_f' \approx 6.5 \times 10^{-17} \text{ cm}^2 \) and \( \sigma_b' \approx 2.5 \times 10^{-17} \text{ cm}^2 \).

The saturation of the aluminium atom data is not sufficiently accurate to establish the form of the aluminium recoil characteristic and we can only estimate the order of forward scattering cross section \( \sigma_f' \). The magnitude of recoil implanted atoms into \( \text{SiO}_2 \) and polythene are similar and by combining these results we find that \( \sigma_f' \) lies between 6.7 \( \times 10^{-18} \text{ cm}^2 \) and 1.4 \( \times 10^{-17} \text{ cm}^2 \).

Nelson's theory of recoil atom implantation (see section 2.1.3) neglects the effects of back recoils and is therefore restricted to low dose calculations. From equation (2.14) we can write \( S_f' \), the ratio of implanted atoms to incident projectiles as

\[ S_f' = C_f' / E_{\text{min}} \quad (4.11) \]
if $E_{\min} \ll E_r$, where $E_r = 4M_1 M_2 E_1 / (M_1 + M_2)^2$.

The constant $C$ is

$$C = \frac{4 \pi a^2 D N_e E_r 2^{1/3} \Omega}{2.72 (M_1 + M_2)^{5/3}}$$

where $D$ is the atomic spacing in the film. An accurate value of $E_{\min}$ is difficult to substitute. $E_d$, the threshold displacement energy for atoms, is usually in the 15 - 25 eV region however it is dependent on recoil atom direction significantly. Therefore as actual values of $E_{\min}$ are uncertain we suggest that they should be larger but not too far removed from the value of displacement energy, $E_d$, say a few tens of eV. By inserting our low dose ratios into equation 4.11, we find that for oxygen, $E_{\min} \sim 27$ eV, for aluminium, $E_{\min} \sim 34$ eV, and for gold, $E_{\min} \sim 25$ eV.

Transmission sputtering data on aluminium gives a sputtering ratio of 5 times greater than that across the thin film substrate interface. In this case instead of $E_{\min}$ being near the displacement energy it is expected that it be near the value for the surface binding energy of an atom; Sigmund (1968) suggests in his calculations of sputtering efficiency an effective surface binding energy $U_0 \sim 10$ eV, which is meant as an average over all directions of ejection. From inserting our experimental values into equation (4.11) we find $E_{\min} \sim 7$ eV for forward sputtering into vacuum.

Although no direct measurement of recoil atom ranges has been made the work of O'Connell (1970) suggests that recoil atoms can penetrate 300 $\AA$ - 500 $\AA$. With the oxygen atom backspattering from silica and Corning 7059 slides into 300 $\AA$ - 500 $\AA$ aluminium films he found a total and seemingly homogeneous conversion of the metal films into a thicker, highly transparent (~90% transmission) and glassy type material (see also the infra-red results, Chapter V, sect. 5.3.2.4 of this thesis). This, together with the fact that recoil metal atom implantation does not significantly change the resistance of dielectric

*Nelson (1970 private communication) has suggested values of 50 - 100 eV.
layers with thicknesses greater than 500 Å (Chapter V, sect. 5.2.3.2) suggests that for the ion target systems used the range of recoils is of the order of 300 Å - 500 Å for incident ion doses of $10^{16} - 10^{17}$ ions cm$^{-2}$.

In using the radioactive measurements of recoil concentrations to calculate metal/dielectric ratios in the following chapter we have thus assumed that the metal atoms are dispersed homogeneously throughout the 400 Å dielectric films.

4.7 Conclusion

It has been shown that with high incident ion doses, of about $10^{16} - 10^{17}$ ions cm$^{-2}$, recoiling atoms near a thin film - substrate interface can cross the interface from a metal film and become embedded in the dielectric substrate and vice versa. The concentrations of recoil atoms are large enough to make the process of recoil atom implantation efficient for the doping of dielectric materials. Furthermore by comparing the calculated values of $E_{\text{min}}$ from experiment with $E_d$, the displacement energy, we suggest that substituting values of $E_d$ for $E_{\text{min}}$ in Nelson's theory can allow at least an order of magnitude calculations to be made of recoil atom implantations for low projectile dose.
5.1 Introduction

In the previous chapter activation analysis and radioactive tracer techniques were used to investigate the recoil collision processes that occur across a thin film substrate interface. Measurements on the number of foreign metal atoms that can be implanted into a dielectric by recoil atom implantation were also obtained. In this chapter we study the conduction properties and microstructure of metal films doped with oxygen atoms by direct ion implantation, and dielectric films doped with metal atoms by recoil implantation.

The mechanisms of transport of carriers through thin dielectric and mixed metal/dielectric films have been the subject of intensive theoretical and experimental investigations for the last several years. These studies have been stimulated by the objective possibilities of the development of a variety of miniaturized solid state devices. The relevant parameters for investigations are usually the dc and ac conductivity and their temperature dependence, ie activation energy, electrical breakdown strength, leakage, dielectric constant and loss tangent as a function of frequency.

In order to understand fully the behaviour of thin solid films it is necessary to characterise them structurally as well as physically as is the case with electrical characteristics. Both electron microscopy and diffraction have been used extensively in the study of ion bombardment phenomena such as radiation damage (Barnes 1961, Westmacott et al 1962, Mazey et al 1962, Beeses and Nelson 1962, Venables and Balluffi 1965), the amorphization of crystalline targets (Trillat et al 1955, Trillat 1962, Ogilvie 1959, Gusev et al 1970), the recrystallisation of amorphous targets (Trillat and Mihama 1960, Pert 1954, Kelly and Naguib 1970) and chemical
effects with active gas ion bombardment (Trillat et al 1956, 1960, Pavlov and Shitova 1967). The shift in infra red absorption bands of material under ion bombardment has been used to determine damage processes by Stein et al (1970). More generally however infra red spectroscopy has been used to investigate the structure of silicon oxide films (Allam and Pitt 1967, Pliskin 1968), glasses (Pliskin 1968) and cermets (Allam et al 1969, Miller et al 1970, Milgram and Lu 1968).

The conduction properties of implanted films in this work were investigated by measurements concerning the voltage-current characteristics and activation energies, and ac conductance and capacitance as a function of frequency. The film structures were studied using transmission electron microscopy and electron diffraction, and infra red transmission and reflection spectroscopy.

5.2 Conduction Properties of Implanted Films

5.2.1 Experimental

5.2.1.1 Sample geometries

In order to investigate electrical characteristics at high electric field strengths, of up to about $10^6$ volts cm$^{-1}$, sandwich structures were used for both oxygen and metal atom implantations, (see figure 5.1).

For the oxygen bombardments two sandwich structure geometries were used, shown in (a) and (b) of figure 5.1. In (a) initially an aluminium or titanium film of about 2000 Å is deposited over an area of about 1.5 cm x 1.5 cm, this designated "layer 1" in the diagram. Then a further 2000 Å film of the same metal, designated layer 2, is deposited on top of the first layer in a circular area of about 1 cm diameter. The sample is then subjected to oxygen ion implantation over an area greater than the top layer 2 but less than the bottom layer 1. This was to ensure that all of the area of layer 2 was uniformly irradiated, such that there would be no low resistance shorting paths around the oxide layer as it was formed. The oxygen ion energies
FIG. 5.1  SANDWICH STRUCTURE CONFIGURATIONS USED FOR OXYGEN IMPLANTATIONS OF METAL FILMS.
FIG. 5.1(c) Sample geometry for recoil atom implantation

FIG. 5.1(d) Planar geometry for oxygen implantations
used were such that the average projected ranges, $R_p$, of the ions were not greater than about 600 Å in the materials. Thus there is left a non-implanted region in layer 2 which was used subsequently as the lower electrode in a sandwich structure, where the implanted metal oxide region was the material under investigation. The upper electrodes were aluminium and titanium discs of 0.2 cm in diameter and 1000 Å thick which were evaporated onto the samples after the implantation. On every implanted metal film nine metal-metal oxide-metal sandwich structures could be fabricated for conduction measurements by this method. These evaporated upper electrodes were not essential when the oxygen dose was relatively low, about $10^{16}$ ions cm$^{-2}$, as then there was a non-implanted region at the surface of layer 2 due to the depth and gaussian nature of the ion range profile. This metal region could then be used as the top electrode. However the electrodes were always evaporated on as a matter of course. Reproducibility of the electrical characteristics from the samples on one implanted film was found to be excellent (see section 5.2.2.3) although occasionally some were found to give short circuits. Examination of the evaporated metal layers in an optical microscope showed that pin-holes did occasionally occur. It is thought that the short circuits were due to the presence of such pin-holes.

In sample geometry (b) used with oxygen implantations the second layer, layer 2, in (a), is not used. Instead metal films, 2000 Å thick, were implanted with oxygen ions across a 1 cm diameter area. After the irradiations upper electrodes of aluminium and titanium were evaporated onto the sample exactly as described above. It is clear looking at figure 5.1 (b) that metallic or near metallic conduction will take place between the electrodes A and B unless the implanted oxide film has "grown" to reach the surface, when a high resistance will then be recorded. The use of this kind of sample geometry then tells at what ion dose, if at all, one edge of the implanted oxide film and the evaporated thin film surface coincide.
The sample geometry used for recoil atom implantations of metal atoms into dielectric films is shown in 5.1 (c). The structure consists of a lower metal electrode of about 1000 \( \mu \) thick, a silicon oxide dielectric layer 300 - 500 \( \AA \) thick, and an upper metal layer of aluminium or titanium about 500 \( \AA \) thick. The use of such sandwich structures with recoil atom implantation provides the advantage that at various stages of the bombardment changes in conduction properties at high fields may be measured without adding or removing contacts.

In order to investigate the effect of radiation damage and surface sputtering of metal films some argon and oxygen irradiations were performed with planar sample geometries as shown in figure 5.1 (d). With this sample configuration metal films 200 - 1000 \( \AA \) thick were deposited on Corning 7059 substrates and subjected to irradiation. Early samples were deposited through a mask to give strips 0.3 cm wide, however, due to the glass at the sides of the strip charging up and the beam then becoming distorted some of the charge was collected by the aluminium film thus making some dose measurements difficult. The difficulty was overcome by covering the whole slide with a metal film except for two .05 cm wide strips which served to define the 0.3 cm wide specimen and earthing the outside film. Connection to the ends of the specimen to measure changes were made through fine wire soldered to the contact lands. The central portion of the 0.3 cm strip to be irradiated was defined by a 1 cm masking slit which was placed across the specimen to give an irradiated area 1 cm x 0.3 cm.

5.2.1.2 Electrical measurements

Most dc characteristics at constant temperature were measured by using a four-terminal method. Known voltages in the 5 mV to 2V range were applied across the film under investigation and the current passing through the film measured with a suitably sensitive ammeter. The voltage across the film was measured by a Keighley 602 model solid state electrometer while the
With careful control of the environment currents as low as about 5 pa could be measured with an accuracy of ± 1 pa. At higher currents the accuracy approached the order of a few per cent.

The current-voltage characteristics were measured at a number of fixed temperatures between 77°K and 450°K. For obtaining temperatures above room temperature a simple laboratory oven was used while for the low temperatures the samples were placed in a protective pyrex tube and immersed in liquid nitrogen. Changes in resistance with increasing or decreasing temperature were then recorded as a graphical trace on a X - Y axis chart-recorder. The temperature of the sample was monitored using copper-constantan thermocouples that had previously been calibrated. Electric fields of up to about 10^6 V cm^{-1} were applied to the sample in the sandwich geometry form.

Ac measurements were carried out using a parallel resistance-capacitance Wayne-Kerr B121 bridge with independent source and detector to cover the frequency range 200 Hz to 20 kHz. Applied signals were kept to below 100 mV rms.

5.2.2 Conduction properties of oxygen implanted metal films

5.2.2.1 Resistivity versus thickness of initial films

The aluminium and titanium films used for the majority of the implantations were in the 300 - 2000 Å thickness region. Sputtering of a surface due to ion bombardment can decrease the thickness of a thin film, and for films whose thickness, t, is of the same order as the conduction electrons mean free path, l, then collisions of the electrons into the surface become important and can have an effect on the resistivity of the films.

* The picomammeter and frequency source and detector used in these experiments were designed by P A O'Connell, AWRE.
At room temperature the mean free paths of electrons in metals are determined almost entirely by lattice scattering, and are of the order of $200 \, \AA$, except in the case of good conductors like Ag and Cu for which they are about $500 \, \AA$.

Figure 5.2 shows the plot of resistivity with film thickness for the aluminium and titanium films used in the implantations. The thicknesses were measured with the quartz crystal monitor, each point being the average of twelve samples. The fact that an increase in apparent resistivity is observed when a film is sufficiently thin implies that some, at least, of the surface scattering is diffuse, and most experimental observations seem to be consistent with the assumption that all surface scattering is diffuse (Rhoderick, 1964). This is not surprising if one recalls that the de Broglie wavelength of the conduction electrons is about $10^{-7} \, \text{cm} (10 \, \AA)$, and that the surface of a metal film is certainly not smooth on this scale.

5.2.2.2 Resistivity of bombarded planar samples

When a metal is bombarded by oxygen ions, or more generally, any active gas ion, both chemical (eg oxidation) and physical (eg radiation damage) processes can take place. In order to obtain the relative magnitudes of these effects, some metal films were bombarded with argon ions only, when the dominant process would be of the physical kind.

The aluminium and titanium films were used in the sample configuration shown in figure 5.1 (a), ie 'planar'. Film thicknesses were such that all the argon ions were stopped in the films. Figure 5.3 shows the small changes in resistance of aluminium films that takes place under argon ion bombardment. The fractional resistance change increases slowly with ion energy as might be expected from the increased depth of ion penetration and the increased damage density. All the curves show a quasi-constant level which we can ascribe to defect production at and below the surfaces and to surface topography (Navinsek and Carter 1968).
Fig. 5.2 Resistivity of Aluminium and Titanium Films

Fig. 5.3 Argon Bombardment of Thick Aluminium Films
The mean projected amorphous range of 80 keV Ar ions in Al calculated from figure 2.3 (a) is approximately 700 Å. An argon primary ion of this energy will produce a displacement cascade. According to the random cascade model (Sigmund and Sanders 1967), the centre of damage lies at 560 Å and has a half width of 350 Å in the direction of the primary. Considering that we can expect damage to about twice the half width, if many damage events are superimposed, we would get a damaged layer that extends to 1260 Å below the surface of the film. This corresponds to about 0.80 of the total film thickness. It is easy to see that due to the shunting action of the undamaged portion of the film the resistance change associated with such a layer of dense damage could at most be 0.80 of the original resistance (size effects neglected). The actually observed total change of the 80 keV argon ion curve is about 0.90 of the original resistance.

When the film thickness is less than the argon ion range, then a plot of resistance change versus argon ion dose results in curves of the form shown in figure 5.4. All show the same characteristic features that have previously been found by O'Connell (1970, private communication), and Collins and Richmond (1970) for 30 keV oxygen and argon ion bombardment of thin metal films for ion ranges of the order of the film thickness. O'Connell has investigated in detail the feasibility of the ion bombardment method for producing stable linear resistors in the resistance region shown by figure 5.4. Figure 5.4 shows that at first the increase in resistance with dose is slow, but once the resistance starts to increase appreciably, the rise with dose becomes very rapid until 'open circuit', ie high resistivity material is reached. The dose required to reach this condition depends on such factors as the initial film thickness, ion energy and ion species, but the final stages are similar in all cases. In all cases the ion beam will penetrate the substrate and it is reasonable to suggest that substrate atoms will be sputtered back into the metal film, as shown by the radioactive measurements in the previous chapter. The author has in fact
FIG. 5.4  ARCON BOMBARDMENT OF THIN ALUMINIUM FILMS

FIG. 5.5  RESISTIVITY CHANGE OF ALUMINIUM FILMS WITH O₂⁺ IMPLANTATION
suggested that the large changes in resistance under ion bombardment are
due to a combination of (a) metal film sputtering, (b) sputtering of
oxygen atoms from the substrates and (c) oxygen ion trapping for the case
of oxygen ion bombardment (Collins and Perkins 1971). The sudden onset of
high resistivity material was then calculated as taking place at a metal
concentration of between 30 - 60 volume per cent.

5.2.2.3 DC measurements on sandwich structures

DC and ac measurements have been performed on oxygen implanted
aluminium and titanium films using sample geometries shown in figures 5.1 (a)
and 5.1 (b). With such sandwich configurations at low doses the small
changes in resistivity of the implanted region discussed in the previous
section cannot be detected. However at a certain dose there was a sudden
onset of high resistivity material leading to metal-oxide system where
conduction behaved as an activated process, similar to discontinuous films
and cermet material. Resistivities in the $10^9 - 10^{12}$ Ω-cm region were
produced with activation energies of about 0.3 eV.

Figure 5.5 shows the resistivity versus dose curves for 100 keV $O_2^+$
implantation into aluminium films with both types of sample configuration.
For convenience the sample geometry in figure 5.1 (a) has been referred to
as S1 and that shown in figure 5.1 (b) as S2. With geometry S1 the
resistivity remained almost equal to that of the bulk metal until an ion
dose of about $6 \times 10^{16}$ cm$^{-2}$ was reached when we had the sudden onset of
high resistivity material with $10^2 \Omega$ cm $< \rho < 10^8 \Omega$ cm. Further
implantation led to a linear increase in resistivity until at about $7 \times 10^{16}$
ions cm$^{-2}$ a saturation resistivity of about $10^{12}$ Ω cm was reached. Even
further implantation led to a saturation phenomena, the resistivity of the
oxide remaining at a constant level. The characteristic curve for geometry
S2 was virtually the same with the one exception that there was not a
gradual increase before the final sudden onset of high resistivity material.
The samples remained conducting until an ion dose of about $6.7 \times 10^{16}$ ions cm$^{-2}$ when the resistivity rose very sharply to reach final resistivities of the same order as found with geometry S1. With samples in the S2 configurations the sudden onset of very low current marks the point at which the edge of the oxide profile has coincided with the surface of the metal film. This top surface has of course always been receding during implantation due to the sputtering process.

Comparing the two curves of figure 5.5 we see that between an oxygen dose of about $6.10^{16}$ ions cm$^{-2}$ and about $7.10^{16}$ ions cm$^{-2}$ there exists a reasonably high resistivity region, $10^2 \Omega$ cm to $10^8 \Omega$ cm, that lies beneath the film surface. That is, there is in effect a "buried layer" of metal oxide material. With the ion energies used this layer could not be made completely insulating, ie with $\rho > 10^{10} \Omega$ cm, without the oxide profile reaching the surface and the layer therefore not being "buried" any longer.

A composite plot of resistivity and temperature coefficient of resistance versus ion dose constructed from sandwich geometry and planar geometry experiments is shown in figure 5.6. As we have already mentioned O'Connell has investigated extensively the $10^{-5} - 10^2 \Omega$ cm region and the detailed conduction properties dealt with in this section concern the oxide material with resistivities in the $10^{10} - 10^{12} \Omega$ cm region only. It should be mentioned here that the curves in figure 5.5 were determined also with oxygen implantation of the titanium films.

In all of the voltage-current plots it was found necessary to recycle the voltages, as shown in figure 5.7, before a completely reversible and stable characteristic could be obtained. The sample in the figure is an implanted titanium film, but this was also observed for implanted aluminium films. The number of cycles needed for this forming process varied from sample to sample but was never more than four in total. The decrease in resistivity that occurred during this process was never greater than a factor of two.
FIG. 5.6 DETAILED COMPOSITE PLOT OF RESISTIVITY AND T.C.R. OF METAL FILMS WITH \textit{O}_2^+ IMPLANTATION
FIG. 57 Effect on voltage-current characteristics of voltage recycling of titanium film implanted with \( \sim 10^{17} \) oxygen atoms \( \text{cm}^{-2} \).
Figure 5.8 shows the plot of the voltage of one polarity required to produce a given current against the voltage of the opposite polarity required to produce the same magnitude of current, for a recycled sample. If the conduction was dominated by a field-controlled emission limited (either from electrodes or traps) mechanism, then a linear plot of unity slope would be expected for each electrode metal pair. If the barrier height adjacent to one electrode metal was different from the barrier height adjacent to the other an intrinsic electric field would exist in the films at zero applied voltage. (Simmons 1963b). The effect of the intrinsic field would be manifest as an intercept of the linear plot along the voltage axes at twice the difference in the barrier targets (Mead 1962). In the case of our films, a single plot of unity slope passing through the origin was obtained for all metal electrode pairs employed, even when Al/Ti, Al/Cr, Ti/Cr pairs were used.

Figure 5.9 shows the sort of variation in the reversible characteristics that typically occurred for, in the present example, seven samples on one implanted area. The low field resistances varied about a mean value by approximately ±20%. This variation decreased as the electric field was increased. In all subsequent results the characteristics shown are the mean values of the various samples on each implanted area. From one implanted area to another the reproducibility of this mean characteristic was always within 10% and usually within 5%, for irradiations carried out under similar conditions. Figure 5.10 shows the doubly logarithmic current-voltage characteristics typical of aluminium-"oxide" systems formed by oxygen implantation of aluminium films and the corresponding characteristics typical of titanium-"oxide" systems, formed by oxygen implantation of titanium films. The resistivities of the titanium-oxide films tend to be slightly lower than those of the aluminium-oxide films for
FIG. 5.8 Forward and reverse voltages needed to give same current
FIG. 5.9 VARIATIONS IN V-I CHARACTERISTICS FOR SAMPLES ON ONE IMPLANTED AREA
Fig. 5.10 V-I characteristics of films implanted with $10^7$ oxygen atoms cm$^{-2}$.
similar doses. The typical variations of these characteristics with
temperature are shown for the Al-Al(O)–Al system in figure 5.11. The
temperature was varied over a range 285 \text{°K} - 400 \text{°K}, and the results were
completely reversible and reproducible from specimen to specimen. The
dotted lines on the graphs mark three regions which are characterised by
specific behaviour. Region I corresponds to ohmic behaviour and is observed
at low fields. It has a strong temperature dependence but the current shows
no tendency to decay with time. Region III will be seen later to correspond
to a linear dependence of the logarithm of current on the square root of
voltage. The temperature dependence is still strong although smaller than
in region I, and again there are no time-dependent phenomena. Region II is
intermediate between regions I and III and may be represented approximately
by a power law \( I \propto V^n \) where the exponent \( n \) is \( 1.0 < n < 1.5 \). The
temperature dependence of this region is intermediate between that of
regions I and III. Throughout the voltage range the absence of any time
dependence together with the absence of any observable material transport
suggests that the current is electronic.

The curves from figure 5.10 are replotted as \( \log I \) versus \( \sqrt{V} \) in
figure 5.12, while the temperature variation shown in figure 5.11 is
replotted in figure 5.13. For both the aluminium and titanium oxide films
the characteristics show linear regions at voltages in excess of about
0.1 volt which corresponds to an electric field strength of \( 10^4 - 10^5 \) V cm\(^{-1}\),
assuming that the oxide is approximately the thickness of the average
projected range of the ions. The slope of the \( \log I \) versus \( \sqrt{V} \) linear region
is less in the case for the titanium than for the aluminium samples. For
a Poole-Frenkel or Schottky type conduction mechanism (see section 2.2.3)
the experimental slope of the \( \log I \) versus \( \sqrt{V} \) curve is inversely
proportional to \( \frac{1}{3} \), the square root of the film thickness, and proportional
to \( \frac{1}{2} \), which is inversely proportional to \( \frac{1}{2} \), the square root of the optical
FIG. 5.11 V-I CHARACTERISTICS AT VARIOUS TEMPERATURES, IMPLANTED ALUMINIUM FILMS.
Fig. 5.12 Log _I_ - _V^1/2_ for same specimens as in Fig. 5.10.
FIG. 5.13 Log. I-V^{1/2} for same specimen as in Fig. 5.11.
dielectric constant). The ion range of 50 keV oxygen ions in titanium films is approximately 0.8 of their range in aluminium. Also the value of $K$ for titanium dioxide is a factor of approximately 2.5 greater than that for aluminium oxide (Heavens 1960). Then assuming that titanium dioxide and aluminium oxide are formed with film thicknesses equal to the ion range we would expect the slope of implanted titanium films to be about 0.7 times the value for aluminium films. From figure 5.12 this ratio is found to be 0.55.

Figure 5.14 shows typical log I versus $10^{3/4}T$ curves for aluminium-oxide samples at high and low fields. For samples with $\rho > 10^9 \, \Omega \, \text{cm}$, the activation energies were not well defined over the temperature range from $77^\circ K$ to $450^\circ K$. This phenomena is common to many non-crystalline materials due to the absence of sharply defined levels (Walley and Jonscher 1968, Walley 1968). The graphs show continuous curvatures with activation energies varying between about 0.06 eV at low temperatures and about 0.55 eV at high temperatures for low applied fields, and between about 0.01 eV at low temperatures and about 0.06 eV at high temperatures for the high applied field measurements. For specimens in the $10^4 \, \Omega \, \text{cm}$ resistivity range the current-temperature plots exhibit the sort of behaviour that was characteristic of samples in the $10^{-1} - 10^5 \, \Omega \, \text{cm}$ region. All showed irreversible variations, which sometimes included a resistance minimum. Sometimes the resistance minimum was observed as a reversible process. These effects are probably due to the combination of resistances due to metallic conduction and that associated with the small gaps between metal particles.

To show the effect of varying the field on the activation energy at and near room temperature the change of current with temperature was plotted at various values of $V$ over a limited temperature range between $300^\circ K$ and $420^\circ K$. This is shown in figure 5.15. As the applied voltage is increased the activation energy for conduction decreases. By plotting activation energy against applied voltage, or the square root of the applied voltage, and extrapolating to zero voltage, a value of the zero field
Fig. 5.14 Current-Temperature Characteristics for Implanted Aluminium Films
FIG. 5.15 CURRENT-TEMPERATURE CHARACTERISTICS FOR VARIOUS APPLIED VOLTAGES

FIG. 5.16 ACTIVATION ENERGY VS. SQUARE ROOT OF APPLIED VOLTAGE
activation energy, $\Delta E$, can be obtained. Figure 5.16 shows the $\Delta E - V^2$ plot from figure 5.15. The experimental points fall on a straight line and extrapolating the straight line to $V = 0$ yields a value of $\Delta E \approx 0.31$ eV for the aluminium-"oxide" system and a value of $\Delta E \approx 0.25$ eV for the titanium-"oxide" system.

5.2.2.4 Ac measurements

The ac conductance and capacitance variations with frequency are shown in figure 5.17. All the films, whether titanium or aluminium oxides showed a frequency dependance of conductance of the form

$$G_{ac} \propto f^n$$

where $G_{ac}$ is the ac conductance of the film, $f$ is the frequency, and $n$ is a temperature sensitive parameter.

The value of $n \approx 0.8$ was typical of all samples at room temperature. The titanium samples which had slightly higher conductivity had a more pronounced dc mechanism at the low frequencies. This frequency dependance is typical of a thermally-activated hopping type of transport between localised centres and has been observed in various types of low mobility solids (Chan and Jonscher 1969, Jonscher and Wally 1969). However, the frequency range used in our experiments is not high enough to establish this absolutely. At the higher frequencies hopping conduction tends to give a $G \propto f^2$ dependance as well. In general the ac conductance was found to be between 10 - 100 times higher than the dc value even with measurements at audio frequencies. This suggests that the ac conduction mechanism differs from the dc mechanism, or that the charge transport is more efficient under ac conditions. The general consensus of opinion seems to be that there is an increase in efficiency due to hopping of electrons from site to
FIG. 5.17 CONDUCTANCE AND CAPACITANCE VS. FREQUENCY OF IMPLANTED FILMS
site in sustaining conduction and that the ac field promotes the hopping electrons to take the least obstructive course (Jonscher and Walley 1969). For frequencies of about $10^4$ Hz and below Chan and Loh (1970) conclude that for room temperatures and below the electrons are thermally assisted to overcome Poole-Frenkel type barriers and then execute several distant jumps into the surrounding centres during the excursion of the ac field cycle. For frequencies greater than $10^4$ Hz hopping is confined to neighbouring sites giving rise to the square law frequency dependence.

All capacitances were of about $1 - 2 \cdot 10^{-8}$ F at a frequency of $10^3$ Hz and had a $C \propto f^{-m}$ dependence, where $m$ was usually $0.3 - 0.5$. For most samples this dependence of capacitance on frequency occurred at values of $f$ greater than about $4 \cdot 10^3$ Hz. Below this value it was relatively independent of frequency. Occasionally however the dependence occurred throughout the frequency range investigated.

For implanted films with lower resistivities, any variations of $G$ with frequency did not occur, the value being constant over the range of frequency investigated.

5.2.2.5 Effect of background pressure

To investigate the effect of background residual pressure on the implantation process some samples were prepared by ion implantation using the ultra-high vacuum beam line. A pressure of about $5 \times 10^{-9}$ torr could then be obtained in the target chamber.

With both aluminium and titanium films the electrical changes during implantation and conduction properties obtained were identical to those described in the previous sections for samples implanted at pressures of about $10^{-6}$ torr. This suggested that residual gas pressure in the target chamber had a negligible effect on sample properties and therefore the use of ultra-high vacuum afforded no great advantages.

No evaporations of thin films were performed at $10^{-9}$ torr as O'Connell (private communication) has found that the implanted characteristics of such films are no different from those evaporated at $10^{-6}$ torr.
Samples were annealed in air at temperatures of up to $500^\circ$K for various times between 5 minutes and 1 hour. For all combinations of time and temperature the detailed conduction properties showed virtually no change at all after the annealing process. There was a change in the initial resistivity as measured at low fields of typically 5 - 10%. However, such parameters as the slope of the log $I - V^2$ curves, activation energies and ac properties were all identical to the pre-annealed samples. It is interesting to note that Balarin et al (1969) established that oxides of silicon, aluminium, tantalum and copper formed by low energy oxygen and air bombardment did not change their electrical properties during annealing up to $500^\circ$K. Freeman et al (1970) similarly found such an insensitivity to annealing with temperatures up to $800^\circ$C and times of up to 2 hours for oxides and nitrides of silicon produced by ion implantation. Usually in dielectric films produced by evaporation processes some heat treatment such as annealing or temperature cycling is needed to stabilise the film structure to some extent (Chan and Loh, 1970). This structural stability in thin films is a prerequisite in obtaining reliable and interpretable data for conduction analysis. The post-bombardment annealing experiments on films would suggest that this structural stabilisation is carried out during the implantation by some induced-bombardment annealing process.

**5.2.2.7 Calculation of the oxide film thickness**

In order to calculate such parameters as the field-barrier lowering coefficient from equations (2.19) and (2.20), it is necessary to have some idea of the oxide film thickness after implantation. No independent measurements of the oxide thicknesses were made.
The majority of the implantations were carried out with the ion energy at 80 keV for O$_2^+$ ions. The molecular ions dissociate into two O$^+$ ions with energies of 40 keV each at the target surface. From the range data we know that for 80 keV O$_2^+$ in Al, then $\bar{R}_p \approx 800 \, \AA$, and the projected standard deviation assuming a Gaussian distribution for the ion range profile, is about 250 $\AA$ (Johnson and Gibbons, 1969). During the implantation the film will be sputtered by the oxygen ions with a sputtering ratio of about 0.5 aluminium atoms atomic oxygen (see section 4.4 and figure 4.10). Therefore as the high resistivity region is reached with a molecular oxygen dose of $6 \times 10^{16}$ ions cm$^{-2}$, the film will have been sputtered by an amount equal to approximately $6 \times 10^{16}$ atoms cm$^{-2}$, is about 100 $\AA$ of aluminium will have been removed. It has been shown from the electrical measurements using various geometries (section 5.2.2.3) that after an ion dose of about $6 \times 10^{16}$ cm$^{-2}$ the edge of the oxide region coincides with the front surface of the film. This cannot be explained by simply assuming that the front surface of the aluminium film has been sputtered away.

Brown and Davies (1963) have shown that the range profile is only near to that from the Lindhard theory when the ion dose is relatively small, $10^{13} - 10^{14}$ ions cm$^{-2}$. They found that for large doses of about $10^{16}$ ions cm$^{-2}$ of Xe$^+$ at 40 keV in aluminium the range was reduced by almost a factor of two. This effect they termed the 'saturation' phenomena. Presumably, at higher energies a comparable reduction in range would occur for larger bombardments. In our case, the final ion dose was of the order of $10^{17}$ ions cm$^{-2}$, and therefore due to such a saturation effect we would expect the range, $\bar{R}_p$, to decrease as the dose increased. We would therefore expect a final profile situated around 300 - 400 $\AA$ depth. In between the initial and final profiles we would expect a series of gaussian distributions centred around range values that were slightly displaced from one another.
The overall effect of this saturation phenomena would then be to move the ion profile's trailing edge nearer to the thin film surface, and at an ion dose of about $6 \cdot 10^{16}$ ions cm$^{-2}$ they seem to coincide. This movement of the trailing edge of a profile at high doses has also been observed by Freeman et al. (1970) with oxygen and nitrogen implantation of silicon. They found that at ion doses of about $10^{18}$ ions cm$^{-2}$ then the insulating layer so formed was elevated about 300 Å above the initial silicon surface.

To estimate the final oxide thickness it is also necessary to determine the movement of the leading edge of the initial ion profile due to the high ion dose.

Freeman et al. (1970) have actually measured the insulating film thickness, $t$, and found that $t \approx 2 \bar{R}_p$, for an ion dose of $10^{18}$ ions cm$^{-2}$ and a current density of 1 ma cm$^{-2}$, with an average temperature rise that did not exceed 600°C. With a gaussian profile centred around $\bar{R}_p$ then at twice $\bar{R}_p$ the concentration would be decreased by approximately two orders of magnitude and a stoichiometric layer would not be produced but for enhanced diffusion due to the large number of defects being formed and assisting deeper penetration of the ions. With our experiments the current density and the final ion dose used were almost an order of magnitude lower than those used by Freeman et al and we would expect enhanced diffusion effects to be much less than in their experiments. We therefore assume that the oxygen implantations form a homogeneous layer of thicknesses given by $\bar{R}_p$ plus or minus the standard deviation. This gives an oxide thickness equal to approximately $300\AA \pm 250\AA$.

A similar analysis for titanium films would lead us to expect an oxide film thickness of approximately $600\AA \pm 250\AA$. 

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Having thus made an estimate of the oxide thicknesses if we now assume that all the oxygen present combines with the aluminium to form $\text{Al}_2\text{O}_3$ and with the titanium to form $\text{TiO}_2$ (this is not unreasonable in view of the electron microscopy and diffraction results, section 5.3.2.1), then we can deduce a plot of resistivity versus volume % insulator or volume % metal. From such calculations we find that the sudden onset of high resistivity material takes place at 40 ± 20 volume % insulator. As well as oxygen being directly implanted into the metal films there is also the secondary process of recoil implantation whereby surface oxide may be "knocked-in" by the incident primary ion (see section 4.5). If this occurs this will contribute to the total number of trapped oxygen. Although measurements have not been made on recoils from surface oxides, by inserting the relevant parameters into the Nelson theory (equation 4.11) and taking $E_{\text{min}} \sim 20 \text{ eV}$, then the recoil concentration can be estimated. The calculation gives at a primary ion dose of $10^{17} \text{ ions cm}^{-2}$ a recoil concentration of about $2 \times 10^{16} \text{ cm}^{-2}$ which would not alter a great deal the above 40 ± 20% volume % insulator value for the onset of high resistivity and negative TCR of the films.

Using the above values of estimated thickness for the oxide layers the capacitance results at low frequencies give values of the low-frequency dielectric constant, $K_0$, of 5 - 10 for the aluminium oxide system and 15 - 20 for the titanium oxide system. These values compare favourably with values of about 9 for aluminium-oxide films prepared by evaporation, sputtering, and anodization (Mier and Buvinger 1969) and 20 - 25 for titanium dioxide thin films (Wasa and Hayakawa 1967).

5.2.3 Conduction properties of implanted dielectric films

5.2.3.1 Properties of evaporated silicon oxide films

The electrical properties of evaporated silicon oxide films are dependent on such parameters as residual gas pressure, evaporation rate and substrate temperature. The evaporation parameters were therefore carefully controlled to enable reproducible properties to be obtained. Infra red
transmission spectra showed that the films were predominantly SiO$_{1.5}$
(see section 5.3.2.2). Film resistivities were of the order of $10^{13}$ Ω cm.

Voltage-current characteristics showed the same form, including the
regions I, II and III found for the oxygen implanted films (see figure 5.10).
There was one difference however, in that for the silicon oxide films
region I had a time-dependent phenomena, the current tending to decay with
time after the application of the applied voltage. This in all probability
is due to ionic conduction, as opposed to an electronic conduction mechanism.
This time dependency decreased as the field was increased, and had in fact
disappeared during region II. The activation energy for conduction in
region II was approximately 0.5 eV, in agreement with other experimentally
determined values (see section 2.2.3) for evaporated silicon oxide films.

Figure 5.18 shows a log I versus $V^{1/4}$ plot of specimens for film
thickness of 400 $\AA$ and 550 $\AA$. There is a strong log $I \propto V^{1/4}$ dependence for
all films, and assuming a Schottky or Poole-Frenkel mechanism we obtain a
value for the field-lowering coefficient, $\beta$, (see equations 2.21 and 2.22) of

$$\beta \approx 2.0 (\pm 0.3) \times 10^{-5} \text{ cm} V^{-1/2} \text{ m}^{1/2},$$

which is in good agreement with values determined by Servini and Jonscher

The capacitance measured at 1592 Hz ($10^4$ radians sec$^{-1}$) gave a
dielectric constant of $5.2 \pm 0.4$. A dielectric constant of about 6 is
expected for SiO films as compared with values nearer 4 for SiO$_2$
(Schenkel 1965).

5.2.3.2 Change in resistivity due to implantation

The variation of the resistances of Al-SiO - Al and Ti-SiO - Ti
structures with the dose of incident argon ions are shown in figure 5.19 for
varying argon ion energies and silicon oxide film thickness. Curves (a)
FIG. 5.18 Log. I - V'^1/2 FOR EVAPORATED SILICON OXIDE FILMS
FIG. 5.19 RESISTANCE vs. ION DOSE OF SILICON OXIDE FILMS DURING RECOIL IMPLANTATION
shows the decrease in resistance for an argon ion energy of 50 keV and aluminium and titanium films of thickness 500 Å. When the ion energy is increased to 80 keV the resistance decreases at much faster rate as shown in curve (b) for aluminium. This can possibly be explained by consideration of the relative ranges of the 50 and 80 keV ions. The average projected ranges, $R_p$, for the 50 and 80 keV $\text{Ar}^+$ ions in Al are 550 Å and 900 Å respectively as calculated from Lindhard's theory. Thus in the higher energy case ions have a greater probability of traversing both the top electrode, and dielectric layer and coming to rest in the lower electrode, than with the lower energy case. So when 80 keV ions are employed the SiO layer has a higher probability of receiving aluminium atoms from displacement collisions in both electrodes thus resulting in a larger change in the resistance per incident ion dose.

When dielectric layers of thickness greater than about 500 Å were used, the resistivity at first falls slowly and then remains constant after an argon dose between 1.2 and $2 \times 10^{16}$ ions cm$^{-2}$ as shown in curves (c) and (d). This indicates that the eventual range of the recoil metal atoms for a high dose level were less than 500 Å, bearing out the fact that recoil implantation is inefficient for deep implantation to the depth of 1000 Å or more.

In order to investigate the conduction properties in detail the parameters giving rise to curves (a) were used throughout. The top metal layer was 500 Å thick, the silicon oxide layer 400 Å thick and the argon ion energy used was 50 keV.

Figure 5.20 shows the variation of the resistance of the dielectric films implanted with aluminium and titanium atoms versus the metal atom density. This was obtained by combining curves (a) from figure 5.19 with the radioactive measurements from figure 4.8. The radioactive measurements were only performed with aluminium, not titanium films, however a value of
Ft<3r.5.20 Resistance change of silicon oxide films with implanted metal atom concentration.
the forward sputtering for titanium can be obtained by using equation (4.11), and substituting into this equation the relevant parameters. We define three regions A, B, C in figure 5.20. In region A where the metal atom density varies from 0 to $2 \times 10^{16}$ atoms cm$^{-2}$ the resistance decreases relatively slowly by three orders of magnitude. In region B however, for a small change in ion dose there is a very rapid change in resistance over 3 - 4 orders of magnitude, whilst in region C the resistance again varies slowly with dose until the resistance measured is that of the leads.

Assuming a dielectric film of SiO$_{1.5}$ with a density of 2.2 gm per cc, calculations show that region B corresponds to a metal concentration of about 35 - 40 volume per cent. From figure 5.20 we see also that the form of the curve is virtually identical for both the aluminium and the titanium metals. That is, to say, a plot of resistance or resistivity versus composition, using volume % metal as the abscissa, should follow the same curve regardless of the metal. This is exactly what has been pointed out by Neugebauer and Rairden (1970). They found that, replotting previous experimental results, regardless of the metal or the deposition conditions, one curve alone gives a good fit for all metal/SiO cermets, and another curve a good fit for all metal/SiO$_2$ cermet films. One must therefore conclude that the resistivity of the cermet films is determined principally by extent of volume dilution of metal by SiO or SiO$_2$ and not the nature of the metal, deposition method or substrate temperature.

5.2.3.3 Do characteristics of implanted films

Figure 5.21 shows the voltage-current plots of dielectric films doped by recoil atom implantation with varying concentration of metal atoms. Unlike the oxygen implanted metal thin films these samples did not need voltage cycling to produce a reversible characteristic. Reversing of the polarity of the applied voltage produced exactly the same characteristics. In the high resistance region designated A in figure 5.20 all films show deviation from Ohm's law at high electric fields. This deviation becomes
FIG. 5.21 V-I CHARACTERISTICS AT VARYING METAL CONCENTRATIONS
less marked as the resistance decreases until in region C the conduction is ohmic up to the breakdown point. For the high resistance samples the voltage-current plots show regions I, II and III as observed for the oxygen implanted metal films and the unbombarded silicon oxide films. No time dependent phenomena were observed indicating probable electronic conduction.

Replotting the curves of figures 5.21 as $\log I$ versus $V^2$ in figure 5.22 we find a strong $I \propto \exp V^2$ dependences for metal concentrations less than about 30 volume %. Again, assuming a Poole-Frenkel or Schottky type conduction mechanism, the field dependency coefficient $\beta$, has values ranging from $3.4 - 3.5 \times 10^{-5} \text{ eV} V^{-1/2} \text{ m}^{2}$ for films with about 10% metal to $2.2 \times 10^{-5} \text{ eV} V^{-1/2} \text{ m}^{2}$ for films with 30% metal. For films above this metal concentration, (i.e. for resistances less than about $10^6 \Omega$) the curves start to show a saturation effect at high fields. This becomes greater as the film resistance decreases.

Figures 5.23 show the temperature dependence of the voltage-current characteristics for films with about 10% metal. The temperature variation is over a limited range $300^0 \text{K} - 400^0 \text{K}$, however we can see that the temperature dependence is stronger at low fields than at high fields. Plotting the values of activation energy versus the square root of the applied field from these family of curves yields a straight line which on extrapolation to $V = 0$ gives a zero-field activation energy of 0.18 eV.

The variation of $\log I$ with temperature for differing values of metallic concentration over a temperature range from $77^0 \text{K} - 500^0 \text{K}$ shows no unique activation energy, as in the case of oxygen implanted aluminium and titanium films; instead there is a distribution of activation energies covering nearly an order of magnitude (figure 5.24). To enable an accurate comparison of activation energies for differing metallic concentrations, the changes in current with temperature in the limited temperature range $300^0 \text{K}$ to $430^0 \text{K}$ were plotted. These results are shown in figure 5.25. The degree of curvature of the slopes and the room temperature activation
FIG. 5.22 Log, I-V₁/₂ for same specimens as in Fig. 5.21.
FIG. 5.23 V-I CHARACTERISTICS AT VARIOUS TEMPERATURES, 10% AL/SiO SAMPLE
FIG. 5.24 CURRENT-TEMPERATURE CHARACTERISTICS FOR METAL|SiO FILMS
FIG. 5.25: CURRENT-TEMPERATURE CHARACTERISTICS FOR METAL ISO FILMS IN LIMITED TEMPERATURE RANGE

CURRENT (AMPS)
energies decreases as the metal impurity concentration increases. For films with low resistances the temperature coefficient is positive indicating metallic conduction even though the conductivity is less than that of bulk aluminium by many orders of magnitude.

These curves show that as with the oxygen implanted metal films (see figure 5.6) the temperature coefficient of resistance (TCR) changes sign at some critical composition at 30 - 50 volume % metal. Figure 5.26 plots the activation energy versus metal atom density in the dielectric from results shown in the previous figure. The critical composition can be taken as the point at which the film structure changes from a continuous metallic matrix to one containing a dispersion of metallic particles. Neugebauer and Raikden state that because of the disproportionation of SiO the insulating phase is really Si + SiO₂ or more correctly SiO₂, since silicon will dissolve in or react with the metal or, if present in excess is relatively conductive compared to SiO₂. Therefore taking

$$\text{SiO} \rightarrow \frac{1}{2} \text{Si} + \frac{1}{2} \text{SiO}_2$$

a comparison of activation energies - composition of metal/SiO and metal/SiO₂ cermets were made and shown to fall on the same line within an order of magnitude. If we assume that

$$\text{SiO}_{1.5} \rightarrow \frac{1}{4} \text{Si} + \frac{3}{4} \text{SiO}_2$$

and replot activation energies of figure 5.26 versus volume % SiO₂, then we find that this too falls near to the data of Neugebauer and Raikden (see figure 5.27). As with the resistivity versus composition data it seems that it is again the volume dilution of the metallic phase by SiO₂ which principally determines the activation energy, and not the nature of the metal or the deposition conditions.
**Fig. 5.26 Activation Energy vs. Implanted Metal Atom Concentration**

- X - Present Work: Al/SiO$_2$, Ti/SiO$_2$
- □ - Au/SiO$_2$: Miller et al. (1970)
- Δ - Cr/SiO$_2$: Milgram and Lu (1968)
- ○ - Best Fit for Cr/SiO$_2$, Au/SiO$_2$, and Au/SiO from Neugebauer and Rainden (1970)

**Fig. 5.27 Activation Energy vs. Volume % SiO$_2$**
5.2.3.4 **Ac characteristics of implanted films**

Ac conductance and capacitance measurements are shown against the variation in frequency in figure 5.28. For all high resistance films whether aluminium or titanium oxide we obtain a frequency dependence of conductance, above $10^3$ Hz of

$$G_{ac} \propto f^n$$

where $n \approx 0.75 - 0.85$. Capacitance values were virtually independent of frequency, and varied between $1 - 4 \times 10^{-8}$ F. The frequency dependence of ac conductance is again suggestive of a hopping conduction as explained for the oxygen implanted metal films.

For low resistances, $G$ was independent of frequency.

5.2.3.5 **Influence of other parameters**

As found with the oxide films produced by oxygen ion implantation of metal films we found that annealing and background pressure did not affect the characteristics of the films produced by recoil atom implantation. Annealing was carried out for up to 1 hour at up to $550^\circ$K in air. The residual pressure during bombardment was varied down to about $5 \times 10^{-9}$ torr.

5.3 **Structure of Implanted Films**

5.3.1 **Experimental**

5.3.1.1 **Electron microscopy and diffraction**

The films before and after implantation were examined by transmission electron microscopy and electron diffraction in a Siemens Elinskop I electron microscope using 100 keV electrons. Using the electron microscope resolutions of about 30 Å could be obtained with magnifications of 160,000X. This magnification was doubled by the use of photographic plates. The microscope was operated in the bright field mode. That is to say the beam as opposed to the diffracted beam for dark field image operation.
FIG. 5.28 CONDUCTANCE AND CAPACITANCE vs. FREQUENCY
The transmission diffraction patterns were utilized to determine the crystal structure following the standard method of X-ray diffraction analysis. Interplanar spacings ("d"-values) are obtained from the relation \( d = \frac{\lambda L}{r} \) where \( r \) is the radius of the diffraction ring or the distance of the diffraction spot from the centre of the pattern, \( L \) is the effective specimen-to-plate distance, called the camera constant, and \( \lambda \) is the wavelength of the radiation, 0.037 \( \text{Å} \) for 100 keV electrons. These numbers were then compared with the tabulated lists (ASTM Index X-ray Powder Data File, revised annually) of "d" values for known structures until identifications were made. With an internal calibration (to determine \( L \)) and for crystallites larger than about 100 \( \text{Å} \), lattice constants may be determined with an accuracy of about 1 - 5 per cent. As the crystallite sizes increase or decrease the diffraction rings decrease and broaden respectively. This "line broadening" is commonly used to determine crystallite size \( t \), which is given by \( t = \frac{\lambda}{D \cos \Theta} \) where \( \Theta \) is the Bragg angle and \( D \) is the angular width at half the maximum intensity. Because of the much smaller value of \( \lambda \) for fast electrons then for X-rays the line broadening of electron-diffraction patterns is considerably less than for X-ray diffraction. The interplanar spacings and line broadening were measured by scanning the photographic negative plates with a commercial double-beam recording photo-microdensitometer and measuring the diffraction ring radii and half peak widths of the diffraction lines.

Electron microscopy may be applied to thin film problems in several modes. Shadowed replicas may be used to study the surface (Bradley 1965); the film may be deposited on a thin electron-transparent substrate so that both the substrate and film can be examined together (McLauchlon et al. 1950, Pashley et al 1964, Poppa 1965) or the more commonly used method for thin films is to remove the film from the substrate by dissolving away the substrate in a suitable solution (Sumner 1966). In these investigations specimens were prepared for examination by a combination of the latter two methods.
In the case of the oxygen implantations of metal films two specimens preparation techniques were used. With the first method, 200 Å self-supporting films of silicon oxide were evaporated onto a thin collodion membrane which had previously been floated onto 3.05 mm diameter AEI type electron microscope grids. Aluminium films, about 300 Å thick were then evaporated onto the silicon oxide, and the collodion suspension dissolved away using amyl acetate (Watt 1969, private communication), leaving the aluminium film supported on the silicon oxide layer on the grid. With the second preparation method, the silicon oxide layer was dispensed with and self-supporting 500 Å aluminium films were condensed directly onto the collodion membrane. After this had been dissolved away the aluminium film was left suspended on the grid. The grids were then placed in the target chamber of the accelerator and the metal films implanted.

Structure of recoil atom implanted silicon oxide films were investigated by using similar specimen preparations. Silicon oxide films, about 500 Å thick, were suspended on grids using the collodion technique. Thin, < 200 Å thick, layers of metal (titanium in this case) were then deposited on the silicon oxide in the vacuum evaporator. Then the grids were placed in the accelerator and bombarded by argon gas ions. The dose was calculated so that after a certain number of metal atoms had been implanted into the silicon oxide, back sputtering of the metal layer had removed the remaining surface metal atoms. Thus when viewed in the electron microscope observation of the implanted dielectric was not interfered with by any superimposed metal surface layer.

A special target holder was used to hold the microscope grids during ion bombardments (figure 5.29). This consisted of a 4.0 cm x 1.8 cm x 0.2 cm stainless steel holder which could be fastened to the target chamber base plate. Four grids could be bombarded at any one time, the grids being held in place in the holder in recessed holes by small cylindrical plugs and a back plate.
**Fig. 5.29** Electron microscope grid holder

**Fig. 5.30** Infra-red reflectance accessory
5.3.1.2 Infra red spectroscopy

Implanted films were examined for composition by transmission and reflection infra red spectroscopy using a two-beam Perkin-Elmer 337 spectrophotometer, which provided a continuous record of the infra red spectra as a function of the frequency in the range $400 \text{ cm}^{-1} - 1333 \text{ cm}^{-1}$ (wavelength range 25 $\mu$ to 7.5 $\mu$).

Radiation emitted by the source is divided into two components, one the reference and one passing through the sample. The two beams are then recombined into a single beam consisting of alternate pulses of radiation from the sample and reference beams. The combined beam is finally dispersed into its spectral components and detected by a thermocouple detector. If the energy in both the sample and reference beams is equal then the pulses from the two beams are of equal intensity. The thermocouple detector therefore produces a dc voltage which is not amplified by the ac amplifier of the instrument. However, at the characteristic absorption frequency of the sample, the intensity of the sample beam is reduced and the two signals become unequal and the combined beam flickers at 11 Hz. The resulting amplitude in the detector is proportional to the difference in intensity of the two beams. The abscissa accuracy of the measurements is $\pm 2 \text{ cm}^{-1}$ in the $400 - 1333 \text{ cm}^{-1}$ frequency region, and the ordinate accuracy is $\pm 1\%$ full scale energy. The noise is less than $1\%$ peak to peak of full scale energy.

The oxidation of metal films was investigated by transmission and reflection methods. With the former method, metal films of about 500 $\AA$ thickness were evaporated onto previously deposited silicon oxide layers, about 300 $\AA$ thick, on polished KBr crystals. KBr transmits all frequencies in the $400 - 1333 \text{ cm}^{-1}$ region and is therefore a good non interfering substrate for infra red absorption work. The intermediate silicon oxide layer although complicating the absorption spectra, was necessary to make sure that any incident oxygen ions that penetrate metal films did not penetrate the KBr crystals and thus damage it.
The reflection technique (Dannenberg et al 1960) involves the use of a specular reflectance accessory in conjunction with the infra red spectrophotometer (figure 5.30). With the accessory in position in the light beam of the spectrophotometer one side of the gold-coated prism deflects the light beam to the sample from which it is then reflected to the second side of the prism such that it reflects the light beam back along its normal path to the spectrophotometer. The sample consists of an evaporated metal film, about 2000 Å thick on a glass substrate, which has been implanted with oxygen ions to a depth of about 600 Å ($R_p$, the average projected range). An absorption spectra of the oxidised region is obtained as the light passes through the region to the reflecting metal portion of the film and then back again through the oxidised region a second time. A similar reflection accessory using a plane unbombarded aluminium film evaporated as the sample was used in the reference beam of the spectrophotometer.

Recoil atom implantations were investigated by using transmission techniques only. The silicon oxide dielectric layer, about 500 Å thick, was evaporated onto KBr crystals, and aluminium and titanium thin, about 100 Å thick, films deposited onto the dielectric. After argon ion bombardment the whole sample was viewed in transmission in the spectrophotometer.

Transmission absorption spectra of evaporated silicon oxide films were recorded for reference purposes, and also so as to determine the composition of the dielectric material used in the study of the conduction properties.

5.3.2 Results

5.3.2.1 Oxygen implanted films

The electron diffraction data obtained from the scanning of the photographic plates by the photomicrodensitometer is shown in tables IV (a) and IV (b). In table IV (a) the "d" values found for the initial evaporated films are presented. Both sets of values agree closely with the
ASTM Powder file data for aluminium and titanium with one exception. The three strongest lines of titanium are not resolved and instead we obtained a very broad band at a "d" value intermediate between the three. The three strongest d values of titanium are at d = 2.24, 2.56 and 2.34 Å, and it is therefore quite probable that with the initial titanium films, due to the slow evaporation rate, the crystallite sizes, ~50 Å are so small that these three lines overlap each other forming one very broad line centred at or near d = 2.4 Å. An interesting feature arises in the diffraction pattern of the titanium films after an oxygen dose of 5 × 10¹⁶ ions cm⁻². The broad line centred around 2.4 Å breaks up into a reasonably sharp line corresponding to a d = 2.56 Å value, and two slightly broader lines giving d = 2.36 Å and d = 2.28 Å. These are the characteristic titanium lines and shows that with the titanium films bombardment has in this case increased the crystallite size, especially for the (010) direction crystallites (ie for d = 2.56 Å). On increasing the oxygen ion dose to 10¹⁷ oxygen atoms cm⁻² the three titanium lines become clearly resolvable with crystallite sizes of about 100 Å as measured by the line broadening method. The other titanium lines were also observed along with six other lines, some strong, some weak which could not be identified completely as a particular oxide phase. We have therefore labelled these as simply 'oxide' lines in table IV (b).

With the aluminium films after 10¹⁷ oxygen atoms cm⁻² had been implanted the diffraction data (table IV (b)) showed that, as with the titanium films, a metal/metal oxide system was formed. Six aluminium lines were identified although their intensities had decreased and the line widths broadened indicating that bombardment had decreased the crystallite sizes. Estimation of this crystallite size using the line broadening gave values of 50 - 150 Å for the aluminium crystallites. Once again the oxide lines could not be completely identified as belonging to any particular oxide phases.
**TABLE IV (a)**

Electron Diffraction Data on Evaporated Metal Films

<table>
<thead>
<tr>
<th>Aluminium</th>
<th></th>
<th>Titanium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Evaporated Film</td>
<td>ASTM Powder File</td>
<td>Evaporated Film</td>
</tr>
<tr>
<td>$d(\AA)$</td>
<td>$d(\AA)$</td>
<td>hkl</td>
</tr>
<tr>
<td>2.34</td>
<td>2.34</td>
<td>111</td>
</tr>
<tr>
<td>2.02</td>
<td>2.02</td>
<td>200</td>
</tr>
<tr>
<td>1.46</td>
<td>1.43</td>
<td>220</td>
</tr>
<tr>
<td>1.26</td>
<td>1.22</td>
<td>311</td>
</tr>
<tr>
<td>1.22</td>
<td>1.17</td>
<td>222</td>
</tr>
<tr>
<td>1.03</td>
<td>1.01</td>
<td>400</td>
</tr>
</tbody>
</table>

* The three strongest titanium lines lie close together at $d$ values equal to 2.24 \( \AA \), 2.56 \( \AA \) and 2.34 \( \AA \). The very broad line observed at $d = 2.38 \AA$ is therefore probably due to the overlap of these three lines.

**TABLE IV (b)**

Electron Diffraction Data on Evaporated Metal Films after Implantation with $6 \times 10^{16}$ O\(^+\) ions cm\(^{-2}\)

<table>
<thead>
<tr>
<th>Aluminium</th>
<th></th>
<th>Titanium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Observed &quot;$d$&quot; value</td>
<td>Identification</td>
<td>Observed &quot;$d$&quot; value</td>
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<td>oxide</td>
<td>4.15</td>
</tr>
<tr>
<td>2.32</td>
<td>Al 111</td>
<td>3.58</td>
</tr>
<tr>
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<td>oxide</td>
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</tr>
<tr>
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<td>oxide</td>
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</tr>
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<td>1.95</td>
<td>oxide</td>
<td>1.99</td>
</tr>
<tr>
<td>1.87</td>
<td>oxide</td>
<td>1.84</td>
</tr>
<tr>
<td>1.81</td>
<td>oxide</td>
<td>1.72</td>
</tr>
<tr>
<td>1.72</td>
<td>oxide</td>
<td>1.60</td>
</tr>
<tr>
<td>1.60</td>
<td>oxide</td>
<td>1.43</td>
</tr>
<tr>
<td>1.43</td>
<td>Al 220</td>
<td>1.34</td>
</tr>
<tr>
<td>1.32</td>
<td>oxide</td>
<td>1.28</td>
</tr>
<tr>
<td>1.21</td>
<td>Al 311</td>
<td>1.25</td>
</tr>
<tr>
<td>1.18</td>
<td>Al 222</td>
<td>1.25</td>
</tr>
<tr>
<td>1.15</td>
<td>oxide</td>
<td>1.03</td>
</tr>
</tbody>
</table>
FIG. 5.3 | ELECTRON MICROGRAPHS OF ALUMINIUM FILMS IMPLANTED WITH $\sim 6 \times 10^{16} \text{O}_{2}^{+} \text{ions cm}^{-2}$ AT 80 KEV. (a) X 80,000 (b) X 320,000
FIG. 5.32. HISTOGRAM OF OXIDE CLUSTER SIZE AND SPACINGS
Figure 5.31 shows electron micrographs of the oxide clusters that have formed after an 80 keV molecular oxygen ion dose of about $6 \cdot 10^{16}$ ions cm$^{-2}$ had been implanted into an aluminium film. The islands were generally randomly scattered over any given area, and were observed to be either well defined polycrystalline aggregates or composed of ill defined areas consisting of many smaller crystallites. Histograms of the oxide island sizes and the gaps between the islands are shown in figure 5.32. The island clusters chosen for the histogram were those of the well defined polycrystalline aggregates. Both the island size and their separation follow approximately a Gaussian type distribution, with an average cluster size of 220 Å.

5.3.2.2 Metal implanted silicon oxide films

Figure 5.33 shows the electron micrograph of a silicon oxide film after being implanted with approximately $8 \times 10^{15}$ cm$^{-2}$ titanium atoms. Titanium, rather than aluminium was used so as a better resolution could be obtained. We see that the metal implanted forms clusters spaced randomly in the dielectric matrix. Histograms of the cluster sizes and cluster separations, shown in figure 5.34 give approximate Gaussian distributions about an average cluster size of 70 Å and an average cluster separation of 80 Å. Table V presents the average cluster size, ($d$) and average separation, ($s$) found for varying doses of implanted metal atoms as measured by the decrease in film resistance, $R_0$.

<table>
<thead>
<tr>
<th>Film Resistance ($R_0$)</th>
<th>$d$(Å)</th>
<th>$s$(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$5 \cdot 10^8$</td>
<td>70</td>
<td>80</td>
</tr>
<tr>
<td>$2.5 \cdot 10^8$</td>
<td>80</td>
<td>50</td>
</tr>
<tr>
<td>$3.0 \cdot 10^7$</td>
<td>90</td>
<td>40</td>
</tr>
<tr>
<td>$10^6$</td>
<td>120</td>
<td>35</td>
</tr>
<tr>
<td>$3 \cdot 10^5$</td>
<td>300</td>
<td>$\sim 25$</td>
</tr>
</tbody>
</table>
FIG. 5.33 ELECTRON MICROGRAPHS OF SILICONOXIDE FILMS IMPLANTED WITH 
\(~ \times 10^{15} \text{ cm}^{-2}\) TITANIUM ATOMS (a) X 80,000 (b) X 320,000
FIG. 5.34 HISTOGRAM OF METAL CLUSTER SIZE AND SPACINGS
Analysis of the microdensitometer trace from the electron diffraction patterns show only the presence of the titanium metal. Calculations of titanium crystallite size from the line widths give good agreement with the electron microscopy data.

5.3.2.3 Bubble formation

In the case of recoil atom implantation if the inert gas ion dose is increased to about $5 \times 10^{16} - 10^{17}$ ions cm$^{-2}$ we obtain inert gas bubble formation. This can be shown in figure 5.35 for the recoil implantation of gold atoms into silicon oxide. The initial film was 300 Å thick and the argon ion energy used was 80 keV. The bubble size varies between about 200 to 800 Å. The gold film is quasi-continuous and shows a positive temperature coefficient, although the conductivity is several orders of magnitude less than that of the bulk material. It is noticeable that the bubbles nucleate around the edges of the gold 'strands'. Because of the considerable vacancy production during ion irradiation and because the strain energy associated with a trapped atom-vacancy aggregate is generally less than that for the atom trapped in a normal substitutional or interstitial site we may expect some gas atom-vacancy agglomeration to occur. The gas probably nucleates into some bubble form by damage events which provide the necessary vacancies (Nelson, 1964). This should be particularly prevalent when the trapped atom and vacancy concentrations are large as in our experiments where large ion doses and high ion energies were used.

5.3.2.4 Infra-red spectroscopy

The stoichiometry of evaporated silicon oxide films is a strong function of the evaporating parameters and can be followed by observation of the SiO stretching bond frequency. Spectrum (a) in figure 5.36 shows the spectrum of a typical evaporated silicon oxide film used in the investigations.
FIG. 5.35  ELECTRON MICROGRAPHS SHOWING BUBBLE FORMATION  (a) x 8,000  
(b) x 80,000
FIG. 5.36 INFRA-RED TRANSMISSION SPECTRA
The film thickness here was about 500 Å, and the evaporation rate was 40 Å sec\(^{-1}\) at a pressure of 10\(^{-5}\) torr. The transmission spectrum of this film shows one strong absorption band at 1040 cm\(^{-1}\), a moderate band at 870 cm\(^{-1}\), a weak band at 930 cm\(^{-1}\) and a weak shoulder in the 1100 - 1250 cm\(^{-1}\) region. The strong absorption occurs at an intermediate position between that of SiO at 1000 cm\(^{-1}\) and SiO\(_2\) at 1085 cm\(^{-1}\), (Hass and Salzberg 1954). This together with the moderate intensity band near 870 cm\(^{-1}\) is interpreted as being due to Si\(_2\)O\(_3\), an oxide intermediate between SiO and SiO\(_2\) (Ritter 1962). The weak shoulder can be attributed to SiO\(_2\) so it is felt that the films consist of mainly Si\(_2\)O\(_3\) with some SiO\(_2\) and probably some SiO although no absorption at 1000 cm\(^{-1}\) is observed. The weak absorption near 930 cm\(^{-1}\) can be attributed to an Si - OH vibration (Pliskin 1968).

When about 2 \(\times\) 10\(^{16}\) cm\(^{-2}\) aluminium atoms are introduced into the silicon oxide films by recoil implantation the transmission spectrum takes the form of that shown in (b) of figure 5.36. The main absorption band weakens and broadens with the maximum absorption shifting from 1040 cm\(^{-1}\) to 1030 cm\(^{-1}\), that is a shift towards SiO. This shift to a lower frequency couples with a broadening of the 1040 cm\(^{-1}\) band can be attributed to a slight oxygen deficiency in addition to the probability of some bond strain and some slight decrease in film density. This has been observed with silicon dioxide to be due to the decreased polymerization of the SiO\(_4\) tetrahedra (Pliskin and Lehman, 1965). It is interesting to note that Chou and Crowder (1970) have observed displacement damage in SiO\(_2\) with O\(^+\) and Ne\(^+\) bombardment manifesting itself in a decrease in oxide density as evidenced by ellipsometric measurements. Also in spectrum (b) there is a broad weak absorption band in the 950 cm\(^{-1}\) - 550 cm\(^{-1}\) region with slightly stronger narrow bands near 730 cm\(^{-1}\) and 630 cm\(^{-1}\). The band at 730 cm\(^{-1}\) could possibly be attributed to the Al-O covalent bond vibration. Kolesova (1959) states that this vibration always appears in the 720 - 780 cm\(^{-1}\) region, regardless of the co-ordination number of the aluminium atoms with respect to oxygen.
atoms. Beck et al (1967) however state that the Al-O vibration band moves to higher frequencies when the co-ordination number is lower than six, ie as for stoichiometric Al₂O₃. Kolesova has found bands at 760 cm⁻¹, 640 cm⁻¹ and 600 cm⁻¹, and Brame et al (1958), at 740 cm⁻¹ for corundum aluminium oxide. Balarin et al (1969) have found a broad absorption band between 500 - 900 cm⁻¹ indicative of amorphous aluminium oxide, for oxygen bombarded aluminium. The SiO₂ band at 870 cm⁻¹ is not observed, but this may well be due to the fact that it is 'lost' in among the broad amorphous aluminium oxide band.

It is interesting to note that a very weak band appears near 950 cm⁻¹ in spectrum (b). Pliskin (1968) has observed this in calciumalumino silicate glasses that have been rf sputtered onto heated substrates. He attributes this to the Si-O⁻ stretching vibration, the presence of which is due to calcium cations in the glass structure. There are calcium impurities in the silicon monoxide used for evaporation, but they are only 1 part in 10⁵ and it is thus difficult to see how they could cause the absorption. A more realistic assumption might be that it is due to an Al-O vibration for non-stoichiometric Al₂O₃. Then, as we have already stated, an Al-O vibrational band is observed at higher frequencies than with the usual frequency range. Recently Vedder and Vermilyea (1969) and Takamura et al (1970) have observed a band at 955 cm⁻¹ which they have attributed to the Al-O vibration from non-stoichiometric Al₂O₃ with co-ordination numbers below six. If we assume that this is the case for our films it could indicate the formation of some suboxide.

The transmission spectrum of an oxygen bombarded aluminium film on a silicon oxide layer is shown in spectrum (c). The ion energy was such that some silicon and oxygen ions will be sputtered back from the silicon oxide layer as the oxygen ions penetrate the aluminium film. The ion dose was about 10¹⁷ oxygen ions cm⁻². The spectrum is virtually identical with that of a boro-alumino silicate glass (Corning 7059), shown in spectrum (d).
Both spectra show a very wide absorption band in the 950 - 1250 cm$^{-1}$ region, and weak narrow bands near 900 cm$^{-1}$, 730 cm$^{-1}$ and 630 cm$^{-1}$. There is more absorption in the 950 cm$^{-1}$ - 550 cm$^{-1}$ region in the bombarded film than with the glass. The bands at 730 cm$^{-1}$ and 630 cm$^{-1}$ have already been mentioned above and Harkins et al (1959) has observed a band near 900 cm$^{-1}$ in an aluminium silicate system. It does appear that the bombardment process produces a thin film with a composition virtually identical with that of an aluminosilicate glass when the ion range is such that the metal thin film is penetrated and substrate atoms backspattered.

Reflection measurements on the oxygen bombarded aluminium films yield weak bands at 625 cm$^{-1}$, 955 cm$^{-1}$ and 730 cm$^{-1}$. No band at 900 cm$^{-1}$ is observed. The 625 cm$^{-1}$ and 730 cm$^{-1}$ band suggests some aluminium-oxide formation and the 955 cm$^{-1}$ band suggests non-stoichiometric oxide formation.

5.3.3 Conclusions regarding film structure

Electron microscopy and electron diffraction studies showed that oxygen implantations of aluminium and titanium films with doses of about $10^{17}$ oxygen atoms cm$^{-2}$ produce a film consisting of a mixture of metal and metal oxide. The metal oxide grew as clusters, the cluster size increasing as the oxygen dose is increased eventually forming both well defined oxide polycrystalline aggregates of $150 \, \AA$ - $300 \, \AA$ diameter and ill defined area consisting of many smaller aggregates. Calculations from electron diffraction line widths gave the aluminium and titanium crystallites as about $100 \, \AA$ in size after the implantation of $10^{17}$ oxygen atoms. The aluminium crystallites had been reduced in size during the bombardment while the titanium crystallites had actually increased in size by a factor of 2 - 3. A complete identification of oxide phases was not possible from the oxide diffraction patterns, and this together with evidence for non-stoichiometric oxide formation from the infra red spectroscopy suggests that the insulating regions between the metallic areas are not completely oxidised, ie they are probably $\text{Al}_2O_x \,(x<3)$ and $\text{TiO}_y \,(y<2)$. 

-152-
For bombardments using argon ions and oxygen ions of such energy that they penetrate a thin metal film, which is on a silicon oxide backing, then infra red studies have shown that a glass like structure is formed within the metal film which is evidence that recoil atoms from a substrate can cross the metal film substrate interface and become embedded in the metal film, as already shown by radioactive measurements in chapter IV.

With recoil implantation the metal implanted into the silicon oxide formed metal atom clusters which grew in size as the metal atom concentration was increased. Infra red spectroscopy indicated that some implanted metal atoms combined with some oxygen atoms from the dielectric to form a few metal oxide molecules. This oxidation process has been found with Cr/SiO evaporated cermet thin films (Allam et al, 1969). These few metal oxide molecules can either be conducting, like TiO, or insulating, like Al₂O₃ and TiO₂. There is no evidence to indicate what phase or phases are formed.

With recoil atom implantation the continued argon ion bombardment results in the eventual formation of argon bubbles. At the level of incident argon ion concentration used in investigating the conduction measurements if bubbles had formed they were too small to be observed under the electron microscope, ie < 30 Å. The high degree of reproducibility, even with the annealing of the films, suggests that the inert gas does not create instabilities in the conduction properties.
6.1 Introduction

The detailed investigation of the conduction properties, structure and composition of thin metal and dielectric films doped by oxygen direct ion implantation and metal recoil atom implantation respectively, has shown that implantation and bombardment methods can be used successfully to control and reproduce accurately a wide range of resistivity material.

In this Chapter following the summary of results a conduction model is suggested to explain the electrical properties in relation to the films' structure. After comparing our results with this model other conduction theories are briefly discussed.

6.2 Summary of Results

6.2.1 Oxygen ion implantation of metal thin films produces changes in the resistance of the film ranging from that of a metal to that of an insulator after a saturation ion dose of approximately $10^{17}$ ions cm$^{-2}$. At high resistances the films had values of $\rho \sim 10^{10} - 10^{12}$ $\Omega$-cm, a factor of $10^1 - 10^3$ down on dielectric films prepared by evaporation, sputtering or anodization. Dielectric constants at low frequency of $\sim 7.5$ for the aluminium-oxide films and $\sim 17$ for the titanium oxide films were measured.

6.2.2 Metal recoil atom implantation has been shown to be a very efficient method in the doping of thin films with thickness less than $\sim 500 \AA$. As in 6.2.1 above by varying the ion dose a wide range of resistivity material, from the dielectric to metallic conductivity, can be obtained.

6.2.3 With both 6.2.1 and 6.2.2 above control over the level of doping can be accurately exercised. This is especially the case of recoil atom implantation in the high resistivity region.
6.2.4 With oxygen implantation the oxide forms and grows in clusters, the clusters increasing in size as the oxygen dose is increased. At high doses, where \( \rho \approx 10^{10} - 10^{12} \Omega \text{ cm} \), the film consists of oxide clusters approximately 200 - 250 \( \AA \) in diameter separated by metallic regions.

6.2.5 Evidence at saturation suggests that the oxides formed are suboxides as no aluminium-oxide or titanium-oxide phase could be identified completely from diffraction patterns.

6.2.6 With recoil implantation the metal atoms form clusters as in the case of the oxygen implantations. The separation between particles decreases as the metal atom concentration is increased. There is evidence that a small percentage of the metal atoms combine with oxygen atoms from the silicon oxide to form a metal oxide system.

6.2.7 The electrical properties of the implanted films are very reproducible. A small degree of "forming" is necessary with the oxygen implanted films to obtain reproducibility in the initial V-I characteristics. The inert gas atoms associated with recoil implantation do not effect film properties.

6.2.8 Conduction is a bulk-limited process and the charge carriers are electronic not ionic.

6.2.9 At high resistances strong \( \ln I \propto F^{1/2} \) dependances were found.

6.2.10 At high resistances the log current-temperature plots do not produce unique activation energies in the \( 77 \text{ K} - 500 \text{ K} \) temperature range. Instead there are curvatures in the plots, giving activation energies that cover nearly an order of magnitude between values at low temperatures and high temperatures.

6.2.11 Also at high resistances \( SE \), the activation energy around room temperature, was found to be proportional to the square root of the field \[ SE \propto F^{1/2} \]. Extrapolation of these curves to \( F = 0 \) yielded zero field activation energies of 0.3 eV for the metal oxide systems produced by oxygen implantation and 0.18 eV for the metal/SiO systems at high resistivity.
6.2.12 There is a change in TCR, from a positive to a negative value, for increasing oxygen ion dose and from a negative to positive value for increasing metal atom dose, which occurs at volume % metal concentrations of 30 – 60%. This composition range corresponds also to the sudden change in resistivity covering may orders of magnitude which is observed in both systems.

6.2.13 Resistivity versus composition plots show that the curves are independent of the metal atom involved, but rather they depend on the insulator concentration.

6.2.14 Alternating current measurements show an ac conductance, G, dependance on frequency of $G \propto f^{0.8}$ below $f \sim 2 \times 10^4$ Hz, for both types of implanted film. This together with the curvature of the current-temperature curves suggests that at high resistances a hopping type conduction between centres might be taking place at low fields.

6.2.15 Annealing and the background residual pressure in the target chamber of the accelerator have a negligible effect on the final conduction properties.

6.3 Conduction Model

6.3.1 Introduction

From the summary of results it can be seen that the conduction problem concerns the conduction between metallic regions through a dielectric matrix. At high resistivities the metallic regions are small and the gaps between them large. When the resistivity decreases this corresponds to an increase in the size of the metallic areas and a corresponding decrease in the gaps between them. This is analogous to the problem of conduction in discontinuous thin metal films where electrons can by the process of quantum-mechanical tunnelling, be transferred between the metal particles through the substrate.
The low fields and moderate temperatures used during the investigations into the conductivity of the implanted films suggest that if the process is not one of quantum-mechanical tunnelling then thermionic emission of charge from a particle into the conduction band of the substrate could be the dominant mechanism. Which process dominates depends on such factors as the measured activation energy for conduction, the average barrier height and the particle spacing. Account of the image effects must always be taken with regard to potential barrier measurements. Two particles forming a gap are very close together so this correction may be large, and will become larger as the gap decreases. If the particle spacing is large ie greater than say, 100 Å, then thermionic emission is likely to be the principle mechanism.

To obtain a conduction model that embraces all particle separation values both thermionic and quantum-mechanical tunnelling processes are considered. The conduction at high electric fields is also considered.

6.3.2 Formulation of model

We consider an array of small metal particles, which we regard as spherical in geometry, embedded in a dielectric matrix. It is assumed that the dielectric resembles a broad band gap semiconductor with conduction and valence bands and somewhere between them a Fermi level as shown in figure 2.4(d). In an amorphous material it is generally accepted that the normally forbidden band contains charge traps and sites distributed near the band edges so that these edges are blurred (section 2.3.1). The particles will normally be neutral unless there are significant charge exchanges between the substrate and the film. The particles however will become charged by removal of a current carrier. The carriers are regarded as being electrons, the ionised particle remaining stationary.
Figure 6.1(a) shows an energy diagram for the contact between a metal and a dielectric. The work function of the metal forming the particles is $\gamma$, the electron affinity of the substrate $\psi$, $\phi_0$ the undistorted barrier height in electron volts and $\bar{\phi}$ the average barrier height. We assume that there are no surface states in the dielectric and that the Fermi level in the dielectric can be defined as that energy with respect to the vacuum level, at which the probability of there being an electron is exactly one half. With bulk metal electrodes normal charge transfer processes align the metal and dielectric Fermi levels. For contact between a small particle and the dielectric however the transfer of each single charge out of the dielectric will raise the Fermi level in the particle by increments of $\delta E_0$ (see equation 6.1) with respect to the Fermi level in the dielectric, (figure 6.1(b)). In equilibrium a small potential step $\delta E$ is left between the Fermi levels.

For an applied field of $F \text{ V m}^{-1}$ the relative Fermi levels in the particles will be displaced by $eV'$ where

$$V' = F(s + d)$$

where $s$, $d$ are the separation and diameter of each particle. As $s$, $d$ are small then $eV' \ll kT$. In order to remove an electron from a particle to infinity we require to do an amount of work (Darmois 1956)

$$\delta E_c = \frac{e^2}{4\pi \varepsilon_0 \varepsilon_r}$$

... (6.1)
FIG. 6.1(a) ENERGY DIAGRAM OF METAL-DIELECTRIC-METAL SYSTEM

FIG. 6.1(b) ENERGY DIAGRAM OF METAL PARTICLE-DIELECTRIC SYSTEM

FIG. 6.2 ILLUSTRATING THE POOLE-FRENKEL EFFECT
If the electron is then brought from infinity and placed on an adjacent particle to the first the work returned to the system is

\[ \frac{e^2}{4\pi \varepsilon_0 \varepsilon_0 (2r+s)} \]

Hence the net work, which we now call the activation energy for conduction, \( SE_0 \), is then

\[ SE_0 = -\frac{e^2}{4\pi \varepsilon_0 \varepsilon_0} \left\{ \left( -\frac{1}{2r+s} + \frac{1}{r} \right) \right\} \]

\[ = \frac{e^2}{4\pi \varepsilon_0 \varepsilon_0} \left( \left( \frac{r+s}{r (2r+s)} \right) \right) \]

\[ = \frac{e^2}{4\pi \varepsilon_0 \varepsilon_0} \frac{r+s}{2r+s} \]

\[ = SE_c \left( \frac{r+s}{2r+s} \right) \]

... (6.2)
6.3.3 Particles separated by small gaps - quantum mechanical tunnelling

If the barrier between two conducting regions is thin enough then electrons can flow through the barrier by quantum mechanical tunnelling. The current density due to this process can be written generally as \( J_q \), where

\[
J_q = \int_{E_m}^{E_n} p(E_x) \xi dE_x 
\]

... (6.3)

and \( p(E_x) \) is the probability that an electron with energy \( E_x \) can penetrate the barrier,

\( \xi \) is termed the supply function, and

\( E_m \) the maximum energy of the electrons in the conducting regions.

The transition probability \( p(E_x) \) is given by (Mott 1954, Bohm 1951).

\[
p(E_x) = \exp \left\{ - \frac{4\pi}{\hbar} \int_{S_1}^{S_2} \frac{1}{2m} \left( \phi(x) - E_x \right) \frac{1}{2} dx \right\} 
\]

... (6.4)

where \( \phi(x) \) is the height of the potential barrier at \( x \),

\( m \) is the mass of the tunnelling electrons,

\( \hbar \) is the Planck constant,

\( S_1, S_2 \) are defined in figure 6.1(a) and

\( E_x \) is the electron energy in the \( x \) direction.

Considering figure (6.1a) when the right hand electrode has a positive bias applied to it and taking the zero of energy as a deep level well below the metal Fermi level the barrier height can be written as \( \phi(x) = \phi + E_F + sE \). Therefore equation (6.4) becomes
\[ P(E_x) = \exp \left\{ -\frac{4\pi}{h} (2m)^{1/2} \int_{S_1}^{S_2} \left( \varepsilon_F + \tilde{\phi} + \delta E - E_x \right)^{1/2} d\chi \right\} \quad \ldots (6.5) \]

This can be integrated to (Simmons 1963a)

\[ P(E_x) = \exp \left\{ -\frac{4\pi}{h} (2m)^{1/2} \Delta S \left( \varepsilon_F + \tilde{\phi} + \delta E - E_x \right)^{1/2} \right\} \quad \ldots (6.6) \]

\[ = \exp \left\{ -A \left( \varepsilon_F + \tilde{\phi} + \delta E - E_x \right)^{1/2} \right\} \quad \ldots (6.7) \]

where \[ A = \frac{4\pi}{h} \Delta S (2m)^{1/2} \quad \tilde{\phi} = \frac{1}{\Delta S} \int_{S_1}^{S_2} \varphi(\chi) d\chi \]

Equation (6.7) can be rewritten as

\[ P(E_x) = \exp \left\{ -A \tilde{\phi}^{1/2} \left( 1 + \frac{\varepsilon_F + \delta E - E_x}{\tilde{\phi}} \right)^{1/2} \right\} \quad \ldots (6.8) \]

and as only electron in levels \( E_x \) close to \( E_F + \delta E \) contribute effectively to the tunnel current then \( E_F + \delta E - E_x \) is small. Thus using the expansion

\[ \left( 1 + y \right)^{1/2} = 1 + \frac{y}{2}, \]

for small \( y \),
then equation (6.8) now becomes

\[ P(E_x) = \exp\left(-A\bar{\phi}^{1/2}\right)\exp\left[-B\left(E_x + \delta E - E_x\right)\right] \]  

(6.9)

where \( B = \frac{A}{2\bar{\phi}^{1/2}} \)

For an array of spherical particles embedded in a dielectric

Hill (1969b) and Kieman and Stops (1969) use slightly different functions for \( \bar{\phi} \). However by substituting either value into equation (6.3) along with equation (6.9) for \( P(E_x) \) results in an equation for \( J_q \) of the form

\[ J_q = \frac{4\pi m^*e}{h^3} \sinh \frac{eV'}{kT} \frac{\pi BkT}{\sin \frac{\pi BkT}{T}} \exp\left(-A\bar{\phi}^{1/2}\right) \]  

(6.10)

for the conditions \( eV' \ll kT \) and \( \delta E > kT \). (see Appendix)

The function \( \exp\left(-\delta E/kT\right) \) represents the activation energy term, but the temperature dependence is modified by that of quantum mechanical tunnelling, \( \frac{\pi BkT}{\sin \frac{\pi BkT}{T}} \).

For the condition \( \delta E < kT \) it is very difficult to obtain a sensible current equation due to the fact that the current flow is not governed solely by the impedance between the gaps. The intrinsic metallic resistance within the large particles must be taken into consideration.

For applied fields of less than about \( 10^4 \) Vcm\(^{-1}\) the potential drop between the particles will be much less than \( kT \) and the function \( \sinh (eV/kT) \) in equation (6.10) can be replaced by \( (eV/kT) \). At high temperatures curvature in the activation energy plot allows the calculation of the parameter \( B \). Substitution of this value into equation (6.10) allows calculation of \( m^* \) and \( \bar{\phi} \) (as \( B \neq m^*/\bar{\phi} \)) unambiguously.
In order to calculate the effect on activation energy of high fields we can write tentatively that the potential energy of an electron in the field of a charged particle can be given by the expression \(- \frac{e^2}{4\pi \varepsilon_0 \varepsilon_0} \), where \(x\) is the distance from the centre (see figure 6.2).

If an electric field is now applied across the film the coulomb potential in the field direction is reduced by a factor \(- eF\). The resultant potential barrier for thermal excitation of a trapped electron into the conduction band is shown by the dashed curve in figure 6.2. The initial unperturbed coulomb potential is shown by the solid line. So we can write

\[
V(x) = -\frac{e^2}{4\pi \varepsilon_0 \varepsilon_0} - eFx
\]

Differentiation gives the maximum in the barrier potential as \(\left\{ \frac{e^3}{\pi \varepsilon_0 \varepsilon_0} \right\}^{\frac{1}{2}}\) so that the activation energy for large fields becomes

\[
\Delta E = \Delta E_0 - \left[ \frac{e^3}{\pi \varepsilon_0 \varepsilon_0} \right]^{\frac{1}{2}}
\]

\[
= \Delta E_0 - \beta F^{\frac{1}{2}}
\]

\[ ... (6.11) \]

with

\[
\beta = \left( \frac{e^3}{\pi \varepsilon_0 \varepsilon_0} \right)^{\frac{1}{2}} = \beta_{PF}
\]

where \(\beta_{PF}\) is the Poole-Frenkel barrier lowering coefficient (see section 2.2.3 and equation 2.13).
This field-lowering in a Poole-Frenkel type field assisted-thermionic emission process (Frenkel 1938), can only be considered to take place for small particles. As the particles increase in diameter we would expect the barrier-lowering coefficient to approach that due to Schottky emission, $\beta_s$, where $\beta_s = 0.5\beta_{PF}$. This factor of two is due to the geometry of the processes. In the case of a Schottky process, (figure 6.3), the image charge is mobile whereas with the Poole-Frenkel effect it is fixed. However, a spherical particle is not the plane surface considered in the Schottky process and the $\beta$ value for this system may lie between the Poole-Frenkel and the Schottky values.

6.3.4 Particles separated by large gaps - thermionic emission

For metal particles separated by large enough gaps such that tunnelling cannot occur, then at low fields either thermionic emission or bulk conduction in the substrate will probably occur. Thermionic emission is the more likely process when the particle separation is less than the "mean free path" length of an electron in the conduction band of the insulator.

In the thermionic emission model only those electrons can be transferred to a neighbouring particle which have an energy of at least the maximum barrier height. The equation for thermionic emission at low potentials can be written as (van Steensel 1967)

$$J_T = 2A_0' T^2 \sinh \frac{eV_0}{kT} \exp \left( -\frac{\phi}{kT} \right) \ldots (6.12)$$

if the barrier height is large compared to $kT$. $A_0'$ is the Richardson-Dushman constant, where
FIG. 6.3 RESTORING FORCE ON ESCAPING ELECTRON (a) THE SCHOTTKY EFFECT. (b) THE POOLE-FRENKEL EFFECT.
\[ A_0^1 = \frac{4\pi \varepsilon_0 mk^2}{\hbar^3} = 120 \text{ am} \text{pm} \text{cm}^{-2} \text{deg}^{-1} \]

For the system of particles under consideration, where \( eV' \ll kT \) equation (6.12) reduces to

\[ J_t = A_0^1 T^2 \frac{eV'}{kT} \exp\left(-\frac{\phi}{kT}\right) \quad \ldots (6.13) \]

At high fields the equation becomes modified by the \( \exp\left(\frac{\beta \gamma^{1/2}}{kT}\right) \) term just as in the case of tunnelling at high fields described in the previous section.

As an amorphous insulator is expected to contain a number of traps we also consider that at low voltages the total current can be made up of a space charge limited component, \( J_s \), as well as the thermionic emission component, \( J_t \). The work of Lampert et al (1964) for the case of injection from a point contact, which we will consider here to be applicable to the case of point metallic islands in a dielectric matrix, gives a value of \( J_s \propto V^{3/2} \).

Thus from equation (6.13) we can write, for low field strengths

\[ J_t \propto V \]

and for space-charge limited conduction,

\[ J_s \propto V^{3/2} \]
The total current can therefore be written as

$$J = A_1 V + A_2 V^{3/2}$$ ...

(6.14)

where $A_1$ and $A_2$ are temperature dependent coefficients.

6.3.5 The image potential

The potential barrier is altered by the effect of image forces. The decrease in the potential barrier becomes greater as the distance between the particles becomes less.

Simmons (1963a) using image force methods has shown that to a good approximation the lowering can be given by

$$\phi_I = -\frac{5.75 s}{Kx(s-x)} \text{ electron volts}$$ ...

(6.15)

where the dimensions are in angstroms, $K$ is the high frequency dielectric constant, and where $x$ is the distance from one electrode of the electron. For $x = s/2$, then

$$\phi_I = -\frac{2.3}{Ks}$$ ...

(6.16)

6.4 Comparison with Results

6.4.1 Oxygen implanted metal films

The zero-field activation energies of the aluminium-oxide films formed by ion implantation was about 0.3 eV and about 0.25 eV for the titanium-oxide films. Calculations of a theoretical activation energy from equation (6.1) assuming metal spheres of radius 50 Å (diffraction patterns give metal crystallites of the order of 100 Å in diameter, see section 5.3.2.1)
Average barrier widths from microscope studies are in the 200 - 300 Å region, and therefore it is to be expected that the dominant conduction mechanism at low fields will be one of thermionic emission.

Analysis of the voltage-current-temperature curves of figures 5.10 and 5.11 in terms of equation (6.13), where

\[ J_T = A_0 T^2 \frac{eV^2}{kT} \exp\left(\frac{-\phi}{kT}\right) \]

yields values for \( \phi_0 = 0.92 \text{ eV} \) for the aluminium-oxide films and \( \phi_0 = 0.80 \text{ eV} \) for the titanium-oxide films.

The value of 0.92 eV is approximately a factor of 2 less than that generally accepted for \( \text{Al}_2\text{O}_3 \), Pollack and Morris (1964, 1965).

Measurements on the slopes of the log I - log V curves at low applied fields do not give a completely ohmic relation. From the curves in figure 5.10 the low field relationship for the aluminium-oxide system is of the form \( I \propto V^n \), where \( n = 1.10 \pm 0.05 \). From figure 5.11 the value of \( n \) is found to alter from \( n = 1.15 \pm 0.05 \) at \( T = 280^\circ\text{K} \) to \( n = 1.00 \pm 0.04 \) at \( T > 360^\circ\text{K} \). A value of \( n \) greater than unity suggests a contribution from space charge limited conduction, as given by equation (6.14). The temperature dependence of \( n \) suggests that in equation (6.14) the second term is negligible at high temperatures and conduction in emission limited. As the temperature is decreased the second term begins to contribute to conduction. The temperature range of investigations was not wide enough to see whether or not the second term begins to dominate the conduction. Then we would expect \( n \) to be about 1.5.
With the titanium-oxide system the slopes at low field gave values of \( n \approx 0.97 \pm 0.04 \), indicating a complete lack of space-charge conduction at room temperature.

At high fields, in excess of about \( 10^5 \text{ Vcm}^{-1} \), the experimental results show a strong \( \log I - \frac{1}{V} \) dependence. This indicates that field-assisted lowering of the barrier to conduction is taking place, as predicted by equation (6.11). From the measurement of the slopes of the linear part of the curves in figure 5.12 the parameter \( \beta \) was found to be equal to \( 5.3 (\pm 1.1) \times 10^{-5} \text{ eV V}^{-\frac{1}{2}} \text{ m}^2 \) for the aluminium-oxide system and \( 2.8 (\pm 0.6) \times 10^{-5} \text{ eV V}^{-\frac{1}{2}} \text{ m}^2 \) for the titanium-oxide system. Film thicknesses, \( t \), used in these calculations were \( t = 300 \pm 250 \text{ Å} \) for the aluminium-oxide films and \( t = 600 \pm 200 \text{ Å} \) for the titanium-oxide films (see section 5.2.2.)

Calculations of \( \beta \) from the \( \xi E \) vs. \( V^\frac{1}{2} \) curve of figure 5.16 for the aluminium-oxide system gave \( \beta \approx 5.5 (\pm 1.2) \times 10^{-5} \text{ eV V}^{-\frac{1}{2}} \text{ m}^2 \) in good agreement with the above estimation from the I-V characteristics.

Using values of high frequency dielectric constant, \( K \), of 2.6 for aluminium-oxide then theoretically \( \beta_{PF} = 2 \beta_s = 4.8 \times 10^{-5} \text{ eV V}^{-\frac{1}{2}} \text{ m}^2 \). Similarly for the titanium-dioxide, \( K \approx 5.7 \), and theoretically \( \beta_{PF} = 2 \beta_s = 3.2 \times 10^{-5} \text{ eV V}^{-\frac{1}{2}} \text{ m}^2 \). Comparison of experimental values of \( \beta \) and these theoretical values shows that a Poole-Frenkel mechanism fits the results better than a Schottky barrier lowering mechanism. The large error that arises in calculating the oxide film thickness does not allow a more detailed interpretation of the experimentally observed \( \beta \) coefficient.

It should be mentioned that analysis of the films in terms of equation (6.20) gave extremely small values for the barrier heights \( (\approx 10^{-2} \text{ eV}) \), indicating that conduction was not by tunnelling.
6.4.2 Metal implanted films

From consideration of the values of s and d from electron microscopy for the implanted dielectric films it is not immediately obvious whether tunnelling or thermionic emission is taking place. Therefore in the resistance range from \( R_0 \sim 5 \times 10^8 \) Ω to \( R_0 \sim 10^5 \) Ω the films have been analysed in forms of both thermionic and quantum mechanical tunnelling processes. The results of this analysis are given in Table VI.

**TABLE VI**

<table>
<thead>
<tr>
<th>2r = d (Å)</th>
<th>S (Å)</th>
<th>( R_0 (Ω) )</th>
<th>Tunnelling ( \frac{\phi}{\phi_0} )</th>
<th>Thermionic ( \frac{\phi}{\phi_0} )</th>
<th>( SE )</th>
<th>( SE_0 )</th>
<th>( SE_0' )</th>
<th>( SE_0'' ) max</th>
</tr>
</thead>
<tbody>
<tr>
<td>70</td>
<td>80</td>
<td>( 5.10^8 )</td>
<td>0.50</td>
<td>0.75</td>
<td>0.88</td>
<td>1.03</td>
<td>0.140</td>
<td>0.062</td>
</tr>
<tr>
<td>80</td>
<td>50</td>
<td>( 2.5.10^8 )</td>
<td>0.61</td>
<td>0.78</td>
<td>0.85</td>
<td>1.05</td>
<td>0.130</td>
<td>0.089</td>
</tr>
<tr>
<td>90</td>
<td>40</td>
<td>( 3.10^7 )</td>
<td>0.78</td>
<td>1.00</td>
<td>0.78</td>
<td>1.02</td>
<td>0.110</td>
<td>0.091</td>
</tr>
<tr>
<td>120</td>
<td>35</td>
<td>( 10^6 )</td>
<td>0.80</td>
<td>1.07</td>
<td>0.66</td>
<td>0.88</td>
<td>0.080</td>
<td>0.028</td>
</tr>
<tr>
<td>200</td>
<td>25</td>
<td>( 3.10^5 )</td>
<td>0.67</td>
<td>1.05</td>
<td>0.67</td>
<td>1.05</td>
<td>0.020</td>
<td>0.016</td>
</tr>
</tbody>
</table>

The column headed \( \phi_0 \) is the corrected barrier height taking into consideration the image potential from equation (6.16). It is this barrier height that should be used in comparing different mechanisms. From Table VI we can see that neither mechanism gives good agreement for \( \phi_0 \) throughout the resistance range. However very good agreement is found if we assume that for \( s > 40 \) Å then thermionic emission is the dominant mechanism and for \( s < 40 \) Å tunnelling is the dominant mechanism. Values of \( \phi_0 \) then give 1.03, 1.05, 1.00 and 1.02, 1.07 and 1.05 eV, showing barrier heights in agreement to within ± 0.03 eV. The fact that both mechanisms can give sensible values of \( \phi_0 \) throughout indicates that both processes are probably occurring all the time. This is reasonable if one looks at the histogram for particle separations for the films with \( R_0 \sim 5 \times 10^8 \) Ω, figure 5.34. Although the average spacing is taken as 80 Å there are a
reasonable number of particles separated by only 20 - 50 Å. For these particles it is quite reasonable to suppose that tunnelling will occur. Similarly for $R_o \sim 10^6 \Omega$ films, where tunnelling is assumed to be the dominant mechanism there will be some particles whose separation will be too large for tunnelling and then thermionic emission will occur. It is interesting to note that for films with $d = 90 \, \AA$ and $s = 40 \, \AA$ the barriers calculated from both conduction mechanisms are almost exactly equal.

For $s < 40 \, \AA$, evaluation of $m^*$ from the tunnelling equations gives $m^* = 0.8$ for $s = 35 \, \AA$ and $m^* = 0.7$ for $s = 40 \, \AA$.

The column labelled $\delta E_o$ gives the activation energy calculated from the particle dimensions, spacings and low frequency dielectric constant of the dielectric from equation (6.2). We see that values of $\delta E_o$ mostly are a factor of two or more below that observed experimentally.

A closer examination of the electron micrographs of the metal clusters show that the majority of them tend to be ellipsoidal in shape. The electrostatic theory of Jeans (1923) shows that the coulombic potential of an ellipsoidal particle of eccentricity $l$ is given by

$$\delta E_o' = \frac{\delta E_c \sin^{-1} l}{l} \quad \text{(6.15)}$$

where $\delta E_o$ is given by equation (6.1). Using typically $l = 0.75$, then for the first case in table VI, $r = 35 \, \AA$, $s = 80 \, \AA$ and $\delta E_o = 0.08$ eV and $\delta E_o' = 0.09$ eV. When $l = 1$, then $\delta E_o' = \delta E_o^{\text{max}} = \frac{\pi}{2} \cdot \delta E_o$. In that case in our example then $\delta E_o^{\text{max}} = 0.13$ eV. Values of $\delta E_o'$ and $\delta E_o^{\text{max}}$ for the cases considered are shown in table VI. For $l = 0$, $\delta E_o' = \delta E_o^{\text{min}} = \delta E_o$. 

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Values of $\delta E_0$ are nearer than $\delta E_0$ to those observed experimentally. For the aluminium-oxide and titanium-oxide system discussed in the previous section $\delta E_{0,\text{max}} = 1.0$ eV, a factor of 2.5 - 3.0 down on the experimentally observed activation energies.

For films with $s > 40 \AA$, where we have assumed thermionic emission to be the dominant mechanism, at high fields a plot of $\ln I \propto V^{1/2}$ yields a straight line at fields in excess of $6 \times 10^4$ V cm$^{-1}$ (see figure 5.22). The value of $\beta$ calculated from the slope of the linear region is $3.5 \times 10^{-5}$ eV V$^{-1/2}$ m$^{3/2}$. Using $K = 3$ for silicon oxide (Heavens 1960), then $\beta \exp \sim 1.6$. $\beta_s \sim 0.8 \beta_{\text{PF}}$. As in the case of the oxygen implanted films a plot of $\delta E$, activation energy, versus the square root of applied voltage, yielded values in agreement with those calculated from the voltage-current characteristics. For films with $R \sim 5 \times 10^{-7}$ the value of $\beta$ has decreased to $3.1 \times 10^{-5}$ eV V$^{-1/2}$ m$^{3/2}$. When the particles become, on average, close enough together for tunnelling to dominate then at high fields the slope decreases even further to give $\beta \sim 2.2 \times 10^{-5}$ eV V$^{-1/2}$ m$^{3/2}$, that is $\beta \exp \sim \beta_{s} \sim 0.5 \beta_{\text{PF}}$.

With both thermionic emission and tunnelling we have shown that at high fields an identical Poole-Frenkel type field lowering process takes place decreasing the activation energy for conduction. The actual value of the reduction coefficient however is not expected to be equal to $\beta_{\text{PF}}$ as the particles are not traps with an immobile image charge as envisaged initially by Frenkel (1938). We have therefore suggested previously that the experimental value, $\beta \exp$, will be somewhere between that for Schottky-emission, $\beta_s$, and Poole-Frenkel emission, $\beta_{\text{PF}}$. This has found to be the case and it is interesting to note that as the particle size increases, from $r = 35 \AA$ to $r = 60 \AA$, then the value of $\beta$ tends towards that expected from Schottky-emission. As the particle size increases it is envisaged that the image force becomes more "mobile" and the true Schottky process is approached although never actually reached.
In the above calculations of the theoretical $\beta$ values for Schottky and Poole-Frenkel type emission processes we have assumed bulk values of dielectric constant for the gaps between the metal particles. Theoretically the dielectric constant of an insulator should be preserved down to a few atomic layers (Kohn 1958). The only experimental verification of this has been in structurally perfect organic films of cadmium stearate down to a monolayer thickness equal to 24.6 Å (Drexhage and Kuhn 1966). However insulator films prepared by vapour deposition and of thickness less than about 200 Å are usually porous and Chopra (1965b) has shown that the dielectric constant decreases as the thickness is decreased. Chopra (1969) however states that although ultra thin oxide film dielectric constants have not been measured bulk like values are to be expected for thicknesses equal to or greater than about 40 Å. We therefore consider the assumption of bulk dielectric constant to be reasonable.

From figure 5.21 we can see that at a film resistance of about $10^5 \Omega$ and below the $F^2$ dependence of current ceases and a 'saturation' effect takes place. Plotting these curves as a log I versus $F$ relation we find that at fields in excess of about $10^5 \text{V m}^{-1}$ a linear relation holds.

This dependence is not explained by the simple Poole-Frenkel type barrier lowering described above but is probably a consequence of the overlap of coulombic fields of centres that are close together (see reference to Hill (1971), following section).

6.5 Comparison of Results with other Theories

Most of the theories that consider tunnelling between particles are based on the electrostatic nature of the activation energy for conduction proposed by Neugebauer and Webb (1962). One would not expect a great deal of difference, therefore, in the theoretical calculations of $SE$ using the experimentally observed values of $r$ and $s$. That this is the case can be seen from Table VII which tabulates experimental and various theoretical activation energies at low applied electric fields. All theoretical values fall below that for $SE_0^1$, which is based upon ellipsoidal particles.
Neugebauer and Webb (1962) suggest that a certain number of microparticles must be charged (or ionized) before tunnelling can take place, with tunnelling occurring between the charged and uncharged microparticles. This is a possible condition but one which is unlikely to limit the ultimate steady current flow. They also neglect the change in potential of the islands involved in the charge transfers. The neutral island model considered in section 6.3 is considered to be more realistic.

Similar comments concerning the conductivity applies to the theory of Weitzenkamp and Bashara (1966). However both these above theories predict the log current $\propto F^{1/3}$ dependence that is experimentally found at high fields.

Hartman's (1963) assumption that conduction could be described by a 1-dimensional model was incorrect. He ignored transitions in the $y$ and $z$ directions and therefore the level spacing difference in energies of the quantized levels within a single metal crystallite were overestimated.

* $N,W$ - Neugebauer and Webb (1962)
$W,B$ - Weitzenkamp and Bashara (1966)
$H$ - Hartman (1963)
$H,R$ - Herman and Rhodin (1966)

### TABLE VII

<table>
<thead>
<tr>
<th>Particle dimensions</th>
<th>Activation Energies</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Experimental</td>
</tr>
<tr>
<td>$d(\AA)$</td>
<td>$S(\AA)$</td>
</tr>
<tr>
<td>70</td>
<td>80</td>
</tr>
<tr>
<td>80</td>
<td>50</td>
</tr>
<tr>
<td>90</td>
<td>40</td>
</tr>
<tr>
<td>120</td>
<td>35</td>
</tr>
</tbody>
</table>

$N,W$ - Neugebauer and Webb (1962)
$W,B$ - Weitzenkamp and Bashara (1966)
$H$ - Hartman (1963)
$H,R$ - Herman and Rhodin (1966)
Consequently the difference in level broadening between ground and excited levels was also overestimated. It was then not possible to explain why excited electron states of the different crystallites should give a band of non-localized states but yet ground states did not overlap in energy. The quantization of energy levels occurred for crystallite diameters of the order of 25 Å or less but Hartman used the model to explain the results of Neugebauer and Webb up to 150 Å diameter crystallites. Hartman's model also predicts a decrease in conduction at high field strengths because of the uncrossing of the \((n + 1)\)th levels. For particle dimensions, \(d \sim 100 \text{ Å}\), this should occur at about \(10^3 \text{ Vcm}^{-1}\). No such decrease in conductance was observed in our experiments at fields of up to \(10^6 \text{ Vcm}^{-1}\).

Van Steensel (1967) considers that the conduction is due to thermionic emission, not tunnelling. The low activation energies obtained being equated with the potential barriers, and the low potential barriers being obtained due to the decrease by image forces which is appreciable for particles spaced approximately 20 Å or less apart.

As we have already pointed out, Table VI shows that thermionic emission does give reasonable values of the barrier height throughout the resistance range investigated for metal implanted dielectric films. However a better agreement is obtained when we assume that for particle spacings of less than 40 Å tunnelling dominates. It is interesting to note that Hill (1969b) has interpreted Van Steensel's results in terms of the model described in section (6.3) and finds a value of \(\Phi = 1.10 \text{ eV}\) and \(m^* = 0.4\), in good agreement with his own results. This again shows that in some cases reasonable agreement with theory can be obtained with either thermionic emission or quantum mechanically tunnelling models. The model of
Van Steensel does not however predict the high field dependence observed experimentally.

Very recently Hill (1970b) has examined the Poole-Frenkel effect by a straightforward conduction calculation. Hill finds for emission into a semi-crystalline material along the field axis,

\[ J \propto T^4 \exp \left( -\frac{SE}{kT} \right) \alpha^2 \sinh \alpha \quad \ldots \quad (6.16) \]

and for uniform emission into a total sphere

\[ J \propto T^3 \exp \left( -\frac{SE}{kT} \right) \alpha^{-1} \left( \cosh \alpha - \sinh \alpha \right) \quad \ldots \quad (6.17) \]

where the latter applies for a truly amorphous material. The term \( \alpha \) is given by \( \beta F^2/kT \). Films can be examined in terms of equations like (6.16) and (6.17), most conveniently, by plotting \( \ln \frac{J}{J'} \) where \( J' \) is given by,

\[ \frac{J}{J'} = J T^{-n} \exp \left( \frac{SE}{kT} \right) \quad \ldots \quad (6.18) \]

against \( \ln \frac{F^2}{T} \), and then superimposing curves of the sinh functions against \( \alpha \). This has been done for both the aluminium-oxide data from figure 5.11 and the high resistance metal/SiO mixture data from figure 5.23. The results are shown in figure (6.4). The consistency between the experimental points over the limited range of temperatures investigated and the agreement with theoretical curves using \( n = 4 \) and equation (6.16) is extremely good. As Hill points out the sinh functions are bulk relationships and clearly show that the limiting process of conduction in these particular films lie within the bulk of the material.
FIG. 5.4 PLOT OF $j'$ VS. $V^{1/2}/T$ FOR (a) 10% METAL/SIO SAMPLE AND (b) IMPLANTED ALUMINIUM FILM
Hill (1971 and private communication) has also shown that when the Poole-Frenkel type centres are close enough together then at high fields \( J \approx \exp \left( \frac{eF_{\text{D}}}{2kT} \right) \). Here \( s \) is sufficiently small such that the coulomb potentials overlap significantly. For \( R_0 < 10^5 \Omega \) in figure 5.21, such a relationship holds, and calculation of the particle spacing gives \( s \approx 50 \AA \), in reasonable agreement with the electron microscopy observations which gives \( s = 30 \AA \).

Considering the impurity band approach Miller and Abrahams (1960) give for impurity conduction with the help of phonons

\[
\sigma = \text{const} \cdot \exp \left( - \frac{\xi E_i}{kT} \right)
\]

with the activation energy \( \xi E_i \), given by

\[
\xi E_i = \left( \frac{\epsilon^2}{K_0} \right) \left( \frac{4\pi N_D}{\epsilon} \right)^{1/3} \left( 1 - 1.35 K_c^{1/3} \right)
\] \( \cdots \) (6.19)

Here \( N_D \) is the donor concentration,
\( N_A \) is the acceptor concentration, and
\( K_c = N_A / N_D \)

The usually favourable range of impurity concentration where impurity conduction may occur is \( 10^{-16} - 10^{18} \text{ cm}^{-3} \).

With the implanted dielectric films, for \( R_0 > 5 \cdot 10^8 \), then \( N_D \sim 10^{20} - 10^{21} \text{ cm}^{-3} \) assuming that the metal particles acts as donors. Then using a value of \( K_c \sim 0.001 \) and using \( K_o \sim 5.2 \) for the silicon oxide films then \( E_i \sim 0.01 \text{ eV} \), a factor of nearly 15 down on the experimentally measured activation energy. In the case of oxygen implanted films, the calculated activation energy, with \( N_D \sim 10^{20} - 10^{21} \text{ cm}^{-3} \) is also much lower than that experimentally observed. With the dielectric material produced by oxygen implantation and the silicon oxide after argon ion bombardment it may be that \( K_c \) is much larger. Incomplete oxidation or a
substantial concentration of defects however can be the source of acceptor like centres in thin films, thus making \( K_0 \) large. Miller and Abrahams quote equations for activation energy with \( 0.02 < K_0 < 1.0 \), and calculations based on our observations give \( \Delta E_1 \sim 0.01 - 0.02 \) eV, again much lower than those observed experimentally.
The conduction taking place in oxygen implanted metal films at high resistivities and metal-dielectric mixtures produced by metal recoil atom implantations has been shown to be in good agreement with models based upon thermionic emission and quantum-mechanical tunnelling.

For aluminium-oxide and titanium-oxide films it is envisaged that conduction takes place between metallic regions in a predominantly dielectric matrix. The electrical conductivity at low fields is then determined by the surrounding amorphous and polycrystalline oxide and suboxide complex. This insulating media has measured low frequency and estimated high frequency values of dielectric constants that are near to those of stoichiometric $\text{Al}_2\text{O}_3$ and $\text{TiO}_2$. At low fields conduction takes place by a thermionic emission process over potential barriers of 0.9 eV for the aluminium-oxide system and 0.8 eV for the titanium-oxide system. There is evidence that a small contribution to the total current at low fields can be attributed to space charge limited conduction.

Above about $5 \cdot 10^5$ Vm$^{-1}$ charge transport via the electric-field-assisted thermal ionization of the metal particles (Poole-Frenkel type effect) dominated the conduction process. This effect was unambiguously identified by the dependence of activation energy and current density on the square root of the applied field.

The above low field and high field mechanism has also been used to explain the conduction in the Al/SiO and Ti/SiO cermets for the regions where the particle separation is more than about 40 Å. Calculations of barrier heights in this region give a value of 1.03 ± 0.02 eV. At smaller particle spacings quantum-mechanical tunnelling dominates and values of barrier heights from this mechanism give 1.04 ± 0.03 eV.
The effective electron mass for tunnelling, \( m^* \), was found to be about 0.75. At high fields the Poole-Frenkel type lowering of the activation energy for conduction takes place with a field lowering coefficient, \( \beta \), that decreases with decreasing film resistance, i.e. smaller particle separations. At a separation \( s \approx 30 \text{Å} \) the value of \( \beta \) is near to that of Schottky emission. As the particles become even closer together the lowering of the activation energy changes from a dependence that is proportional to \( F^{\frac{1}{2}} \) to one that is proportional to \( F \).

Good agreement is found between the observed activation energies and theoretical values based upon ellipsoidal particles, calculated by assuming that the activation energy is due to coulombic field surrounding the charged particle.

7.2 Possible Technological Applications

With both thermal evaporation and sputtering techniques to produce elemental or multi-component thin films the electrical and chemical properties of the films are very strongly dependent on many environmental factors. For example with the production of mixed metal-dielectric (e.g. Cr/SiO) thin film cerments, good reproducibility and stability depend upon constant pressure and composition of the residual gases, fast and reproducible deposition process, constant temperature of the boat and more often than not the proper thermal treatment of the films. With sputtering, usually the sputtering atmosphere, the substrate bias and temperature, the target composition and sputtering rate and the inert gas content are prime factors in determining the type of film that is eventually produced. With so many variable parameters it is not surprising to see why films with widely differing properties are produced although production is carried out under similar conditions. Comparison of the results of Rozgonyi and Polito (1969) and of Raimondi and Kay (1970) on the electrical properties of ZnO films illustrate this point. Rozgonyi and Polito report
for ZnO films grown by dc reactive sputtering from oxide targets, resistivities ranging from 0.1 to $10^6 \Omega \text{ cm}$. Also by dc reactive sputtering Raimondi and Kay were able to reach film resistivities in the $10^{13} \Omega \text{ cm}$ range. Similar variations occur in evaporated cermet films.

Ion implantation and metal recoil atom implantation doping of thin films has shown that highly reproducible electrical properties can be obtained with a bare minimum of environmental control. For this reason alone the use of implantation to fabricate passive devices in thin film form could be of great benefit. Implantation could be used either throughout the complete operation by itself or used in conjunction with more conventional techniques. As an example of the latter case initially a metal/metal oxide mixture could be produced, with electrical properties in the required region, by say thermal evaporation with not too strict environmental controls; then the film could subsequently be subjected to an ion beam treatment to "trim" the resistivity and/or temperature coefficient of resistance so as to obtain the precise value needed. The variation in resistance of cermet films prepared by evaporation processes has in fact necessitated some "trimming" method so as to produce precision resistors for silicon integrated circuits. One technique that has been favoured is that of laser adjustment because of the ability to either increase or decrease the resistor (Berg and Locd, 1968). However there is a change of structure (recrystallization) of the film material which might be a disadvantage in some applications.

If in fact the ion beam accelerator was substituted by a high-energy discharge, say in a 0 - 50 keV, chamber, then by proper design any initial evaporation and final ion bombardment "trimming" could take place within the same vacuum. This would be a great advantage. Processes that require gas ion bombardment would then be the easiest to perform as a metal ion discharge would be more difficult to produce and would probably
lead to difficult cleaning problems. Thus the recoil atom implantation techniques would prove beneficial.

The oxidation experiments have shown that a semi-insulating layer can be produced beneath the metal surface. That is to say, a "buried layer" was produced. This layer could not be made completely insulating due to the energy-range profiles that were used in this work. However with a high enough energy, say 1 MeV or more, it is envisaged that oxide or nitride insulating layers could be produced at reasonable depths beneath the surface. By choice of ion energy or by programming a series of ion energies the actual depth and profile of the layers could be reasonably controlled. Such a buried layer could prove to be of use for many applications.

The fact that recoil atom implantation eventually produces a conducting path through a dielectric layer is useful for the production of contacts through protective dielectric layers. Such a technique has important applications in the field of thin film transistors (Anderson, 1968 private communication).

Another big advantage of ion implantation is that a very wide range of ion-target combinations are available for investigation. Metals that are difficult to oxidise by more conventional methods could be oxidised by ion implantation; alloys that are difficult to produce could be produced by implanting one or more elements into a single elemental target in thin film form; metal/metal oxide cermet systems that are difficult to produce could be easily achieved. The technique therefore offers a much wider choice of materials for study. The technique of recoil atom implantation even allows the use of materials for doping that are not very easily ionizable.
Ion implantation, apart from producing desired electrical properties, can also enhance the adhesion of thin films to their substrates. Ni, Au and Al films on Al₂O₃, Corning 7059 and SiO₂ substrates have had their adhesion increased by at least an order of magnitude using recoil atom implantation techniques, (Collins et al, 1969, Stroud, private communication). Work is in fact in progress at the Edwards High Vacuum Central Research Laboratories with a view to improving the adhesion of optical coatings. Collins (1970 private communication) has shown that very narrow highly adhesive aluminium lines produced by recoil atom implantation can be made to remain on a substrate after the rest of the film had been removed by mechanical stripping or by an acidic solution. This has possibilities in the field of interconnections in microcircuitry.

The use of ion beams as a method of modifying or producing thin film circuits will be significantly enhanced if the ion beam could be controlled and made to "write" circuits. By careful programming of the beam, regions of different electrical properties could then be produced and even isolated from one another. Lamouroux et al (1970) have recently described such a micro-machining method using a laser beam for application to microcircuits. The use of a focused ion beam would eliminate the need for masks as all processes would be done in one operation and the possibility of contamination would be reduced.

Consider the implantation to give an impurity concentration of \(10^{18}\) atoms cm\(^{-3}\) and a penetration depth of 1 \(\mu\)m. The density is \(10^{14}\) cm\(^{-2}\) assuming 100% trapping in electrically active sites. This is \(1.6 \times 10^{-5}\) coulomb cm\(^{-2}\) and if an implantation time of 10 sec is required this needs a current of \(1.6 \mu\)a cm\(^{-2}\) for a stationary beam. If the beam is not stationary but is say 1 \(\mu\)m square and a total device area of 0.01 cm\(^2\) has to be covered then \(10^6\) operations are needed to cover the area and if the time is still restricted to 10 sec then this requires a current density of \(1.6\) amp cm\(^{-2}\). The current would be 16 nA (\(1.6 \times 10^{-8}\) A).
The effect of aberration and space charge is to limit the size of the circle of least confusion. Space charge tends to neutralize the effect of spherical aberration (Kanaya 1965). From the space charge equation, if the beam had an initial diameter of 1 cm, and for \( E = 90 \text{ keV} \) and \( M = 100 \), then space charge can be shown to be not important (Collins, 1968 private communication). Spherical aberration is then the main limitation. With low aberration lenses a circle of least confusion of 1 \( \mu \text{m} \) can be obtained with an angle of \( 0.4^\circ \) (\( \sim 0.007 \) radians). The beam from an ion source, say RF source usually has a half-angle of about 0.1 radian.

If the current density distribution is uniform the current will be in the ratio \( \left( \frac{\lambda_1}{\lambda_2} \right)^2 \), where

\[
\left( \frac{\alpha_1}{\alpha_2} \right)^2 = \left( \frac{0.007}{0.1} \right)^2 = 4.9 \times 10^{-3}
\]

Thus in order to produce the required current a total current of only \( (1.6 \times 10^{-8})/4.9 \times 10^{-3} \approx 3 \mu\text{A} \) is sufficient. The calculation does show that theoretically ion beam writing is feasible, although sophisticated ion beam optical systems have to be developed.

7.3 Future Work

In the previous section we discussed the possible technological applications of ion implantation that were immediately evident from the work performed in this thesis. In this section we now discuss some other areas where ion implantation into thin films may possibly prove to be fruitful. We consider some uses in the field of glassy and amorphous insulating and semiconducting films and metal films.

Although glasses such as pyrex 7740, Corning 7059 and soda-lime silicate can be sputtered to give amorphous films, oxide glasses containing, for example lead, are extremely difficult to produce by sputtering because of the ease of reduction of the lead ions to lead atoms. (MacKenzie, 1970)
This makes the control of optical and electronic properties of such complex films a formidable task. With ion implantation techniques the basic relatively simple glass structure could be sputtered in thin film form and the lead, or in fact any other material, could then be implanted to depths and concentrations of one's own choice. The implantation could then be ceased at the precise point the required electrical and/or optical properties of the glass were reached.

Other interesting experiments could be performed on the conductive oxide films such as Sn $O_2$, Zn $O$, BaPbO$_3$, NiO and the vanadium and titanium oxides. With these films the amorphous and crystalline conductivity usually differ. The doping of NiO with Li$_2$O to give highly conductive ceramics is well-known (Morin, 1954). Frey and Mackenzie (1970, to be published) and Frey (1969) have recently produced both amorphous and crystalline NiO films by RF sputtering, the stoichiometry of which is very dependent on substrate temperature. As far as conductivity was concerned the stoichiometry was much more important than the crystallinity for the films. Ion implantation of Ni$^+$ and O$^+$ ions would be an excellent method for changing the stoichiometry very accurately and in very small stages. This coupled with detailed electrical measurements would lead to a better understanding of the material involved.

In the investigation of oxide materials any conduction instabilities that occur at high field strength should be noted. Many films such as SiO$_2$, SiO, Al$_2$O$_3$, Ta$_2$O$_5$, TiO$_2$, NiO, Nb$_2$O$_5$, VO$_2$, ZrO, Fe$_3$O$_4$, exhibit such instabilities after which their conductivity undergoes considerable change giving rise to what are termed "switching" phenomena (Chopra, 1970). However, the switching ratio and speed vary enormously from case to case and only switches based on the chalcogenide glasses have reached the degree of overall effectiveness required for practical devices (Henisch et al, 1970). They permit the construction of bistable and monostable switches which can be used for a variety of computer and control applications.
The glasses used are usually 2-5 component mixtures of Ge, Si, Se, S, As, Te, In etc, and deposition accomplished by flash evaporation or sputtering. Compositions and procedures used tend to be empirically optimized and the significance of the various proportional parameters and their relation to the electronic processes taking place is not yet well understood. Here is a field in which ion implantation techniques could be of a great deal of use, as has been pointed out by Mott (1970). An accurate change in composition of the films could be easily accomplished by implantation, or alternatively the components could be built up one by one in slowly varying stages by implantation into an initially one element thin film. All the while this build up is taking place detailed diagnostic measurements should be taking place. The high level of bombardment and therefore induced disorder that would occur need not be a complication as work in this thesis indicates that with polycrystalline and amorphous films no adverse effect is observed. Indeed after bombardment all films showed a complete insensitivity to annealing. This would be an advantage in device production.

It is interesting to note that the author has in fact observed switching phenomena in a few samples of evaporated silicon oxide films doped with about $10^{21}$ cm$^{-3}$ nitrogen atoms by ion implantation (unpublished work). The characteristics follow closely those found by Tronc (1970) for boron-doped silicon oxide films. At a certain voltage the film switches from a low conductive state ($\rho \sim 10^{12} - 10^{13} \Omega$ cm) to a highly conductive state ($\rho \sim 10^{-1} - 10^{2} \Omega$ cm). It remains in this state until a reverse voltage of about $-10$V is applied. Then a lower conductivity state is obtained, with $\rho \sim 10^{8} - 10^{10} \Omega$ cm. Successive voltage cycling then switches the film between this latter state and the highly conducting state. The switching speed was not measured however and the number of voltage cycling operations before complete breakdown occurred.
was not very great. However, this does suggest that ion implantation may have a role to play in the field of thin film switching devices.

Another important feature of the $N_2^+$ implanted SiO was that the dielectric breakdown strength had been slightly increased. This has also been found by Fritz Sche et al (1970) for SiO$_2$ films implanted with $P^+$ and $N_2^+$ ions and is obviously of practical importance.

Another field where implantation may prove fruitful is in that of thin film superconductors. It has been known for some time that evaporation of a metal film in an oxygen atmosphere, resulting in a film with a granular structure, enhanced the transition temperature, $T_c$, in the superconducting region (Abeles et al, 1966). The more elegant technique of cosputtering metal and dielectric has yielded the highest known enhancement of $T_c$ for a given metallic crystal structure; the $T_c$ of BCC Mo is increased from 0.9 to 6.4°K (Hanak et al, 1969). These granular materials are bona fide superconductors because Josephson tunnelling permits lossless currents to flow from grain to grain. Such a concept does break down if sufficient dielectric material separates the metallic grains. Cohen (1970) shows that in a granular system $Al_{1-x} (SiO_2)_x$ for $x > 0.4$, then $T_c \to 0$. Abeles (1969) has proposed that this disappearance of superconductivity is caused by the decrease of the coupling energy for Josephson tunnelling with increasing tunnelling barrier material. The individual grains may still be superconducting above $x = 0.4$, although macroscopic supercurrents do not flow from grain to grain.

We have shown that implantation can precisely control such factor as particle spacing in metal/dielectric granular structures, thus the method lends itself to an investigation of the superconducting properties of such systems. A wide range of material combinations could be investigated.
Also in the field of superconducting thin films Spitzer (1970) has recently reported the highest known $T_c$ value to date for solid solution alloys with a Ti-V alloy in thin film form. A $T_c$ value of about 11°K was obtained for a 70 at % V composition. Such alloys and other combinations could easily be produced by ion implantation.

An interesting extension of the above two aspects of superconducting thin films is the combination of an alloy (Ti/V say) in a granular state. This combines the conditions for the highest $T_c$ together with those for the highest enhancement. The enhancement in the case of the Ti/V alloy in thin film form is only about 3°K compared with about 5.5°K for the granular Mo system reported by Hanak et al. We have shown that titanium implantation produces clusters of titanium atoms in a dielectric matrix. The relevant question now is whether or not one can by implanting Ti and V in sequence produce clusters of Ti-V alloy in a dielectric matrix close enough together to enable macroscopic supercurrents to flow.

Finally, an aspect of ion implantation and bombardment that could well be put to greater use is that of bombardment induced recrystallisation and amorphization. Both in this thesis and in other work (for example Kelly and Naguib 1970) it has been shown that bombardment does not decrease crystallite sizes of all materials. In some materials the initially amorphous material is made polycrystalline or even monocrystalline by bombardment. As the current interest in piezo-electric and optical application grows, more research is appearing which is directed towards the growth of orientated or epitaxial dielectric layers (Francombe 1970). As candidates for piezo-electric film transducers, the orientated and epitaxial growth of insulating compounds belonging to the wurtzite structure class has received special interest, and considerable success is now being achieved using sputtering methods (Noreika et al, 1969, Rozgonyi and Polito 1969, Foster 1969). Ion bombardment should not be ruled out as a method for producing such layers.
No doubt other future applications of ion implantation to the understanding and production of thin film devices will appear, and some of those suggested above might never yield anything of benefit. There is no doubt however that ion implantation could have a big future in the field of amorphous and polycrystalline thin films generally.
APPENDIX

Tunnelling between metal particles and the supply function

Considering a system of particles as shown in figure A1 the potentials of the source and drain are not fixed and the supply function is given as being proportional to the density of full states in island $i$ and the density of empty states in island $j$, therefore (Neugebauer and Webb, 1962)

$$\sum \alpha \int f_i (1 - f_j) dE \ldots \quad (A1)$$

The more familiar factor $(f_i - f_j)$ in the ordinary tunnelling equation is only appropriate for tunnelling between two electrodes whose potentials are held fixed, such as by a battery. Neugebauer and Webb describe charge transfer where some islands are initially charged - a possible condition, but one which is unlikely to limit the ultimate steady current flow. Keiran and Stops (1969) adopt the neutral island model of Hill (1969b) but modify distribution functions of electrons associated with the islands to allow for charge transfer on the basis that the initial distribution of any excess charges is unlikely to limit the steady current flow. Keiran and Stops then give for the supply function,

$$\sum \alpha \int f_i (1 - f_j) dE - \int f_j' (1 - f_i') dE \ldots \quad (A2)$$

where the unprimed functions relate tunnelling from island $i$ to island $j$ in the direction of the field, and the primed values to transfer in the opposite direction. Then using Simon's expression for the transmission probability, equation (6.9), the current becomes
FIG. A1  ENERGY DIAGRAM OF THREE PARTICLES $h, i, j$. 
\[ J_q = \frac{4\pi m e}{B^2 h^3} \frac{e^{B kT}}{\sin (\pi B kT)} \exp(-A \phi^2) \]
\[
\times \left[ \frac{1 - \exp\left( B(\delta E + eV')/kT \right)}{1 - \exp\left( \delta E/kT \right)} + \frac{1 - \exp\left( -B(\delta E - eV')/kT \right)}{1 - \exp\left( \delta E/kT \right)} \right] \quad \text{... (A3)}
\]

where the plus signs in the right hand bracket hold for $\delta E < eV$ and the negative signs for $\delta E > eV$.

When $\delta E > eV$, and for $\delta E > kT$ equation (A3) becomes modified and can be written as

\[ J_L = \frac{4\pi m e}{B^2 h^3} \frac{\sinh (eV'/kT)}{\sin (\pi B kT)} \exp(-A \phi^2) \]
\[
\times \exp\left( -\frac{\delta E}{kT} \right) \quad \text{... (A4)}
\]

and is the same as that derived by Hill (1969b), using a supply function of the form

\[ \sum \alpha \int f_i (f_h - f_j) dE \quad \text{... (A5)} \]
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LIST OF PUBLICATIONS

The following is a list of the author's publications and conference papers based wholly or in part on work presented in this thesis.


2. Perkins J G and Stroud P T (1970) "Thin Film Cermet Structures Formed by Ion Bombardment", UKAEA, AVRE Rept 09/70


