THE FORMATION OF THIN FILM RESISTORS

BY ION IMPLANTATION OF METAL FILMS

by

PATRICK A. O'CONNELL

Work carried out in collaboration between
the Department of Electronic and Electrical Engineering
of the University of Surrey and AWRE Aldermaston.

Submitted for the degree of
Doctor of Philosophy to the
UNIVERSITY OF SURREY
Guildford, Surrey
1975
SUMMARY

A form of ion implantation has been applied to the formation of high value thin film resistors of low temperature coefficient.

The material produced by this process may be continuously controlled in resistance, from an initially low value to more than many mega ohms per square. The temperature coefficient of resistance is changed simultaneously and goes from an initial positive value, of a metal film, to a negative value at high resistance values. At sheet resistances near to 10,000 ohms per square, the temperature coefficient makes a transition through zero, and thus provides a potentially very useful resistor material.

The process requires a large dose of ions and involves considerable sputtering. In addition to the normal processes of direct implantation and loss of material by surface sputtering, the film material is recoiled forward by the impinging ions into the substrate and substrate atoms recoiled backward to implant the film. An analysis of the electrical behaviour of the film indicates that a dielectric and metal island matrix is formed, in which the dielectric component dominates the impedance of the structure at high resistance, and then provides a negative temperature coefficient of resistance. In an intermediate range the metallic and dielectric phases complement each other to provide a very low temperature coefficient. In addition the recoil collision processes greatly enhance the adhesion of the film to the substrates.

An analysis of the general behaviour of a two-phase material of mixed conduction characteristics is presented, and is used both to analyse the material produced in this work, and to indicate possibilities in other forms of "transition material".

Other phenomena produced by the ion implantation process are the modification of optical reflection and transmission and the change of secondary electron emission coefficient during ion implantation.
It is concluded that this process is capable of producing a useful resistor material which can be controlled over a wide range in resistance, temperature coefficient, optical transmission and geometry by an ion beam.
ACKNOWLEDGEMENTS

The work described in this thesis formed part of a programme of research conducted collaboratively by the Department of Electronic and Electrical Engineering of the University of Surrey, Guildford, and the Ion Effects Group in the Superintendency of Nuclear Effects, Atomic Weapons Research Establishment, Aldermaston, Reading, between the years 1967 and 1970.

The author wishes to thank his University Supervisor Dr. K. G. Stephens and his Industrial Supervisor Dr. L. E. Collins for their advice and many useful discussions. He also wishes to acknowledge the valuable discussions with Dr. P. T. Stroud, Dr. J. G. Perkins, A. W. Tinsley, Dr. A. C. Douglas, P. R. C. Stevens, Dr. P. L. F. Hemment, and F. R. Pontet. Special thanks are due to J. L. Wankling for his invaluable assistance with computer programming, to T. D. J. Cameron for expert electronics assistance and the use, on occasions, of his laboratory, and to P. J. Cracknell and P. Simms of the University for their valuable assistance with the vacuum equipment.

The author also wishes to thank the management of A.W.R.E., especially Dr. R. Batchelor, Dr. H. R. Hulme and Mr. J. J. McEmhill for their co-operation and the use of their facilities during the research and preparation of this thesis. Finally grateful thanks are due to Mrs. Karen Jones for typing the final draft, and to Mrs. Beryl Whyatt and Mrs. Helen Trowell for their patient assistance in the preparation and typing of the manuscript.
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LIST OF SYMBOLS

The symbols used frequently in the test are listed below. Other symbols may be used occasionally and when this occurs they are explained fully in the text.

A  Arbitrary constant - defined when used
A_n  Avogadro's Number
Ar_1^+  Singly charged ion of atomic Argon
B  Arbitrary constant - defined when used
C  Capacitance (Farads)
d'  Density
E_1  Energy of incident ion
e  Charge on electron
eV  Electron-volt
F(x)  Fuchs-Sondheimer size effect function for conduction in thin metallic films
f  Frequency (Hz)
G  Conductance
h  Planck's constant
I  Current (Amperes)
K  Arbitrary constant - defined when used
k  Boltzmann's constant, also used as arbitrary constant when so defined
M  Atomic mass
M_1  Atomic mass of incident ion
M_2  Atomic mass of target atom
m  Mass of electron
mC  $10^{-3}$ Coulomb, charge unit frequently used as unit of ion dose.
N  Atomic density of target material
N_1^+  Singly charged ion of atomic Nitrogen
Singly charged ion of atomic Oxygen

Singly charged ion of molecular Oxygen

Parts per Million

Total ion range

Mean ion range

Mean projected ion range

Resistance

Sheet resistance of film

Resistance component of a model

Sputtering coefficient (atoms per ion)

Absolute temperature (°K)

Temperature Coefficient of Resistance

Film thickness

Average film thickness

Applied voltage (volts)

Width of film

Ratio of film thickness to electron mean free path (t/λ) - also used as arbitrary variable when so defined

Arbitrary variable - defined when used

Electrical impedance

Temperature coefficient of resistance of bulk metal

Temperature coefficient of resistance of metal film

Coefficient of secondary electron emission for ion bombardment (electrons per ion)

Debye temperature

Mean free path of conduction electrons

Resistivity (Ω.cm)
\( \rho_o \) Bulk resistivity

\( \rho(T) \) Component of resistivity dependent upon absolute temperature

\( \rho_f \) Component of resistivity dependent upon size effect

\( \rho_i \) Component of resistivity dependent upon impurity concentration

\( \sigma \) Conductivity \((\Omega^{-1}.\text{cm}^{-1})\)

\( \Phi \) Recoil atom flux

\( \Phi_f \) Incident ion flux
CHAPTER I
INTRODUCTION

Ion implantation is the introduction of atoms into the surface of a solid, in vacuo, using a directed stream of ions. The implantation technique has become established over the last decade as a new and powerful method of fabricating semiconductor devices (1-16). The principal advantage of ion implantation is the accuracy of control it confers to the introduction of electrically active impurities into semiconductors. When ions with initial energies of typically 10 KeV to 100 KeV, finally come to rest within the host material and are implanted, they may have travelled distances of hundreds to several thousands of Angstroms. Their depth and distribution is determined by the nature and species of the host and ion, and the ion energy. Thus by accurate measurement of the ion dose and by adjustment of the ion energy and bombardment conditions, precisely controlled impurity doping profiles of almost any desired shape and concentration may be built up.

However ion implantation has not displaced conventional techniques, such as thermal diffusion, but is used in the critical fabrication stages where precise control is impossible by other means. In most implanted devices, annealing is required subsequently to remove radiation damage and make the implanted impurities electrically active. An interesting application of the ion implantation technique would be control of electrical properties in materials in which radiation damage is not deleterious but may be of advantage. Examples of such materials are resistor materials, surface insulating layers, e.g. oxides, capacitor dielectrics, and amorphous semiconductor and glassy devices such as switches and memories. These materials and devices have received much attention elsewhere, but little in the field of ion implantation. The use of thin film resistors and amorphous devices in microcircuits can improve performance and simplify circuitry, and can
provide more rugged devices which are resistant to radiation and therefore of considerable importance in military and space applications.

1.1. Objectives of Research

Ion implantation allows the formation of a wide range of unusual compounds and solid solutions (17) with a high degree of control over concentrations, and therefore lends itself to the fabrication of new electrical materials; the object of this research project is to investigate its application to passive electronic devices. Thin film resistors were chosen for this research because the electrical properties of resistance materials are notoriously sensitive to impurity concentrations, and are generally improved by the presence of crystalline disorder, thereby allowing the electrical effects of implantation to be studied without recourse to annealing procedures.

Many ion implantation and bombardment studies have reported small changes in the resistance of metal films when using heavy ions, and these changes were attributed to radiation induced changes (18), surface sorption and sputtering (19-22), radiation induced defects (23-25), and damage (26). Active gas ions have been used to produce chemical changes in surface layers, for example oxide layers on silicon (27), on copper (28), and nitrate on nickel (29-31).

The effect of implantation on resistance was carried much further by Collins and Richmond (32) who found that prolonged bombardment with oxygen ions could increase the sheet resistance of aluminium films controllably over a very wide range. In this dissertation the process was extended and examined in detail. In addition to the dramatic changes in resistance it was also discovered that the temperature coefficient of resistance was changed over a wide range and from positive to negative; other physical properties that changed significantly as the result of ion implantation were optical transmission and reflection, the coefficient of secondary electron emission, the film thickness and the adhesion of the film to the substrate.
1.2 Review of Thin Film Resistor Materials

It is generally known that film resistors are improved, that is the resistivity increased, the temperature coefficient and noise reduced, by the controlled introduction of stable impurities and disorder (33). Most film resistor requirements are met with films having a sheet resistance in the range 10 to 1000 Ω/sq. Resistors below 10Ω are rarely needed, whereas values in the megohm range are achieved through the use of large geometrical length to width ratios and by meandering techniques. There remains, however, a limited but pressing need for films with sheet resistivities of greater than 1000 Ω/sq., and much current research is devoted to finding a solution to this problem. In the effort to find an ideal material, the producers of thin film resistors have examined a very wide range of materials and methods of fabrication. No single material or process has yet emerged, but instead the choice available for any given application has become wide indeed.

To allow comparison with the ion bombardment technique, some of the significant materials and methods that have been reported in resistor production are outlined in the following sections, and are classified according to their structure and the type of conduction process that is observed.

1.2.1 Alloy Films

One of the first materials to be used in modern thin film applications and most extensively studied was the alloy Nichrome which is a popular resistance wire material (Nichrome, 80% Ni, 20% Cr), and was investigated during the Second World War for the production of microwave attenuators (34, 35). The resistivity and TCR obtained with Nichrome provides sheet resistances of up to 300 Ω/sq, at 50 Å thickness and a TCR of 100 to 200 ppm/°C, which depends upon the alloy composition. A problem with Nichrome is maintaining the required composition since in direct evaporation from the alloy, each constituent, which has a different melting point, evaporates at a vastly different rate unless relatively
high temperatures are used, in which case the overall rate is so high that control of deposition thickness becomes difficult. It is not surprising, therefore, that a variety of methods of vacuum deposition of this material are in common use, e.g. evaporation from resistance heated tungsten wire (36), from RF induction heated crucible (34), by sublimation from the wire (37), by electron beam heating (38), by flash evaporation (39), and by sputtering with argon gas from a Nichrome cathode (40); the inclusion of oxide phases by, say, slow evaporation, may assist in reducing the TCR. Annealing proves essential, however, to stabilise the resistance, and high resolution microscopy (41) showed that the film was an island structure of sub-crystalline Ni-Cr, with a connecting skin of chromium oxide which became semi-continuous at a critical thickness of about 150 Å, and it was suggested that on annealing the resistance was stabilized by the removal of defects in the metallic phase.

Stainless steel as a tertiary alloy containing 8% Ni and 18% Cr has been investigated (42) since the material could be easily etched in thin film circuit production, and did not require a high substrate temperature during deposition to ensure stability. The resistance range was limited however to 100 Ω/sq for better than 1% stability per 1000 hr.

In the attempt to produce alloy films with higher resistivities than Nichrome, silicon and titanium have been used in place of the nickel component (43-45). An alloy of 24% Cr and 76% Si, prepared by flash evaporation proved most promising, with a maximum sheet resistance of 10000 Ω/sq. Over the range of resistivities of 100 to 4000 Ω/sq, the TCR was within ± 200 ppm/°C, and after thermal ageing the films were found to be rugged and stable. Recently this alloy has been investigated as a substitute for Nichrome films in radiation hardened microcircuits and does not present problems of contact with aluminium metallisation normally experienced with Nichrome.

Nickel films alloyed with phosphorus have been reported (46)
with a sheet resistance of up to 2000 $\Omega$/sq and a TCR of less than 100 ppm/$^\circ$C. However the high resistance, due to the phosphorus concentration of between 0.5% and 1.3%, proved difficult to control and for close tolerances individual adjustment was required.

Other alloys for high quality resistors have been described by Jackson et al (47) and the resistivity and TCR they quote for various systems were as follows:

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Resistivity ((\mu\Omega.cm))</th>
<th>TCR (ppm/$^\circ$C)</th>
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<tbody>
<tr>
<td>Pd - Ag</td>
<td>38</td>
<td>± 50</td>
</tr>
<tr>
<td>Cu(83)Mn(13)Ni(4)</td>
<td>48</td>
<td>± 10 (Manganin)</td>
</tr>
<tr>
<td>Ni(80)Cr(20)</td>
<td>110</td>
<td>± 85 (Nichrome)</td>
</tr>
<tr>
<td>Ni(75)Cr(20)Al(3)Cu(2)</td>
<td>130</td>
<td>± 20</td>
</tr>
<tr>
<td>Ni(76)Cr(20)Al(2)Fe(2)</td>
<td>133</td>
<td>± 5</td>
</tr>
<tr>
<td>Pd - Au - Fe</td>
<td>158</td>
<td>10</td>
</tr>
</tbody>
</table>

In summary, alloys of metals can provide low temperature coefficients of resistivity, but composition and heat treatments must be carefully controlled for good reproducibility. The sheet resistance obtainable is limited, however, and falls in the "metallic region", that is below the "transition zone" of figure 1.1 on page 23.

1.2.2 Single metal systems refer to those materials which start from a single evaporant and achieve high resistivity, low temperature coefficient and good stability by incorporating impurity phases during formation, e.g. oxides or nitrides, or by forming a new structure, e.g. β-tantalum and low density tantalum. A higher range of resistivity and lower TCR are achieved for single metals than for metal alloys. Heat treatment is applied to stabilise the resistance of the metallic bulk of the films, although the metals more frequently used, e.g. Ta, Hf, Mo, are refractory and have a low atomic mobility so that little change in structure occurs over the operating temperature range even without
Belser and Hicklin (48) investigated a number of single metal systems likely to be useful in thin film resistor production and these included noble or semi-noble metals (Au, Pt, Ir, Rh, Pd, Ni), refractory metals (Mo, Ta, W), semi-refractory metals (Cr, Ti, Zn) and aluminium. The most promising results were those of the refractory metals; these gave high sheet resistances and low TCR's. It was found that a wide range of values could be obtained by controlling the oxygen partial pressure in the argon-oxygen atmosphere used for cathode sputtering the films and electron diffraction studies revealed that those films with the lowest TCR had the highest oxide content. Semi-refractory metals with low TCR's, which were deposited by vacuum evaporation, were also found to have a high oxide content.

Similar results have been observed for tungsten (49), hafnium (50), and molybdenum (51). In contrast with tantalum-like systems rhenium may be used to form high resistivity films which are just on the edge of agglomeration (52). The additional resistivity is provided by the finite space between the deposited metal particles and normally such films are unstable owing to atomic mobility. Rhenium however is so refractory that films can be formed that are only about 40 Å thick with a sheet resistivity of 1000Ω/sq and are stable up to 500 °C in vacuo.

Zimmerman (53) compared aluminium, chromium, tungsten and rhenium, and concluded that, by a considerable margin, rhenium was the best choice for a thin film resistor material. He reported sheet resistivities of up to 5000Ω/sq and a TCR of -200 ppm/°C for films deposited at 450°C, and resistance changes of -15 to -20% during heat treatment.

Interest has grown in refractory metals since, due to their high melting points (in excess of 2000°C), metals such as tantalum, tungsten, rhenium and niobium remain quite stable at ordinary
temperatures displaying very low atomic mobility. Thus any defects and imperfections "frozen in" during deposition do not anneal-out in use. The high melting points give rise to deposition difficulties and, normally, electron beam heating or sputter deposition are used. Tantalum has been used very widely as a film circuit material, but its highly reactive nature causes it to acquire considerable contamination when deposited unless special precautions are taken. Such contamination is however desirable in controlled amounts to achieve high resistivities and low temperature coefficients. Normally tantalum resistors are stable up to 200 Ω/sq and TCRs of 150 ppm/°C, and are aged thermally at up to 300°C for several hours to ensure less than 1% drift under operation below 100°C. Tantalum nitride deposited by reactive sputtering in an argon-nitrogen atmosphere also provides a highly stable material (54-56). Films of up to 100 Ω/sq and TCR's less than -100 ppm/°C were made with a resistivity of 250 μΩcm, i.e. about 20 times bulk. The deliberate introduction of oxygen in reactive sputtering results in films of higher resistance, 1000 to 2000 Ω/sq, higher TCR -300 to -350 ppm/°C, and poorer stability than the nitride forms (55). Reactive sputtering with methane or carbon monoxide produces Ta2C or TaC films which also display high sheet resistance and low TCR (56).

New crystalline forms of tantalum have been reported (57,58) and is referred to as β-tantalum. This form is only observed when the deposition is free of gaseous contamination with a substrate temperature less than 600°C, which contrasts strongly with the normal α-tantalum form (25-50 μΩcm and TCR's +500 to +1800 ppm/°C). Frequently films contain both forms and generally tantalum films are difficult to deposit to the required value of resistivity.

1.2.3. Cermets

It is seen that in order to produce a stable high resistance resistor material with a low temperature coefficient, some form of impurity or discontinuity is introduced into a metallic phase. The
impurity phase may be an insulating material such as a ceramic, and when the concentration of the insulator becomes large the mixture is referred to as a "cermet". The advantage that cermets have over alloys and impure metals is that their resistivity can be sufficiently high that thicker and more rugged films can be used for a given resistance instead of ultra thin layers susceptible to atomic mobility and oxidation. The insulator phase of the cermet, generally an oxide, protects the metal grains from oxidation, and provides high mechanical strength since the grain boundaries are stabilised by the oxide phases. Electronic conduction occurs either through a network of touching metal grains or by electron transport through the intermediate oxide layers.

In a survey in 1961 (60) several metal dielectric mixtures were compared, i.e. gold-silicon oxide, gold-magnesium fluoride, chromium-silicon oxide, chromium-magnesium fluoride, and of them only Cr-SiO proved stable under thermal and load tests and was hard and abrasion-resistant. Silicon monoxide (SiO) and magnesium fluoride (MgF₂) are also popular dielectrics and are frequently used in thin film capacitors. However, in mixtures using MgF₂ the metal grains exhibited considerable recrystallisation, leading to a rapid increase in resistance at low metal concentrations, and this made the control of resistance difficult. In contrast SiO suppressed appreciable migration of the metal content, resulting in a thermally stable structure. By varying the relative proportions of chromium and silicon monoxide the resistance of the mixture could be varied over a wide range, typically three to five orders of magnitude between zero and 50% SiO (60,61), but for stability the sheet resistance was limited to 600Ω/sq with a TCR of ±100 ppm/°C, using 65% Cr - 35% SiO and protective silicon oxide overlays (13).

Other cermet systems possess sheet resistivities considerably larger than the Cr-SiO system. Using a two source reactive sputtering arrangement and heated substrates Farrell and Lane (14) produced noble
metal-refractory oxide mixtures viz. Pt-WO₃, Pt-Ta₂O₅, Au-WO₃, and Au-Ta₂O₅. Of these the Au-Ta₂O₅ provided the widest resistance range, 10⁻¹Ω/sq to 10⁵Ω/sq, with the lowest TCR range +350 to -200ppm/°C, but the resistance increased on heating and stabilised with loss of control of value possibly due to contact difficulties. Miller and Shirn (62,63) produced Au-SiO₂ films using direct rf sputtered SiO₂ which displayed resistivity values of an order of magnitude higher than evaporated Au-SiO₂ mixtures of equivalent metal-dielectric composition. Also investigated were Nichrome-SiO₂ mixtures and in the TCR range +500 to -3500 ppm/°C the resistivity ranges were 10⁻² to 10 Ω.cm and 10⁻⁴ to 10³Ω.cm for NiCr-SiO₂ and Au-SiO₂ systems respectively. A triple compound mixture (64) was produced from equal amounts of Cr, Si and TaSi₂ with increasing amounts of Al₂O₃. Baking in air at up to 490°C was used to stabilise and trim the films to about ±10%. A resistivity range of 10⁻³Ω.cm to about 5 x 10⁻²Ω.cm was found with the corresponding TCR range of +30 ppm/°C to -800 ppm/°C. Zero TCR was observed at just over 10⁻³Ω.cm, with a sharp rise above -200 ppm/°C ( ~ 2 x 10⁻³Ω.cm).

Riddle (65) attempted to ease the evaporation procedure for cermet mixtures of similar vapour pressure, so that steady rather than flash evaporation could be employed possibly leading to better control. He reported results of experiments on cermet mixtures selected from metal and insulator components of similar vapour pressure, suitable for co-evaporation from a single source. Among those mixtures tested were germanium-chromium, aluminium-silicon monoxide, silicon-silicon dioxide, chromium-silicon, aluminium-silicon, and aluminium-aluminium oxide. Preliminary results showed that Cr-Ge cermet to be stable at 10⁻³Ω.cm, but that at higher resistivity the stability worsened and could be improved by annealing. The Al-Al₂O₃ cermet also proved stable at 10⁻³Ω.cm, requiring thermal ageing for stability at higher resistivities, and Riddle suggested that the
Al-Al₂O₃ insulator form could find application as dielectric and passivating material in the fabrication of semiconductor microcircuits.

Head (66) reported interest in silicon-iron oxide, silicon-manganese oxide and silicon-titanium oxide mixtures. The iron cermets displayed very large negative TCR's, eg -4000 ppm/°C at a 2.5 kΩ/sq sheet resistivity, whereas the manganese mixtures produced very low TCR and titanium oxide cermets appeared very stable, but no figures were given.

Cermets provide one of the most interesting forms of high resistance material in that they represent a "molecular engineering" approach to the control of electronic conduction properties. A very wide range of suitable metal and insulator materials are available and many have yet to be exploited or proven commercially. The range of electrical properties obtained overlaps that of single metal systems and although very high resistance can be obtained, it is at the sacrifice of temperature coefficient, so that the useful high stability range covers almost the same region as that of the "single metal". The most significant use of cermetstoday is possibly in the field of thick films where it proves amenable to screen printing techniques of deposition. Production by vacuum deposition is bedevilled by the necessity and difficulty of compositional and structural control, although sputtering techniques can be stable. Reproducibility is normally achieved at the loss of flexibility in the choice of sheet resistance so that a very careful evaluation of the process is required for any application.

1.2.4 Semiconducting Films

In applications where large temperature coefficients and non-linearity can be tolerated in the interest of high resistance values, semiconductors still hold considerable promise in film resistors. Among the materials now used are the conventional semiconductors, e.g. Si and Ge, and also carbon and tin oxide films.
Carbon Films

Carbon has probably been the most popular resistor material ever used for discrete components, but because of high processing temperatures and difficulty in precise sheet resistance control it has not proved compatible with microcircuit applications. Films are normally deposited on ceramic substrates at high temperature (e.g. ~1000°C) using pyrohydrolytic decomposition of a carbon bearing gas such as methane, and the film thickness is adjusted by varying temperature, gas composition, etc. The final resistance value is obtained by selection and by trimming, by abrading or groove cutting, for close tolerance. The TCR obtained is of the order of -250 ppm/°C at 10 Ω/sq, and -400 ppm/°C at 1 kΩ/sq. The electronic conduction processes in the carbon film may be characteristic of the graphite band structure when deposited at very high temperatures (i.e. >1900°C) but at the normal lower temperatures no unique band structure is evident and the grossly disordered film displays properties associated with conduction by finite energy gaps (67). The TCR is often reduced by the addition of Boron, introduced into the gas stream. At 4% boron the TCR of the film is as low as -20 ppm/°C at 10 Ω/sq and -250 ppm/°C at 1 kΩ/sq.

Tin Oxide

Most film resistor systems appear susceptible to oxidation to varying extents, but a fully oxidised material should be free of this defect. Tin oxide is such a material, providing high resistance, and because of its refractory nature even the effects of thermal agglomeration and annealing are low. The normal method of deposition is by spraying stannous chloride on to hot glass, the oxide film being formed by surface hydrolysis, and this provides exceedingly adherent and robust films.

Tin oxide has the characteristics of a wide-band gap semiconductor. Oxygen deficiencies and chloride ions or antimony dopant
atoms act as donor centres giving an n-type semiconductor, whereas indium acts as an acceptor which compensates the donor centres to increase both resistivity and TCR (68). A sheet resistance of 1000 $\Omega$/sq may be obtained with films of 1$\mu$m thickness, and may be used without detriment to 450°C (69). Antimony doping greatly improves the stability of films, particularly in highly oxidising atmospheres, as it prevents oxygen vacancy refilling. Films between 10 $\Omega$/sq and 300 $\Omega$/sq may be produced with TCR in the range 0 to -200 ppm/°C with antimony doping between 7% and 9% (70). Tin oxide resistors feature a very high degree of transparency and have found application in window heating elements, electrodes for liquid crystal displays, etc. The high temperature hydrolytic deposition process normally used provides a coarse grained, rough material and has therefore found little favour in integrated circuit manufacturing processes. A low temperature process, e.g. evaporation or sputtering, results in a smooth film but a post-deposition heat treatment stage to 800°C is required (71).

1.2.5 Conclusions

From the preceding sections it is seen that the two major parameters of a thin film resistor, namely resistivity and temperature coefficient of resistivity (TCR), are closely inter-related and whatever the material or processing technique the general trend of these parameters follows that of figure 1.1, due to Halaby (72). Useful thin film resistors materials, however, are normally those with highly stable properties and low temperature coefficients of resistance, i.e. less than 200 - 500 ppm/°C. This also limits the useful range of sheet resistivities and to illustrate the relative usefulness of the materials discussed in the previous sections the author has compiled a pictorial summary shown in figure 1.2 and based on the format of Halaby.

Of modern applications of thin film components, that of microelectronics manufacture, in particular that of monolithic integrated
Temperature Coefficient of Resistivity

$-4 \times 10^{-4}$ ppm/$^\circ$C at 20$^\circ$C

Fig. 1.1 Variation of Resistivity and Temperature Coefficient of Resistivity for Single Phase Materials; after Halaby (72).
Fig. 1.2 Illustrating typical "working ranges" of sheet resistance and temperature coefficient of resistance for high quality thin film resistor materials.
circuits, is probably the most important. In conventional micro-
circuits diffused semiconductor resistors are used, typically at a
sheet resistance of 100-200Ω/sq, and p-type base, or n-type collector
type diffusions, are used for compatibility and ease of manufacture.
Higher values of sheet resistance, e.g. 1-50 kΩ/sq may be formed by
constructing, say, a base diffusion with an emitter zone, but because
the resistor thickness is then the result of a small difference between
two large depths, precise control is very difficult. The structure of
such a resistor is analogous to that of the channel in a junction-gate
field effect transistor and consequently experiences "pinch" effect which
increases the resistance with operating voltage and considerable non-
linearity is introduced. Film resistors, although more expensive since
they add further processing stages, have the great advantages of low
noise, low TCR, high resistance, low parasitic capacitance, high
isolation resistance independent of polarity, possible saving in area,
and are almost unaffected by nuclear radiation. The use of thin films
also allows independent variation of resistor and device processing in
integrated circuit fabrication so that, for example, speed and power
consumption may be varied throughout a range of circuit in a logic
family.

Normally the geometry of microcircuit thin film devices is
determined by photolithographic resist-etch techniques rather than by
masking, since it is more compatible with conventional processing steps
and is in consequence more accurate and easy to apply. Two main
techniques exist, (1) coating the entire substrate with the resistor
film and etching away the undesired material, (2) forming a resist
"negative" first of the required pattern, and after depositing the
resistor film removing the excess coating when the resist is washed
away.

Any film that has been proved satisfactory on glass substrate
(a silicate) is likely also to be satisfactory in microcircuity
(normally a silicon oxide bed). Nichrome has been used in the range 200-300Ω/sq, and therefore takes approximately the same geometry as conventional diffused resistors although some contact problems have been experienced between nichrome and the aluminium metallisation. Tin oxide (5) and simultaneously evaporated cermets (61) have been used experimentally. Reactively sputtered tantalum (15), and more recently silicide compounds, e.g. MoSi$_2$, SiCr, and CrSi$_3$ (16) have shown promise in the 1 kΩ/sq range.

Ion implantation techniques have also been used to improve semiconductor resistors e.g. neon ion bombardment has been used to damage thin diffused resistor layers of up to 50 kΩ/sq which proved stable to 500°C (73). Direct impurity implantation has been applied to the formation of resistors of 800 to 11000Ω/sq, at -800 to -4000 ppm/°C using boron ions of 30 to 55 keV at a dose of $10^{14}$ ions/cm$^2$ with SiO$_2$ masking and post bombardment annealing (74). Since the resistor took the form of a conventional, but very shallow semiconductor layer, non-linearity was still present.

Thus in recent years new requirements have been made upon the performance of microcircuits, in particular in space and military applications, which require high tolerance to nuclear radiation. Present day circuits have several limitations in these respects, and as a result techniques and materials have been developed which can offer radiation resistance, and these include ion implantation, and amorphous and thin film devices.
CHAPTER II
REVIEW OF THEORY

2.1 Introduction

In the ion bombardment of thin films to form the electrical materials studied in this research, the interaction between the ion and the target, and the behaviour of the electrical properties of the target may, to some extent, be predicted. In this chapter the principal theoretical descriptions of ion–target interactions, and of thin film conduction are reviewed.

2.2 Heavy Ion Bombardment

Two important phenomena of ion-target interaction are relevant to this study. These are:-

(1) Penetration and stopping of incident ions. The mechanisms involved determine the depth, profile and concentration of the implanted dopant species.

(2) Target atom displacement. This gives rise to surface sputtering losses, radiation damage, recoil implantation, and controls the structure of thin surface layers.

2.2.1 Ion Penetration and Range

When an ion penetrates a solid, or lattice of atoms, they interact and energy is lost from the ion, and the ions slows down. When the ion energy reaches about 20 eV it is stopped. There are two main processes by which energy is lost:-

(1) Excitation of outer valence electrons – "in-elastic collisions"

(2) Interaction between the nuclei of ion and target – "elastic collisions"

In-elastic collisions occur when the ion has a high velocity, for example a high energy heavy ion, or a lower energy light ion. For the
low energies (~30KeV) and heavy ions (atomic number 32 to 40) used in this research in-elastic collisions may be ignored, and nuclear stopping predominates. This is illustrated qualitatively in Figure 2.1.

In its course through a solid lattice a slow heavy ion suffers a sequence of collisions with lattice atoms which deflect its path, as represented schematically in Figure 2.2. The two extreme cases of collision sequence are (i) the random collision sequence in an amorphous material, and (ii) the regular spatially correlated collisions which occur if the ion is directed into an open direction of a crystalline lattice which "focus" or "channel" the ion to anomalously large ranges. Some channelling effect may also be detected in poly-crystalline material, but for high ion doses the accompanying radiation damage permits the assumption of near amorphous material, and only this case will be considered.

In recent years a comprehensive theory of atomic stopping has been developed by Lindhard and his collaborators (75-77), and sufficient corroborative experimental evidence has been accumulated to justify the present general acceptance of the Lindhard, Scharft and Schiott or "LSS" theory. The "LSS" theory assumes a screened potential, between two atoms, of the Thomas-Fermi type. That is it takes the form of Coulomb's Law for two point charges, modified by a function which accounts for the finite dimensions of the screened atomic core for very close approach. Lindhard derived dimensionless range and energy parameters (76) in terms of a single screening parameter, the density of the target, the energy of the ion and their atomic numbers and masses. The depth at which the ion stops is less than the total range (R) owing to its random collision path, and a term called the mean projected range (Rp) is used and Lindhard gives the ratio of \( \frac{R}{R_p} \) as:-

\[
\frac{R}{R_p} = 1 + \frac{M_2}{3M_1}
\]
Specific Energy Loss

\[ \frac{dE}{dx} \]

**Fig. 2.1** Qualitative Illustration of Specific Energy Loss \((\frac{dE}{dx})\) as a function of Ion Energy \((E)\).

**Fig. 2.2** Illustrating Projected Range and Path of Ion in Solid.
The statistical nature of the collision process causes the mean projected range of individual ions to "straggle" about the mean. The profile of the resulting distribution is approximately Gaussian in the region where nuclear stopping predominates and expression for straggling was derived by Lindhard as:

$$\langle \Delta R^2 \rangle_{av} = \frac{2M_1 M_2 (R_p)^2}{3(M_1 + M_2)^2} = \frac{1}{h^2}$$

where $h^2 = \frac{1}{2\sigma^2}$

and $\sigma^2$ is the variance of the normal distribution.

The variation of the concentration of stopped ions with depth, that is the "profile" illustrated in Fig. 2.3, is approximated by the expression:

$$n(x) = \frac{h}{N \sqrt{\pi}} \exp \left(-\frac{h^2 (x - R_p)^2}{N}\right)$$

where $n(x)$ is the concentration of implanted ions at depth $x$

$N$ is the number of implanted ions.

Several workers have employed the LSS theory in the calculation of ranges for a wide range of ion-target systems, eg Johnson and Gibbons (78), Matthews and Holloway (79), and theoretical ranges for the systems employed in these studies, were obtained from published values and from those computed by Stevens and Wankling (Private Communication). The projected range and energy are plotted in Fig. 2.4, and compared, where available, with published measured values.

2.2.2 Displacement and Sputtering

In the previous section only the effect of energy loss on the ion was considered. In this process energy is given up to the target lattice and where elastic scattering occurs, target atoms can receive
Relative Ion Concentration

Fig. 2.3 Typical Gaussian Profile of Implanted Ion Concentration predicted for Nuclear Stopping Processes.

Mean Projected Range (Å)

Aluminium Target

Fig. 2.4 MeanProjected Range as a Function of Ion Energy for Aluminium Target for Ions of Oxygen and Argon computed by Johnson and Gibbons (78); experimental data are for Argon after Davies et al (140).
considerable energy, greater than the threshold for displacement (25 eV) and become dislodged, and in turn dislodge further atoms by collision. Near to the surface such energetic atoms may remove themselves into vacuum and this is termed surface sputtering or back sputtering. Atoms may also be projected forward out of a thin lamina (forward sputtered). Material sputtered backwards and forwards at an internal interface can give a doping (81) or mixing effect and provides implantation by a recoil process. A form of radiation damage occurs when atoms are dislodged within a crystalline material and at quite low doses the material is reduced to amorphicity or polycrystallinity; although the reverse process, recrystallisation has also been reported in some materials. The target materials used in the present work were polycrystalline thin films and since radiation damage could therefore have only a small effect it will not be treated in detail here. Sputtering was however significant and is reviewed briefly in the next sub-section.

2.2.2.1 Surface Sputtering

The sputtering yield of a material is defined by the quantity of matter, in atomic mass units, molecules or atoms removed for each incident ion. The yield varies with ion energy, ion and target species, crystallinity and orientation of the target and sometimes with charge state. Sputtering yield, for instance, is found to follow variations in the electron concentration of the outermost 'd' shells of the target species, and also bears some resemblance to the reciprocal of the heat of sublimation of the target(82). The yield changes with the atomic number of the ion species so that it rises to a maximum at each inert gas species, and then falls within each group of elements in the periodic table (83,84). Accordingly only qualitative trends will be described and quantitative detail only introduced where relevant.

Sputtering is basically a momentum transfer process and does
not operate until some threshold energy of a few eV is exceeded. Yield then rises quadratically with energy but quickly becomes linear over the "low-energy" region to about 1 KeV. At higher energies the yield saturates or flattens, eventually falling to zero when inelastic collisions dominate at the target surface (Figure 2.5). Ion penetration into the target then places elastic collisions too deep for dislodged atoms to emerge at the surface.

Various theories have been derived to explain sputtering (84 - 88). Brandt and Lambert (89) employed the theories of Lindhard et al for energy loss of heavy particles using the Thomas-Fermi potential, and derived dimensionless representations of sputtering yield which showed good agreement with data from 100 eV to 200 keV for target-ion combinations of high sputtering rate (eg Au-Kr, Cu-Ar, Cu-Kr). More recently Sigmund (90) has treated the subject rigorously using the LSS collision theories. Sigmund split ion energy into two ranges divided at a limiting energy, $E^*$, normally a few hundred eV, below which the Thomas-Fermi potential over-estimates interaction and a Born-Mayer potential is more appropriate.

Both Brandt and Sigmund show that the variation of sputtering yield with ion energy follows approximately the variation of stopping power derived from the LSS theory. It is generally found that low energy particles predominate in the sputtered yield owing to their large population density near to the ejection site relative to higher energy particles. Thus most sputtered particles come directly from within only a few Angstroms ($\sim 5 \AA$) of the surface. However interactions in much deeper layers influence the total yield so that bulk values would not be expected from films of material less than several tens of angstroms.

When a thin film of depth less than the range of incoming ions is placed on a substrate, particles which would have been ejected by
Fig. 2.5 Sputtering Yield as a Function of Ion Energy for Argon Ions and Aluminium Target.

Key:

- Laegrid and Wehner (120)
- Schirrwitz (121)
- Carlston et al (122)
- Almen and Bruce (83)
- Perkins (101); data points for Oxygen Ions also shown.
forward sputtering can now be caught in the substrate. Also since the primary ion may cross into the substrate with considerable energy then substrate particles can be back sputtered and held in the film. For a metal film and an insulating substrate this provides a means of doping the film to produce a mixed phase or cermet-like material and has been termed "Recoil Implantation" by Nelson (81).

2.3. Conduction in Thin Films

2.3.1. Introduction

It is not only resistivity that is of importance in a high stability resistor material but also the way resistivity varies with temperature, electrical stress, and time. Of these the temperature coefficient of resistivity (TCR) represents perhaps the most important parameter in classifying a material of a given resistivity. Unless the TCR is low and near to zero (i.e. \( \approx 100 \text{ ppm/}^\circ\text{C} \)) the material cannot be considered in the context of high stability. The TCR also provides a physical description of the conduction processes present, e.g. for example a high positive TCR characterises metallic conduction, whereas high negative TCR indicates an activated conduction as found in impure dielectrics or in semiconductors. Low values of TCR are not found in pure single-phase materials but are normally obtained by making impure metals, such as alloys and oxides, or by employing surface scattering in very thin films, or by combining opposite phases of materials such as metal and dielectric, in a structure in which positive and negative temperature coefficients compensate each other over the operating temperature range.

Defects and foreign atoms within the lattice of metal atoms disturb locally the lattice potential function and behave as "ion-like" centres, and the scattering effect of such centres is independent of temperature.
The separate causes of electron scattering each contribute to the total resistivity of a metal according to Matthiessen's Rule (91).

For an impure metal Matthiessen's Rule is applied thus:

$$\rho = \rho (T) + \rho_1$$

where $\rho(T)$ represents the resistivity due to lattice scattering which is a function of temperature, and $\rho_1$ represents the residual resistivity due to impurities and defects.

Maissel (33) has tabulated the approximate maximum contribution to the residual resistivity of various types of defect and these are given in Table 2.1. below:

<table>
<thead>
<tr>
<th>Type of Defect</th>
<th>Approx. Contribution to residual resistivity $\mu\Omega$.cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dislocations</td>
<td>0.1</td>
</tr>
<tr>
<td>Vacancies</td>
<td>0.5</td>
</tr>
<tr>
<td>Interstitials</td>
<td>1.0</td>
</tr>
<tr>
<td>Grain Boundaries</td>
<td>40</td>
</tr>
<tr>
<td>Impurities in Equilibrium</td>
<td>180</td>
</tr>
</tbody>
</table>

Since most pure metals of interest have resistivities in the region of a few $\mu\Omega$.cm even when polycrystalline, it can be seen that only the addition of impurities provide a significant increase in resistivity.

The temperature coefficient of resistivity, normally given the symbol $\alpha$, is given by:
TCR = \alpha_o = \frac{1}{\rho_o} \frac{\partial \rho}{\partial T}

where \rho_o is the resistivity at 20^\circ C, and \alpha_o the TCR.

For an impure metal

\frac{\alpha_i}{\alpha_o} = \frac{\rho(T)}{\rho(T)+\rho_i} \quad \text{Schwartz and Berry (92)}

and as the residual resistivity, \rho_i, increases, the TCR is reduced by the ratio:-

\frac{\alpha_i}{\alpha_o} = \frac{\rho(T)}{\rho(T)+\rho_i}

2.3.2. Conduction in Thin Metal Films

When one or more of the dimensions of a metal conductor are reduced to the same order as the mean free path of conduction electrons, a new scattering term is introduced, due to the surface, which greatly increases the resistivity of the metal. This is termed "size effect". Surface scattering is always present in the bulk material but is only significant when a large proportion of free electrons can make collisions with the surface. Fuchs (93) presented a strict analysis of metal films which was revised by Sondheimer (94) and is referred to as the Fuchs-Sondheimer theory. The distribution function of electrons with a dimensional limitation imposed in one direction due to the film boundaries was considered. Then by repeated integration of the current density of the limited distribution function, an expression was derived for the ratio of resistivity of a film to that of bulk, in terms only of the
ratio of film thickness to electron mean free path:

\[
\frac{\rho}{\rho_0} = \frac{1}{1 - \frac{3}{8x} + \frac{e^{-x}}{16x} (x^3 - x^2 - 10x + 6) - \frac{x}{16} (x^2 - 12)E_i(-x)}
\]

\(E_i(-x)\) is the exponential integral

\[E_i(-x) = -\int_{-x}^{\infty} \frac{e^{-u}}{u} du\]

and \(x = t/\lambda\), where \(t = \) film thickness

\(\lambda = \) electron mean free path

The temperature coefficient of resistivity due to size effect is not zero, but is much lower than bulk. The ratio of film TCR to bulk TCR given by Campbell (95) due to Swanson is:

\[
\frac{\alpha}{\alpha_0} = \frac{1 - \frac{3}{4x} + \frac{e^{-x}}{8x} (x^3 - x^2 - 8x + 6) + \frac{x^2}{8} E_i(-x)}{1 - \frac{3}{8x} + \frac{e^{-x}}{16x} (x^3 - x^2 - 10x + 6) - \frac{x}{16} (x^2 - 12)E_i(-x)}
\]

These equations were incorporated in their complete form in the computer programs used in the analysis of the electrical effect of ion implantation on thin films during this project.

The variation of resistivity and TCR ratio with film thickness to mean free path ratio are shown in figs. 2.6 and 2.7 respectively. The general dependence of resistivity both for diffuse scattering size effect, and impurity scattering are shown in fig. 2.8 and the ratio of electron mean free path to film thickness is indicated. The electron mean free path in metals at room temperature is limited by thermal vibration of the lattice and is therefore of the same order as the average wavelength of
Fig. 2.6 Variation of Resistivity Ratio with Ratio (x) of Film Thickness to Electron Mean Free Path.

Fig. 2.7 Variation of Ratio of Temperature Coefficients of Resistivity (TCRs) with Ratio (x).
Fig. 2.8 General variation of Resistivity with Temperature Coefficient of Resistivity (TCR) for impurity scattering and diffuse surface scattering, showing various values of thickness to mean free path ratio (x); after Schwartz and Berry (92).
sound waves in the metal, or by imperfections such as impurity atoms to the order of the distance between impurities (Sondheimer 1952). Thus the electron mean free path ($\lambda$) is normally a few hundred Angstroms or less, so that $\lambda/t$ ratios of greater than $10^2$ are unrealistic and demand a sub-monolayer film thickness, where the structure of the film is discontinuous. Similarly impurity introduction in a metal may eventually exceed the equilibrium state and the material splits into a two phase composite, e.g. if the impurity is a ceramic dielectric, a cermet type film composed of metal islands in a dielectric matrix can result.

2.3.3. Conduction in Mixed Phase Materials

In order to increase the resistivity of a metal film and at the same time reduce its temperature coefficient the metallic content can be diluted by incorporating a high concentration of insulating material, or by spreading the metal in an extremely thin layer on an insulating substrate. For a normal continuous film it would be expected that the resulting temperature coefficient of resistivity would remain positive and tend towards a low, limiting value (fig.2.8.). In practice, however, it is found that at a critical point the continuous structure breaks down. The metal then takes up an island-like form and becomes dispersed on the surface of the substrate, as in the so-called ultra-thin films, or distributed through the dielectric matrix as in metal-insulator or "cermet" films, and similar conduction processes are found to apply to each (95, 96).

The change in conduction at the critical point at which a metal film takes up an island form is dramatic and is typified by a very rapid rise in resistivity and a change in the temperature coefficient from a low positive value to a negative value typical of a dielectric which increases rapidly with change in structure as the proportion of metal is reduced. The useful range of the material so formed for resistors is that
which is close to zero TCR, where small changes in the dielectric concentration can produce large changes in the properties of mixed phase films. The substrate temperature and the rate and process of deposition, affect the structure of the mixed material, and therefore influence the conduction properties of the material. Thus the successful production of a cermet structure relies upon very strict process control.

2.3.4. Discontinuous Films

When a film is deposited on a substrate its growth is generally found to start at localised sites or nucleation centres. As deposition continues islands grow at the nucleation sites until they attain a sufficient size to overlap neighbouring islands and form a continuous film. When the film is still in the discontinuous phase, i.e. before islands touch, conduction may be measured in the film which is dominated by the impedance of the "gaps" between islands. If these gaps are filled with dielectric and many similar layers are placed one on top of the other, a three dimensional mixture of metal islands in a dielectric matrix results which is termed a cermet. Thus the discontinuous film and the cermet are equivalent(96), and indeed show many similarities in their equations of conduction and features of tunnelling, field and thermionic emission may be observed. The most important features of conduction in the discontinuous film are related to the relative geometry and size of the metal island and the gaps. Particles or islands are defined as "small" when their Coulomb potential energies are greater than their thermal energies (usually below $\sim 100 \, \text{Å}$), and gaps or separations are defined as small when they are less than the tunnelling path lengths for electrons ($\sim 40 \, \text{Å}$).

Discontinuous films may then be categorised under four headings with the associated dominant conduction processes.
(i) Small particles, small gaps - Quantum Mechanical Tunneling

(ii) Small particles, large gaps - Thermionic emission with bulk (semi) conduction in the substrate.

(iii) Large particles, small gaps - Tunnelling predominates but if island resistance is large the TCR becomes positive.

(iv) Large particles, large gaps - Either thermionic emission or bulk conduction in the substrate.

All mechanisms of dielectric conduction are characterised by dependence upon electric field and temperature such that a negative TCR and non-linearity with voltage can occur if high fields and large impedances are used.
CHAPTER III

APPARATUS

3.1 Introduction

In the experiments of this study a small 30 kV positive ion accelerator equipped with a gas ion source was used to bombard and implant thin film specimens.

The accelerator was adapted by the author* from an ion source test bench, which had only a rudimentary target system. Part of the experimental work therefore involved fitting new pumping and beam handling equipment, and several different target handling and measurement systems were devised by the author for the implantation experiments. Particular attention was paid to the electronic monitoring equipment, and items of original design were incorporated by the author to improve the accuracy and reliability of measurement.

One of the instruments designed by the author, an electronic current integrator with low input impedance, has been put into use both at Surrey University and AWRE. Several of these instruments have been built and used both as a beam monitor and integrator for electrons and ions, and as a high sensitivity (i.e. picoamp) current detector for measurement of electrical characteristics of thin film structures (100,101).

The thin film deposition equipment was initially considered to be of secondary importance, but improvements in measurement techniques demonstrated that more consistent starting materials were required for repeatable experiments. Accordingly a system capable of providing ultra-high vacua was designed at Surrey University, and was used at AWRE in conjunction with the conventional systems. After some development by the author a preparation and evaporation procedure was evolved which provided extremely reproducible thin film specimens. A vital part of the process was the provision of reliable, low resistance contacts of

*With the assistance of the staff of AWRE, and Mr. P. Simms of the University of Surrey.
precise configuration on the substrate to provide four-point resistivity measurements. The contacts had also to be sufficiently tough to withstand the rigorous cleaning schedule. For this purpose a titanium-gold evaporation technique, developed by the author, fulfilled the requirements excellently.

Measurements of temperature coefficient, voltage-current characteristics, film thickness, optical properties, frequency response etc. required for the analysis of implantation and bombardment effects made use of equipment and techniques designed or developed at the Ion Effects Group, AWRE, during the course of these studies. In the following sections the techniques and apparatus of general importance to this work are described.

3.2 Preparation Techniques

In the majority of experiments the bombarded targets were metal films evaporated on glass substrates. Thin films are notoriously sensitive to contamination and difficult to control accurately in thickness. Thus in preparing the films care was taken to ensure reliable reproducible results by evolving a thorough and standardised method of preparing the glass substrates, by maintaining cleanliness and low pressures during evaporation, and by precisely monitoring film deposition thickness by a number of different methods. The techniques used are described in the following sections.

3.2.1. Substrate Cleaning

To ensure freedom from contamination the substrates were well cleaned immediately prior to use. A standard schedule was evolved, which was found to be satisfactory in that it provided consistent films and good adhesion. During the entire cleaning process the batch of substrates was mounted with each slide separate in a spot welded nickel wire frame-basket, to prevent inadvertent fluid trapping and
permit easy access to the cleaning fluid. The procedure used was:-

1. Wash in detergent (Teepol) and hot water with ultra-sonic agitation for 15 minutes,
2. Rinse thoroughly in distilled water, with ultra-sonic agitation (15 minutes),
3. Clean in absolute ethyl alcohol in ultra-sonic bath (½ to 1 hour),
4. Hot drying in alcohol vapour (½ hour).

If required the titanium-gold contacts were applied at this stage. The whole cleaning process was then repeated prior to the deposition of the film specimen. Any poor cleaning procedures were readily demonstrated by poor adhesion of the titanium-gold contacts, since "bad" areas could be stripped from the substrate by ultra-sonic agitation.

Other methods of cleaning were attempted, but this procedure was found to be the most reliable.

3.2.2. Vacuum Evaporation

The deposition of the thin film targets was performed using two basic systems; a conventional bell-jar coating plant was used for preparing contacts and normal specimens, and a bakeable stainless steel UHV system was used to prepare low contamination aluminium films with highly reproducible characteristics.

3.2.2.1 Conventional System

This consisted of a twelve inch diameter bell-jar chamber pumped by a 6 inch diameter liquid nitrogen trapped oil diffusion pump with a maximum pumping speed of about 500 litres sec⁻¹. The pump and chamber were separated by a baffle-type isolation valve so that the pumping system could operate continuously when the chamber was opened to atmospheric pressure. The diffusion pump was backed by
a 50 litre min⁻¹ rotary pump which also functioned as roughing pump for the evaporation chamber when valved off from the diffusion pump (see Holland (36), Spinks (102).) The vacuum flanges, bell jar, and vacuum valves were sealed by 'Neoprene' rubber in the form of 'O'-rings, 'L' rings or valve flaps. The chamber pressure was measured with a triode type hot cathode ionisation gauge, and for rough and backing-line pressures a Pirani gauge was used. Electrical power for heating the evaporation sources was supplied to the chamber by shielded heavy duty 'lead-ins', which also served as supports for the heavy gauge copper source holders. The source to substrate distance was normally kept large to ensure uniform deposition, and to prevent collection of the contaminants which evolve as the source is heating-up; a shutter operated manually through a Wilson rotary shaft seal, shielded the substrates until evaporation was under way.

3.2.2.2 Ultra High Vacuum Chamber

The UHV chamber was designed as an evaporating chamber which could also be adapted for use with an ion accelerator as a target chamber, to permit single pump down and bombardment experiments for future low-contamination applications.

The 12 inch diameter bakeable stainless steel chamber was mounted on a titanium sublimation pump with a pumping speed of 3000 litres sec⁻¹, and connected to a 1200 litre sec⁻¹ Ferranti getter-ion pump. To extend the life of the getter-ion pump it could be isolated by a baffle valve and maintained under vacuum while the chamber was opened at atmospheric pressure. The baffle was a totally enclosed type operated manually by a screw using a stainless steel bellows to transmit motion without breaking the vacuum seal. The chamber was brought up to atmospheric pressure by admitting dry nitrogen, to prevent absorption of unwanted gas and vapour from the air. While any
vacuum port was removed for changing specimens or recharging the evaporation unit, the interior pressure was maintained just above atmospheric by pressurised dry nitrogen, in order to prevent in-flow of airborne contamination. Figure 3.1 shows an overall view of the UHV apparatus.

The chamber was rough pumped to about $10^{-5}$ Torr by sorption pumps containing M X 13 molecular sieve material, cooled with liquid nitrogen. The pump down schedule included a medium-low temperature bake-out at $70^\circ$C for 24 hours. The temperature was limited to $70^\circ$C because Viton seals were used in some frequently-opened ports, otherwise metal seals employing indium, aluminium, gold or copper (Conflat) were fitted. The chamber temperature was regulated by a microcircuit controller, fig. 3.2, with a chromel-alumel thermocouple sensor placed in the warmest part of the chamber. The controller was linked into the heater relay switch and timer units. The getter-ion pump was operated continuously and augmented by operating the titanium sublimation pump periodically. In this way a pressure of 1 or $2 \times 10^{-9}$ Torr could be attained within 48 hours of sealing the chamber, and held for many days.

The pressure was measured using a Vacuum Generator type IGl Bayerd-Alpert gauge, and an experimental version of the Edwards mass spectrometer was used to analyse the residual gases present in the chamber. Measurements were made before and after outgassing and during evaporation to check for contamination. The main contaminants were water vapour ($\text{H}_2\text{O}$, mass 18) and nitrogen ($\text{N}_2$, mass 28) although some other materials ($\text{N}$, $\text{O}$, $\text{OH}$, Ne, $\text{O}_2$, Ar) and several others were also evident, but were reduced considerably by outgassing. During evaporation nitrogen was evolved as the major residual gas.

Evaporation was performed using an electrically heated helical
FIG. 3.1 U.H.V. APPARATUS AND CONTROL UNITS
Input from Thermocouple

Thermocouple Amplifier

Input from Thermocouple Amplifier

Level Comparator

Output to Oven Control

Fig. 3.2 Microcircuit Controller for Bakeout Oven
tungsten filament. It was found that the operation and life of the filament were improved considerably by pre-melting the aluminium charge onto the filament, in a conventional vacuum chamber, prior to loading into the UHV evaporator. To prevent evaporated film building up in the chamber where it could flake off and damage the seals and pumps, the evaporator was surrounded by a chimney-shaped shield, fabricated in nickel wire and sheet, fig. 3.4. The evaporator was specially designed, by the author, in a coaxial pattern to fit on a small flange and after loading into the chamber the much larger chimney shield was press-fitted in place through the large diameter specimen holder aperture. The substrates were carried, in batches of eight, on a rotary specimen holder, operated from outside the chamber by a Vacuum Generators type RDL rotary drive. The holder also carried a quartz crystal monitor for measuring the thickness of films deposited, Fig. 3.3.

The deposition rate achieved in this apparatus was generally greater than 10 Å sec⁻¹, at a background pressure of better than 10⁻⁸ Torr. The "ratio of incidence" (10³) of metal to gas atoms, mainly nitrogen, was then about 10³: 1. The use of tungsten filaments with aluminium may be accompanied by contamination of the film by a tungsten-aluminium alloy (Holland 1956). The tungsten content of a UHV evaporated film was examined by a charged particle Rutherford back-scatter technique using 1.5 MeV He⁴ (Tinsley, private communication) and was found to be below the limit of detection, which was less than 1 part in 500. Properties of the materials used in the evaporations are given in table 3.1. The tungsten helical coil filaments used to evaporate aluminium and titanium were manufactured from multistrand wire to provide good 'wetting' with the evaporant and uniform evaporation (104). Copper and gold were evaporated from
**FIG. 3.3 U.H.V. ROTARY SPECIMEN HOLDER**

**FIG. 3.4 U.H.V. EVAPORATOR WITH COAXIAL CONDUCTOR MOUNTING AND DEMOUNTABLE CHIMNEY SHIELD.**
heaters made from molybdenum foil, bent into a bridge shape for strength (36) and dimpled to hold copper pellets or gold wire balls. An electron gun source was used for the evaporation of tantalum since it is so highly refractory. This was of the AWRE pattern described by Arnison (105) and used a tantalum rod held at high tension, 3-4kV, heated by electrons emitted thermionically by a ribbon filament cathode, and surrounded by a water-cooled collimating radiation shield. Silicon monoxide for passivating coatings was evaporated from a tantalum-foil tube source, the vapour issuing from a narrow slit. The composition of vapour deposited silicon monoxide depends upon the source temperature (106) and densities can vary between 2 and 2.3 gm cm$^{-3}$, compared with 2.15 gm cm$^{-3}$ for the source material. To maintain the correct composition the source temperature was measured using an optical pyrometer and kept at 1250°C for all evaporations.

TABLE 3.1

<table>
<thead>
<tr>
<th>Material (Purity, %)</th>
<th>Melting Point (°C)</th>
<th>Evaporation Temperature (°C) $p = 10^{-2}$ Torr</th>
<th>Evaporation Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium (99.99)</td>
<td>659</td>
<td>1220</td>
<td>W, helical coil</td>
</tr>
<tr>
<td>Copper (99.9)</td>
<td>1084</td>
<td>1260</td>
<td>Mo, dimpled-foil</td>
</tr>
<tr>
<td>Gold (99.99)</td>
<td>1063</td>
<td>1400</td>
<td>Mo, dimpled-foil</td>
</tr>
<tr>
<td>Chromium (99.9)</td>
<td>1900</td>
<td>2400</td>
<td>W, conical basket</td>
</tr>
<tr>
<td>Titanium (99.9)</td>
<td>1700</td>
<td>1750</td>
<td>W, helical coil</td>
</tr>
<tr>
<td>Tantalum (99.9)</td>
<td>3000</td>
<td>3060</td>
<td>electron-gun*</td>
</tr>
<tr>
<td>Silicon Monoxide (99.9)</td>
<td>1200-1250</td>
<td></td>
<td>Ta, boat</td>
</tr>
</tbody>
</table>

*AWRE pattern electron gun (105)

High purity materials obtained from Koch-Light Laboratories, Colnbrook, Bucks.
According to the application different geometries were chosen for the film samples and these were obtained by the use of masks specially fabricated in metal foil and wire and held in aluminium frames. The standard substrate size was 1 inch square and since the source to substrate distance was large, several samples could be deposited side-by-side with less than 10% spread in thickness between extremes.

3.2.3 Contact Formation

In a study of this nature, it was essential to make reliable and repeatable low resistance contact to the thin film specimens. In many cases a simple pressure-contact was acceptable but for very thin films thick contact areas were required to avoid damage. A separate evaporation was required and in some aluminium films the resulting structure changed resistance in an anomalous manner. Another method is to soft solder leads to the contact areas but this is not possible with metals which readily form highly protective oxides (e.g. Al, Ta, Ti) and those which do not wet with solder or adhere insufficiently well to the substrate. Silver loaded paste was used to bond lightly loaded thin wires, but the contacts were difficult to position accurately, and when dry were brittle.

A method of making contacts which overcame most of these difficulties was developed by the author by using a two layer method employing titanium and gold. Gold has a low resistivity and a low contact resistance but poor adhesion to glass. Adhesion between gold and many metals is good however, particularly for titanium, and this combination is used in some microcircuit fabrication techniques because of its high etch resistance (Rathbone, Private Communication). Titanium can adhere strongly to glass and was readily available for evaporation as a bonding under layer or "metallurgical glue" for thick gold films. Only about 100 Å of titanium was required but it was
essential for titanium and gold to be evaporated in sequence in the same pump-down, with the least possible delay and the use of shutter-shielding (section 3.2.2.1) to prevent inadvertent contamination. Any contamination or incomplete substrate cleaning resulted in non-adhesion.

The edges of the contacts were "shadowed" by the use of out-of-contact and round-wire masks to give a ramp edge. Step edges are to be avoided when layered contacts are made since they can result in weak or broken connections. The contact patterns made with the titanium gold method were sufficiently robust to provide very strong solderable contacts, and could withstand the cleaning schedule (Section 3.2.1) thus permitting large batches to be prepared well beforehand and cleaned immediately before use.

3.2.4 Measurement of Film Thickness

Several techniques were employed in the measurement and monitoring of the thickness of vacuum films.

These were:-

1. Fizeau Fringe optical interferometry
2. Optical transmission and reflection
3. Quartz crystal microbalance (three types used)
4. Talystep

Quartz crystal microbalance and optical transmission methods had the advantage that they could be used in situ during vacuum deposition to determine film thickness and growth rate, but were dependent upon knowledge of the film composition.

Fizeau fringe interferometry and the Talystep machine recorded only the film profile, and had the practical disadvantage of damaging the film and destroying their further use as resistors.

3.2.4.1 Optical Transmission

This method of measurement employed a modified Edwards High
Vacuum unit in which a mechanically chopped light beam was aimed through film substrate with a mirror system and picked up using a photocell and frequency selective amplifier.

An advantage of the system was that the detecting apparatus was never contaminated by the evaporant, unlike the quartz crystal microbalance. However, calibration was required for each material, setting up was lengthy and measurements were limited to transparent films (≤ 200 Å of Al). Because of these disadvantages the optical method was limited to use in non-precision applications.

3.2.4.2 Fizeau Fringe Interferometer

The interferometric method of measurement of film thickness (107) was initially our sole means of assessing the evaporated film. The apparatus required was simple and a microscope was adapted for the purpose of viewing the fringes. The light source was a mercury vapour lamp restricted by a pin hole and placed distant from the interferometer, to provide a near parallel beam. The beam was then reflected down onto the specimen by a glass beam splitting plate, half silvered on its front face. Above the specimen a half silvered optical flat was supported at a very shallow angle, and optical interference could then occur between light reflected from the silvering of the reference plate, formed by the underside of the optical flat, and the specimen surface. The microscope was then used to view the interference pattern of dark and light fringes. For a flat specimen the fringes are equally spaced and occur at each half wavelength increment in the difference between the optical paths of the interfering beams. When the fringes cross a step in a surface the light and dark bands are displaced. The height of a step in the film simply adds to the path length and displaces the fringe along the optical flat. The displacement in the fringes is proportional to the film step height, and if \( t \) is film thickness, \( x \)
the displacement and s the spacing of the fringes then given by:

\[ \frac{t}{\lambda/2} = \frac{k}{s} \quad \therefore \quad t = \frac{k}{s} \frac{\lambda}{2} \]

where \( \lambda \) is the wavelength of the light, in this case 5461 Å, the mercury green line.

The displacement \( x \), and fringe spacing \( s \) were measured by inspection, or from photographic plates and enlargements. The accuracy of measurement was about one tenth of a fringe spacing, that is about 250 Å.

### 3.2.4.3 Quartz Crystal Monitor

Quartz piezo-electric crystals have become widely used as frequency determining elements in high stability precision oscillators. When the crystal plates are cut in line with particular crystallographic orientations, e.g., AT and BT cuts, they possess the very useful property of zero temperature coefficient of frequency of resonance near to room temperature.

The AT and BT cuts promote piezo-electric vibration in the "thickness shear" modes, in which the major surfaces of the crystal are antinodal. In this condition it is possible to add material to either or both of the crystal surfaces and cause a change in the frequency of resonance in proportion to mass, and independently of thickness, density, elastic constant or stiffness of the added material. The inherent stability of the crystal oscillator system and the sensitivity of frequency measurement techniques permits the detection and measurement of very small masses deposited on the crystal faces. Thus quartz crystals may be made into almost ideal deposition monitors for thin film experiments.

Several models of quartz crystal monitor were used.

The first unit was designed by Muggleton and Howe (108) of the Special techniques Group, AWRE Aldermaston. 1 MHz crystals were
employed and for aluminium deposits the thickness-frequency sensitivity was 10 Å Hz⁻¹. The method of measurement of frequency deviation was as follows. Two oscillators using initially identical crystals were operated so that one was a reference and the other the mass sensing unit. The two oscillator outputs were then mixed electronically and filtered to obtain a signal representing the difference frequency. The difference frequency was then displayed on a digital frequency meter. Unfortunately the circuitry permitted a coupling between the two oscillators that allowed each to "pull" the other when the difference frequency was small. This caused an anomalously low determination of deposited mass at small difference frequencies.

Another, more sensitive and more complex circuit was built* to a design due to Lawson (109). Quartz crystals of 4.15 MHz resonant frequency were employed and these provided a thickness-frequency sensitivity of 1 Å Hz⁻¹ for aluminium. The crystals were obtained from the Quartz Crystal Co. Ltd., New Malden, Surrey, and were manufactured with specially bonded 4-point edge contacts. The principle of operation was as described above, and both a linear analogue meter and digital frequency meter were used. This proved quite satisfactory in operation, except for the one shortcoming that some crystals appeared to cease oscillation when only a small amount of deposit had been accumulated. However when this occurred the evaporated deposit was removed chemically. As a simple precaution aluminium was made the initial deposit on each crystal. A solution of warm caustic soda (sodium hydroxide) could then be used to take off the deposited layer without attacking either the quartz crystal or the gold electrode. The crystal unit was then rinsed in distilled water and dried with ethyl alcohol and warm air.

The third quartz crystal monitor used was a commercial unit

*Mr. T.D.J. Cameron, AWRE, Ion Effects Group
manufactured by Edwards High Vacuum. It is described in detail by Steckelmacher (110) and Holland (111) and differs from the above units in that its reference crystal frequency is deliberately chosen to be 500 kHz above that of the mass sensing crystal, nominally 6.0 MHz; A second mixer with a low frequency variable reference oscillator is then used to enable the zero beat condition to be reset at will, regardless of the deposit accumulated on the sensing crystal, up to the limit of frequency change linearity (typically 100 kHz total deviation).

This monitor was used in the UHV evaporator and the frequency output voltage was recorded on a graph plotter to show evaporation rate, and a digital frequency meter was wired into the circuit via a filter network to measure beat frequency directly and with high accuracy.

3.2.4.4 Talystep

The "Talystep" machine is manufactured by Rank-Taylor-Hobson, and provides a mechanical measurement by means of a moving stylus transducer. The output of the moving coil transducer is amplified electrically and presented upon a conductive paper strip recorder. Using the Talystep a 2mm length could be scanned and the profile recorded on a strip chart.

The sensitivity of this machine (maximum vertical amplification of x 10^6) was so great that disturbances on the sample surface due to grit and dust and long undulations in the substrate could cause problems when examining very thin films. The former disturbances could be minimised by careful preparation, storage and handling of the samples, but the latter occurred in the original manufacture of the substrate. The normal microscope slides manufactured by Chance display considerable roughness, whereas the Corning 7059 Borosilicate glass slides display a very smooth but slightly undulating surface. (Corning 7059 glass is one of the Corning Microsurfacer range of glasses
and features both a smooth surface and a very low electrical conductivity).

The talystep measurement was used for three significant measurements:

1. Film thickness calibration
2. Bombardment profile of film
3. Sputtering removal of film and substrate

3.3 ION BOMBARDMENT

3.3.1 Ion Accelerator

The accelerator used for the irradiations is shown schematically in Fig. 3.5 and a photograph of the beam line target apparatus and control equipment is shown in Fig. 3.6. Ions were generated in a gas plasma in a radio frequency type ion source, using capacitive coupling to excite the plasma from a double triode oscillator, running at 85 MHz and a power level of about 100 watts. The source was similar in construction to that described by Collins et al (112), the canal length being kept short in order to reduce positive ion losses due to charge exchange. The ions were extracted from the source by applying up to +4 kV to the water-cooled probe electrode, and the beam was accelerated and focussed by a two cylinder gap lens with up to 30 kV applied across the gaps. A Cockroft-Walton type multiplier driven by the 50Hz supply was used to generate the EHT.

Power to the equipment at EHT in the "bun" was supplied by an isolating transformer.

The beam was mass analysed using 20° magnetic deflection with a maximum usable flux density of about 0.5 Tesla. After analysis, the beam was passed through two sets of deflector plates set at right angles so that the beam was swept across the specimen by two independent free running oscillators, with frequencies of about 2 Hz and 50 Hz. The scanned area was much larger than the specimen so that the irradiation of the specimen was uniform.
FIG. 3.6 VIEW OF 30KeV ACCELERATOR FROM TARGET END.
The source, accelerator and magnet box were pumped by a 6-inch diameter liquid nitrogen-trapped oil diffusion pump. A beam stop after the magnet, which also acted as a pumping restriction isolated the target chamber region, which was pumped by another 6-inch liquid nitrogen-trapped oil diffusion pump. The pumps were connected to the beam line manifolds by water cooled baffle valves and were run continuously, and in this way pressures better than $10^{-6}$ Torr were readily attainable. The pumps were fitted with automatic cutout valves to protect the system in the event of mains failure.

Most of the work was conducted with two ion species $O_2^+$ and $Ar_1^+$. The $O_2^+$ beam was selected since it had a higher intensity than the $O^+$ beam. However since molecular ions dissociate into two particles on striking the target surface, the effective ion energy is only half the original ion energy, i.e., 15-17 keV. Ion current densities of $5-10 \mu A \ cm^{-2}$ were available with $Ar_1^+$ and $O_2^+$ at 30 keV.

3.3.2 Target Techniques

Many different parameters of the target material were measured during bombardment in addition to the continuous measurement of ion dosage. Some parameters eg resistance, could be measured easily in situ and without interruption of bombardment. Other measurements required specialised techniques which could not be applied to the specimen without removal from vacuum. In order to facilitate such measurements the target chamber was designed with a very small volume for rapid pumping and turn round. The chamber was connected to the beam line by a 2 inch baffle valve. The target chamber was separately pumped to rough vacuum by means of a backing pump by-pass line. The target chamber was then connected to the main pumping manifold by opening the 2 inch baffle valve, and the large evacuated volume of the manifold acted as a vacuum reservoir and provided a very rapid pump down in conjunction with the wide pumping path to the diffusion pump.
The target chamber was also provided with a Pyrex glass coldfinger liquid nitrogen trap. The trap was capable of reducing the pressure of the target chamber by one order of magnitude below that provided by the diffusion pump, i.e. to about $10^{-7}$ Torr, and was essential for the removal of hydrocarbon vapours which can otherwise be decomposed by the ion beam and build up many monolayers on the specimen surface.

The target specimens were normally mounted on a stainless steel plate bolted to the target chamber and sealed by a Viton O-ring. The methods of in-situ monitoring will now be described.

3.3.2.1 Measurement of Ion Current

When a current of heavy ions strikes a target many types of secondary emission occur, and these may cause error in the measurement of ion current.

The main emission phenomena are:

1. secondary electron emission
2. secondary negative and positive ion emission
3. reflection of ions.

Other particles may be emitted by sputtering, but these are uncharged, and therefore do not, in themselves, modify target current. A masking baffle was used to define the area of bombardment, and this can also give rise to secondary currents which may be collected by the target. The measured target current is given by

$$I_T = I_P + I_o$$

where $I_o = \text{total current error}$

$I_P = \text{true primary beam current}$.

The largest component of the error current is normally found to be that produced by secondary electron emission ($I_S$), and may be as large as or larger than the primary ion current. The ration $I_S/I_P$ is known as the secondary electron emission coefficient and will be termed $\gamma$. 
The γ term was measured to be as great as 10 in value in some cases. The energy distribution of secondary electrons is such that the majority of electrons have only low energy, i.e., <25 eV.

Secondary ions are known to emit at only about 1% of rate of secondary electrons, and the yield of reflected ions is normally of the order of 1% of the secondary ion rate (113). The most serious error, therefore, is caused by secondary electron emission. In order to remove this error secondary electron suppression electrodes were incorporated in the target assembly, as shown in Fig. 3.7.

The secondary electron control electrode was built in the form of a rectangular section tube and was mounted close to the target. Application of negative bias voltage to this electrode suppressed electron emission from the target, while positive bias permitted electron emission, and provided a measure of secondary emission. A screen was placed between the control electrode and the masking aperture, in order to suppress any current scattered from the masking aperture, which could be accelerated or rescattered on to the target by the secondary electron control electrode. An auxiliary screen was also incorporated to further impede the passage of scattered particles. For biases greater than +25 volts the characteristic was virtually constant to several hundred volts, and normally a potential of -100 V was used to suppress secondaries, and +100 V to measure secondary emission effects.

In all cases the ion beam fell at normal incidence on to the target within a deflection angle of ±0° 8'.

3.3.2.2 Dosimetry

Current picked up by the target was monitored by an electronic nanoammeter and the output was integrated electronically to provide a measurement of total dosage. The ion beam was scanned across the target so that the target current was composed of pulses. The acceler-
FIG. 3.7 TARGET CHAMBER BASE FLANGE

FIG. 3.8 SUBSTRATES IN STAGES OF PREPARATION
ator and analysing system were subject to a small drift with time which was sufficient to misalign the beam. As a visual aid for correcting drift the output of the current monitor was displayed on an oscilloscope whose horizontal amplifier was coupled to the horizontal ion beam scanning waveform. Then, by centering the oscilloscope trace with manual adjustment of the analysing magnet system the ion beam could be maintained accurately in alignment with the centre of the target.

The current monitor circuit was designed by the author and had advantages over the commercial units used previously. The amplifier was designed as a direct current meter and by using a virtual earth circuit presented only a very small voltage drop across its input terminals. (This may be thought of in terms of low input impedance.) The current sensitivity on each range, \( \frac{\text{voltage output}}{\text{current input}} \), was defined by feedback employing high stability precision resistors. The input current ranges for full scale deflection were arranged in decade steps from 10 mA to 1 nA, with a multiplier on the output meter to increase the reading sensitivity by a factor of ten, ie 100 pA. The advantages of low input impedance for this type of instrument are:

1. avoidance of large voltage drops, therefore the target is maintained very close to earth potential. This avoids excessive secondary emission due to autobias.
2. the capacitance of screened cables, carrying the target current to the amplifier, does not distort the time dependent current waveform.
3. the effects of stray impedance and leakage currents in the connection to the amplifier are minimised as the voltages are always very low.
4. stray signal pickup and hum is minimised.

A further advantage of this system was that a "voltage-
clamping" overload protection network could be incorporated into the input circuit, and so prevent damage by even quite large current and voltage pulses. It was found later that in the presence of poor earth- ing systems voltage breakdowns in some accelerators could cause extremely large mains borne surges, and protection against such surges was also devised.

The electronic current integrator was constructed as part of the same current monitoring instrument and was also designed by the author. The circuit functioned as a voltage-to-frequency converter in that it provided output pulses at a rate proportional to the voltage input. It was connected directly to the output of the current sensitive amplifier. Each output pulse then corresponded to an increment in dose and by counting the pulses in, say, a Nucleonic scaler a digital record of the total dose was obtained. The limit to the total measurable dose was set by the number of decades available in the scaler instrumentation, and in this case up to six decades could by used. The design of the instrument is described later in Section 3.5.

3.3.2.3 Resistance Measurement

The resistance of the target film was monitored continuously during bombardment. At low resistance values, eg, a few ohms, conventional resistance meters could be employed (eg Avometers) but at the highest values of resistance an insulation-tester was used. When continuous recording of resistance was required at values of resistance below about 100 kΩ, a simple electrical circuit was used in conjunction with a chart recorder. The very simplest circuit shown in Fig. 3.9 supplied current to the target film and voltage drop across the specimen was taken to the y-axis of an X-Y recorder. The x-axis was driven by the output of the current integrator so that a resistance-versus-dose curve was drawn automatically. The digital current integrator signal
Fig. 3.9 Simple Current Source for Monitoring Film Resistance during Implantation

Fig. 3.10 Potentiometer for Continuous Recording of Resistance and Temperature for TCR Measurement
from the nucleonic scaler was converted to an analogue signal for the
recorder and since the curve consisted of steps of integrated dose, the
resistance corresponding to any particular dose could be read quite
accurately.

3.4 POST BOMBARDMENT DIAGNOSTICS

3.4.1 Temperature Coefficient of Resistance

The change of resistance with temperature in devices of
interest to this study is small, i.e. of the order of tens or hundreds of
parts per million per degree centigrade change in temperature
(abbreviated to ppm/°C)

\[
1 \text{ ppm/°C} = 10^{-4} \% / ^\circ C
\]

The method of measurement, therefore, has to be sensitive to
a few parts in a million and to achieve this sensitivity a potentiometer
method was chosen. A minimum off balance indication of better than
10 ppm, with a bridge supply voltage of 10 volts, was achieved by using
a sensitive X-Y recorder and precision reference resistors in the circuit
shown in Fig. 3.10.

Thus for small deviations, \( R_x \) the out-of-balance signal is
directly proportional to the change in resistance. Note that the supply
voltage and potentiometer connections are arranged so that increases in
the resistance \( R_x \) cause a positive out-of-balance signal, and decreases
in \( R_x \) caused negative signals, thereby removing possible ambiguity from
determination of the sign of temperature coefficient.

In order to permit continuous recording of the resistance-
temperature characteristic a thermocouple was placed as close as
possible to the sample resistor and clamped on to the resistor substrate.
The output of the thermocouple was then used to drive the one axis
(x-axis) of an X-Y recorder, while the out-of-balance voltage from the
potentiometer circuit was measured on the other axis (y-axis) of the
recorder.

Heating or cooling the specimen then produced a continuous recording of its resistance-temperature behaviour. In general the procedure adopted was to cool the specimen to liquid nitrogen temperature, then to heat in boiling water, and finally to permit cooling to room temperature. In this way any hysteresis or thermal lag in recording temperature resistance characteristic was detected and could be taken into account in assessing experimental errors. The specimen was clamped by contacts on an aluminium holder and enclosed in a cellulose nitrate 1\(^{\text{st}}\) diameter test tube for protection. The tube was partially sealed, and half immersed in the cooling or heating bath. An advantage of this system noted during cooling experiments was that of low vapour contamination. Since the tube was cooler than the sample the moisture contained within the sample ambient atmosphere was condensed on the tube walls, and not on the sample. Such contaminating vapour could cause leakage currents in the sample, and to test the effect of contamination in this system a measurement of leakage resistance during the cooling cycle was measured. With an applied voltage of 500 volts a resistance of greater than 10\(^{13}\)\(\Omega\) was measured throughout the cycle.

On completion of a thermal cycle on a specimen, the resistance axis of the plotter was calibrated by directly substituting a standard resistance box for the sample. Thus any non-linearities that may have occurred for large resistance deviations were compensated by the calibrated scale.

At high resistance values the temperature coefficient of resistance could be large and negative. In this case the resistance scale was so grossly non-linear that the potentiometer method was quite inappropriate. The currents involved in resistance measurement were low
and required very sensitive detection, and for this the current-sensitive section of the current integrator system, devised originally for ion beam measurement was used. The output of the amplifier was then used to drive the Y-axis of the chart recorder, and when the specimen was supplied from a fixed voltage the chart plotter provided a direct measurement of conductance against temperature. The wide range of the current sensitive amplifier, and the low input impedance, made it an ideal instrument for this purpose.

3.4.2 Measurement of Electrical Noise

The procedure used followed the recommendations of the DEF-5115 (118) specification in which the R.M.S. noise generated in one decade bandwidth centred on 1KHz is measured in microvolts referred to one volt bias across the resistor. The specimen under test was biased from a decoupled variable battery source, to avoid mains pick up, through a high value low noise resistor for isolation. The bias voltage was measured with a Digital Voltmeter, which was removed during noise measurement. The resistor noise was amplified and filtered by a low-noise band limited amplifier; and then indicated on an oscilloscope and measured on an RMS Voltmeter. The amplifier centre frequency was variable so that the resistor noise output could be measured against frequency. The equipment did not permit measurement of the change of noise amplitude with temperature and this was not investigated. The limit of measurement of noise voltage by this apparatus was of the order of 0.1 \( \mu \)V RMS. The apparatus is shown schematically in Fig. 3.11.

3.4.3 Measurement of Optical Properties

The optical transmission and reflection of specimens mounted on glass slide substrates were measured using a specially adapted* Cook binocular microscope, which was equipped with a filtered light source and reflection and transmission facilities. A photocell detector was

*by T.D.J. Cameron, Ion Effects Group
Fig. 3.11 Apparatus for Resistor Noise Measurement
made for fitting to one eyepiece, permitting viewing and focussing through the other, although this was covered during measurement to cut out stray light. The output of the detector was amplified and indicated on a meter. With this apparatus the lower limit of detecting was about 0.5% for transmission or reflection, and areas as small as 0.1 mm dia. could be measured.

3.5 Description of the Design of a Digital Current Integrator

3.5.1 Current Sensitive Amplifier Section

The instrument was designed for beam current measurement in charged particle accelerator work over the current range 10nA to 10mA positive or negative. A D.C. amplifier is used with overall negative feedback to define the current sensitivity and to provide a low input impedance. The voltage at the amplifier input (which is connected to the target) does not exceed 10mV and thus avoids any significant voltage biasing on the target.

An output of 10 volts f.s.d. is provided at low impedance and feedback ensures that drift does not exceed 0.2% f.s.d. The frequency response of the amplifier extends into the mid audio frequency range in order that beams scanned at up to several cycles per second may be followed faithfully on an oscilloscope.

3.5.2 Theory

The circuit is essentially a differential d.c. amplifier with its non-inverting input grounded (see Fig. 3.12). The feedback resistance is placed between the output and the inverting input terminals.

\[ V_o = A (V_x - V_i) \]
\[ V_x = 0 \]
\[ = R_f \cdot I_t + V_i \]
\[ I_f + I_{in} - I_j = 0 \]
\[ V_o = -R_f \cdot A (I_{in}) / (A+1) \]

if \( A \gg 1 \) then

\[ V_o \approx -R_f \cdot I_{in} \]
Fig. 3.12 *Virtual Earth Feedback with D.C. Differential Amplifier*

\[ V_o = -A(v_1 - v_2) \]

Fig. 3.13 *Method of Magnifying Effective Value of Feedback Resistance, by using Attenuation in Feedback Path*
Thus the output voltage is directly proportional to the input current, and the current sensitivity is defined by the feedback resistor, \( R_f \).

On the very low current ranges the feedback resistor (\( R_f \)) may require an impractically large value and to avoid this an attenuator is used between the amplifier output and the feedback resistor on the most sensitive ranges. The effective value of the actual resistance is then multiplied by the inverse of the attenuation ratio, \( k \), and the theoretical circuit must be modified so that in Fig. 3.13

\[
R_f I_4 = k V_o - V_i, \quad V_o = -A V_i, \quad I_i = -I_4
\]

if \( kA \gg 1 \)

then \( V_o \approx -I_i (R_f/k) \)

3.5.3 **Input Impedance**

It is normal practice with current measuring instruments to provide a low input impedance so that current may be passed without introducing any unnecessary voltage drop. The type of feedback employed in this instrument (viz. shunt-current-negative-feedback) provides a low input impedance and its value is given by:

\[
Z_{in} = |\frac{\partial V_o}{\partial I_i}| = \left(\frac{1}{A}\right) \left[\frac{\partial V_o}{\partial I_i}\right] \quad \therefore Z_{in} \approx R_f/kA
\]

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<thead>
<tr>
<th>CURRENT RANGE</th>
<th>( R_f ) ohms</th>
<th>( A )</th>
<th>( k )</th>
<th>Effective ( R_f ) ohms</th>
<th>Zin ohms</th>
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</thead>
<tbody>
<tr>
<td>10 mA</td>
<td>1 K</td>
<td>-1000</td>
<td>1.0</td>
<td>1 K</td>
<td>1</td>
</tr>
<tr>
<td>1 mA</td>
<td>10 K</td>
<td>&quot;</td>
<td>&quot;</td>
<td>10 K</td>
<td>10</td>
</tr>
<tr>
<td>100 uA</td>
<td>100 K</td>
<td>&quot;</td>
<td>&quot;</td>
<td>100 K</td>
<td>100</td>
</tr>
<tr>
<td>10 uA</td>
<td>1 M</td>
<td>&quot;</td>
<td>&quot;</td>
<td>1 M</td>
<td>1 K</td>
</tr>
<tr>
<td>1 uA</td>
<td>10 M</td>
<td>&quot;</td>
<td>&quot;</td>
<td>10 M</td>
<td>10 K</td>
</tr>
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<td>1 M</td>
</tr>
<tr>
<td>1 nA*</td>
<td>-</td>
<td>&quot;</td>
<td>-</td>
<td>-</td>
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</tbody>
</table>

Note that on any range the input VOLTAGE for f.s.d. current is 10 mV. *Amplifier used without feedback on this range.
3.5.4 Circuit Description

The circuit diagram of the current sensitive amplifier is shown in Fig. 3.14, and is described in detail in the following sections.

3.5.4.1 Input Stage

The input stage is constructed from a matched pair of n-channel Junction gate silicon planar field-effect transistors (Texas Instruments Type 2N3819). F.E.T.s are used in this position because they have very high input impedance, and thus may be employed where very small currents are to be measured. The F.E.T.s (T1 and T2) form a long-tailed-pair differential stage and their source electrodes are fed at constant current by transistor T3 thereby ensuring stable bias current independently of variations in gate-source voltages. A potentiometer (VR1) is provided in the drain circuit so that balance may be set initially and take any component mismatch.

3.5.4.2 Second Stage

The differential output derived from the drain electrodes of T1 and T2 drives a second long tailed pair differential stage which is constructed from p-n-p silicon planar bipolar transistors T4 and T5 (S.G.S Fairchild Type V205). Again a transistor (T6) is used to provide a constant current 'tail' for the long-tailed-pair in order to reduce common mode amplification, but the main purpose of T6 is to provide isolation for the set-zero resistor VR2 so that it may be mounted remotely from the circuit without introducing spurious interaction in the signal circuitry.

3.5.4.3 Output Stage

The output is taken from the collector of T5 and a complementary transistor White-emitter-follower is employed here to provide a low impedance of medium power. This stage has to supply a large
Fig. 3.14 Circuit Diagram of Current Sensitive Amplifier Section
voltage and current swing and in order to provide sufficient bias current at extreme positive voltage without excessive power dissipation at the negative extreme, the normal emitter resistor has been replaced with a transistor constant current source (T9). Transistors T8 and T9 are run at a medium power level, and to ensure that these devices do not experience any large temperature rise due to power dissipation they are fitted with small finned heat sinks.

3.5.4.4 Frequency Response

This amplifier is designed for use in the frequency range of zero to a few kilohertz and to avoid possible instabilities outside this range the response is designed to cut-off at about 8 KHz by the use of step-networks across the collector resistors of T4 and T5. The output transistor T8 is stabilised by capacitive feedback from collector to base to remove a low level spurious oscillation occurring at several megahertz, and the main feedback resistors are shunted by small capacitors to reduce the gain by negative feedback outside the normal signal band, and prevent RF breakthrough from the radiation of the high power RF oscillator used in the accelerator ion source.

3.5.4.5 Over-voltage Protection

Input and output circuits are protected from damage by connexion to external high voltages by reverse biased catching-diodes. At the output diodes D5 and D6 prevent the output voltage exceeding either supply line voltage (i.e. + or - 15 Volts). At the input the maximum signal voltage occurs at about 10 millivolts and so the catching diodes D1 and D2 are biased to roughly half a volt using D3 and D4 in forward bias as low impedance low voltage reference points. An additional advantage of using such low voltage biasing is that the leakage current in D1 and D2 is made low, and by using especially low leakage types (S.G.S. Fairchild Type FD300) in this balanced configuration extremely low input leakage current levels may be obtained. The
output circuit is also protected against temporary short-circuit by the same 100 ohm series limiting resistor that forms part of the output over-voltage protection network.

3.5.5 Digital Integrator Section

The circuit shown in Fig. 3.15 takes the form of a voltage-to-frequency convertor and the input voltage is made proportional to the beam current. The output pulses are counted on a scaler which in so doing fulfils the integrating action to provide a digital representation of total charge.

Now $V_{in} = (R_f)I_{in}$ where $V_{in} =$ input voltage to integrator

$I_{in} =$ beam current

and $F_{out} = K.V_{in}$

$R_f =$ conversion constant

$F_{out} =$ output frequency (Hz)

thus $F_{out} = K(R_f). I_{in}$

$K =$ conversion constant

Since $F_{out}$ represents the number of pulses occurring in one second then the number of pulses occurring in a time $T$ is given by:

$$N = \int_0^T F_{out}.dt$$

Ignoring conversion inaccuracies $N$ will be the count on the scaler to the nearest integral number, with an error in this total of one digit in the least significant digit. This error is equal to the basic charge unit used, and in the interests of low error the unit is made as small as practicable. In this instrument the charge unit is one hundreth of the one-second-integrated value of the current range in use on the current sensitive amplifier.

Thus $N = \int_0^T F_{out}.dt = K R_f \int_0^T I_{in}.dt$, where $T$ is in seconds

and $(\text{basic charge unit})(N \pm 1) = \int_0^T I_{in}.dt$

giving: basic charge unit = I range x (one second) / 100 = $1/(K,R_f)$ Coulomb

3.5.6 Circuit Description

The voltage to frequency convertor operates as two distinct sections viz:—
1. a controlled current generator, which charges a capacitor

and

2. a fast discharge circuit which is automatically triggered when the capacitor voltage reaches a pre-determined level.

3.5.6.1 Controlled Current Generator

This circuit produces an output current proportional to its input voltage. The current controlling element is a junction-gate field effect transistor incorporated in a feedback loop, as shown in Fig. 3.16. The bias voltage on the F.E.T. gate controls the width of the conducting channel between source and drain electrodes and thus the apparent resistance of the device. The FET behaves in fact like a voltage controlled resistor. The field effect transistor is significantly better than the bi-polar transistor for this purpose. The bi-polar is limited, particularly at low currents because it relies on 'transistor action' (i.e. the multiplication of base input current to produce an output current) which becomes poor at low levels. As current flowing into the control electrode produces an error, comparable with leakage currents in the controlled output, in some circuit configurations the bi-polar transistor can be quite unsuitable (as was discovered by the author).

The wide range of control possible with a FET can be gauged from Fig. 3.17

The operation of the control circuit is as follows:-
referring to Fig. 3.15 the current flowing in the FET (T6 or T7) is sensed by means of a resistor (R15) placed in its source circuit. The voltage drop produced by the current is compared with the input voltage by the differential FET pair (T1 and T2). Any difference in the two voltages is amplified by T1 and T2, and then by a second differential pair T4 and T5 and this error voltage is fed back to the gate electrode of the current control FET in such a way as to reduce the initial error. The magnitude of the eventual error in this feedback system is small when...
Fig. 3.16 Schematic Diagram of Controlled Current Generator

Fig. 3.17 Characteristic of Junction Gate F.E.T. used as a Current Control Element
the gain of the amplifying stages is high. Referring to the generator
circuit represented schematically in Fig. 3.16:-

at the amplifier output \( V_o = A(V_i - V_2) = V_g + R_4 I_s \)

for the F.E.T. \( I_s = g_m V_g + I_{so} \) where \( I_s = \text{source current} \)

\[ g_m = \text{mutual transconductance} \]

Thus:-

\[ A(V_i - R_4 I_s) = (I_s - I_{so})/g_m + R_f I_s \]

differentiating w.r.t. \( V_i \) :-

\[ A (1 - R_4 (d I_s/dV_i)) = d I_s/dV_i (1/g_m + R_f) \]

\[ d I_s/dV_i = A g_m / (1 + g_m R_f (1 + A)) \]

if \( g_m R_f A \gg 1 \), then \( d I_s/dV_i \approx 1/R_f \)

or, using small signal notation

\[ I_s = V_i / R_f \]

Thus for a high gain circuit the output is defined by the input voltage
and the feedback resistor.

The input to the circuit is attenuated by a factor 2, by the
network \( R_1 \) and \( R_2 \), because the output of the current sensitive amplifier
can be large, i.e. an appreciable proportion of the supply voltage, and
if used directly it would unnecessarily restrict the voltage swings
available for the operation of the integrator circuitry.

3.5.6.2 Discharge Circuit

This uses an Unijunction-Equivalent (UJTE) comprising
complementary bi-polar transistors \( T_9 \) and \( T_{10} \). The trigger voltage
level is set by the potentiometer network \((P_3, T_{22} \text{ and } R_{23})\) and when the
voltage at the emitter of \( T_9 \) is equal to the potentiometer voltage the
circuit triggers into a conduction state. The current then flows through
\( D_3 \) to discharge the capacitor \( C_{11} \), and when this discharge is complete
the current drops to zero and the circuit returns to the initial non-conducting state. The diode $D_3$ is a low leakage type and is used to maintain good isolation of the discharge circuit from the capacitor prior to triggering. In addition $D_3$ protects $T_9$ from breakdown caused by excessive reverse bias across the emitter-base junction since as little as 4 volts may cause breakdown. The circuit is augmented by $T_8$ which further amplifies the current in the $T_9$, $T_{10}$ pair and improves the discharge characteristics when there is a high d.c. charging current.

At each discharge performed upon $C_{11}$, a pulse appears at the output, taken from the potentiometer network. The pulse is amplified and shaped by the output transistors $T_{15}$ and $T_{16}$, where $T_{16}$ provides both inverted and non-inverted forms of the pulse formed at $T_{15}$. The pulse has a fast rise, and an exponential decay controlled by $R_{30}$ and $C_{19}$.

The whole of the discharge is duplicated in complementary form for operation on the opposite sign of input and the required polarity of integration is selected by a front panel switch. The circuit for the integration of negative inputs has an additional transistor ($T_{14}$) to invert the output of the UJTE to drive the common output circuit.

3.5.7 Performance

The d.c. performance of the circuit can be seen in Fig. 3.18. The characteristic measured was that of output pulse period vs. input voltage since it was possible to measure time intervals more accurately than frequency at the very low frequencies generated by the circuit. Frequency is the reciprocal of the output period.

The voltage-frequency conversion performed by this circuit is linear to within about 1% over 2.5 order of magnitude, and the circuit operates with an increasing error at low input levels over a total of more than 3 order of magnitude.
Fig. 3.18 D.C. Response of Voltage to Frequency Converter Section of Integrator

Fig. 3.19 Overall Response of Instrument to Typical Pulsed Current from Ion Bombarded Target
The response of the circuit to pulsed inputs is shown in Fig. 3.19. For this measurement an approximately Gaussian shaped pulse of a constant amplitude and repetition rate was reduced in width to vary the average current. This is the most usual form taken by the beam current of an accelerator when it is scanned across the target. In Fig. 3.19 the average current is plotted against average pulse period and it can be seen that the characteristic is linear over a wide range. Errors arising from non-infinite gain in the current control amplifier, and from FET gate leakage currents (typically 30nA) amount to about 0.3% over the working range. Other sources, e.g. component tolerances, give a proportional error which is accommodated by a setting up procedure and calibration.
CHAPTER IV

OBSERVATIONS OF PROPERTIES OF ION IMPLANTED THIN FILM RESISTORS

4.1 Introduction

When heavy energetic ions were incident upon a thin metal film the bombardment phenomena described earlier caused physical changes in the film thereby modifying many important properties. The main properties of interest in this study were those which go to make a high quality electrical resistor material, i.e. sheet resistance, temperature coefficient of resistance (TCR), electrical noise and stability.

In this chapter the characteristics of the change of resistance during ion bombardment are described in detail for aluminium films and the resulting properties of the bombarded films when tested as electrical resistors are also described and compared with those of more conventional processes of manufacture. The results of subsidiary experiments on other materials are described in the Appendix. The most important effects of ion implantation upon thin films were:

(a) Increase in the sheet resistance over a very wide range, e.g. \(1 \Omega/\text{sq} \) to \(10^{12} \Omega/\text{sq}\).

(b) Change in the magnitude and sign of the TCR, i.e. a reduction in the initial positive value to zero, with further bombardment the TCR became negative and progressively larger.

(c) Increase in the current noise generated by the resistance as the value of sheet resistance was increased.

The physical processes causing these effects will be discussed in the next chapter where models of the formation and conduction processes are discussed. Only the experimental observations are described in this chapter.

Many other physical effects of bombardment could be observed. Amongst these, changes in thickness and optical transmission were detected, and generally quite significant increases in both quantities
were found. Optical reflection was decreased, and surface roughness increased. The coefficient of secondary electron emission could also be observed during the course of a bombardment by reversing the suppression field, and the coefficient was also found to vary with ion dose.

The adhesion of the film to the substrate, a quality of great importance in thin film electronic circuits, was also increased to a remarkable degree. Other workers have shown that the atomic structure of these films is altered considerably with bombardment to become a mixture of polycrystalline metal regions and a glassy matrix made up from material from the substrate and compound insulating phases incorporating metal from the film, and that conduction processes can be correlated with the new structure (101, 126).

4.2 Characteristics of Resistance Formation by Ion Implantation

4.2.1 Aluminium Films

Aluminium is used extensively for interconnection layers in integrated circuits and held promise for adaptation to thin film microcircuit resistor applications. It was used during preliminary work and was the most suitable and convenient material for the implantation experiments. The 30 KeV positive ion accelerator was used for bombarding the film specimens and the process first envisaged was by implanting oxygen to react chemically with the film to produce an oxide impurity phase.

The main requirements for the ion and target species, which were met by the oxygen-aluminium system were:-

(i) ion-target reaction producing a stable insulating phase

(ii) complete penetration of ion for films of typical resistor dimensions (i.e. a few \( 100 \, \text{nm} \) thickness)

(iii) an electrically stable starting material, capable of being manufactured reliably and reproducibly in thin film form.

The molecular oxygen beam (\( O^+ \)) at about 30 KeV was used for
its high intensity. On impact each ion splits into two atoms each having half the initial energy, and the mean projected range of 15 KeV oxygen ions in aluminium, by calculation using LSS theory, is about 300 Å. The sputtering rate for aluminium is relatively low and to examine the influence of sputtering on resistance formation without reaction with the ion, argon ions were used. Argon (Ar) has approximately the same calculated range and straggle as molecular oxygen ions of the same energy.

4.2.2 Effect of Oxygen Implantation on Film Resistance

The change in resistance with oxygen ion dose of an aluminium film was typified by the curve of Fig. 4.1. The slope of this characteristic changed during bombardment, Fig. 4.2., and displayed three distinct stages:

I an initial rapid rise of resistance with dose during which the film resistance roughly doubled and the slope reduced, followed by:

II a slower but linear increase in resistance with dose persisting until about half the "saturation" or "infinite" resistance dose, and

III a final extremely rapid rise in resistance at a rate which increased as very high resistance values were approached so that changes of many orders of magnitude occurred within the final few percent of the total dose.

The "saturation dose" is defined as the dose required to produce very high or near-insulator resistance values. It was found to vary with the initial film thickness, shown in Fig. 4.3., and was determined to within a few percent by taking the vertical asymptote to the dose-resistance curve. During the third stage an exponential rise of resistance with dose was found, but near to the saturation dose the exponent also increased.

Thus the resistance of a metal film could be increased over several orders of magnitude in a controlled manner by ion bombardment, but at high values great care is needed to obtain a particular value.
Fig. 4.1 Variation of Sheet Resistance of Aluminium Film with Dose of Oxygen Ions

Fig. 4.2 Slope of Dose vs. Resistance Curve of Fig. 4.1
Fig. 4.3 Initial Film Thickness vs. Ion Dose for High Value of Sheet Resistance or 'Saturation Dose'
because the rate of increase is very rapid.

When the film thickness was greater than the range of ions a completely different characteristic was observed. This situation is illustrated diagramatically in Fig. 4.4, showing that the film can be regarded as two layers with only the top layer being converted by ion implantation. The two layers, R1 and R2, are in parallel and the resistance becomes approximately the value of the lower layer, R2, and approaches a constant, or slowly increasing value, and no "saturation" occurs. This structure has other applications in implantation experiments, for example the upper layer may be used as a capacitor dielectric, (see Appendix A) in the investigation of conduction processes in implanted material (101), in ion range estimation, as a passivating layer or for trimming the value of thin film resistors.

The resistance-dose characteristics for a wide range of initial film thicknesses between the thinnest stable film and those thicker than the ion range are shown in Fig. 4.5, and their slopes in Fig. 4.6. In the thinnest films the linear stage II was absent.

4.2.3 Argon Bombardment

Argon ion bombardment was used to investigate sputtering alone in the absence of the reactive gas implantation obtained with oxygen. It was found however that for films thinner than the ion range no significant difference could be detected between the effects of argon and oxygen bombardment upon the electrical properties of the films. Some results for argon bombardment are shown with those of oxygen in Fig. 4.7. The figure is plotted to show the dose necessary to cause a given change in sheet resistance against the initial value of film resistance, and the good fit of the argon results with those of oxygen is evident. This result provides evidence that direct implantation from the ion beam does not make a significant contribution when films are thinner than the ion range, and that surface sputtering, and back sputtering at the film-
Fig. 4.4: Layered Structure and Equivalent Circuit for the case where Ion Range is Less than Film Thickness
Fig. 4.5 Sheet Resistance vs. Ion Dose for a Range of Film Thicknesses
Fig. 4.6 Slopes of Sheet Resistance vs. Dose Curves of Fig. 4.5 on page 95
Fig. 4.7 Ion Dose for a Given Change in Sheet Resistance vs. Initial Film Thickness
substrate interface (i.e. "recoil implantation") make the real contribution.

4.2.4 Temperature Coefficient of Resistance

The coefficient of the change of resistance with temperature is a vital parameter of resistor materials as it serves not only to denote the quality of the material but also to signify the nature of the conduction processes that are present.

The change of the TCR and the corresponding value of sheet resistance with ion dose for a typical film are shown in Fig. 4.8. An unbombarded continuous metal film possesses a high and positive value of TCR and a relatively low sheet resistance, which are changed from pure, bulk values by the presence of size effect and impurities. At the commencement of bombardment the TCR dropped rapidly, corresponding with the rapid rise in resistance during stage I (section 4.2.1). The temperature coefficient then tended towards a constant value of about +400 p.p.m./°C for the remainder of stage I and through stage II. At the onset of stage III, the rapid rise in resistance, the TCR dropped towards a zero value of TCR, and then became increasingly negative. This latter change in the sign of the TCR is typical of the addition of a semi-conducting or dielectric phase and is seen in many cermet type resistor compounds (section 1.2.3).

The transition through zero TCR is of particular interest as it offers a potentially high stability material with a relatively high value of sheet resistance. The TCR is really an average change taken over a specified temperature interval and closer inspection of the change of resistance reveals that a zero or very low value of TCR is the result of a change in the slope of resistance with temperature from positive to negative within the measurement interval (Fig. 4.9). In fact no physical process of conduction is independent of temperature, instead two opposing processes compensate over a narrow range and average to zero. The
Fig. 4.8 Variation of Sheet Resistance and TCR with Ion Dose
Fig. 4.9 Variation of Resistance with Temperature near to Zero TCR

Fig. 4.10 Variation of TCR with Sheet Resistance of Ion Implanted Aluminium Films
change in the spot values of TCR over the measured interval of 100°C was normally less than \( \pm 80 \) p.p.m./°C for a nominally zero average value.

The TCR and sheet resistance were found to be interrelated and followed the general trend for conventional resistor materials outlined in section 1.2.5, and shown graphically by a plot of sheet resistance against temperature coefficient. In Figure 4.10 several representative films of different initial thicknesses are shown. The thinner films possessed a higher initial resistance and lower temperature coefficient, and were generally found to attain near zero values of temperature coefficient at higher sheet resistances. Thus for low TCR at low sheet resistance initially thick films should be used, whereas for low TCR at high sheet resistance, thin films are preferable.

4.2.5 Drift and Annealing

The ion implanted aluminium films were tested under various forms of ageing and heat treatment to explore the stability of this process of resistor formation. The number of specimens available for testing was limited so that only small numbers were involved in each type of test precluding statistical correlations. The types of test were room temperature storage, which permitted largest numbers of specimens to be examined, testing under normal electrical loading, accelerated ageing and annealing heat treatments. It was found that, whereas drift in room temperature storage and on-load testing was of the order of a few percent for films below about 20KΩ/sq., films approaching 100KΩ/sq. and with large T.C.R.'s showed large drifts approaching 40% (Fig. 4.11). No correlation was found between the direction of drift and method of manufacture, that is bombardment temperature, ion species, or initial film thickness, but the number of samples in each category are too small to permit statistical analysis, and these results serve to indicate the potentialities of this process rather than an expected manufacturing tolerance.
Fig. 4.11 | Drift in Resistance value of Test Samples
Artificial or accelerated ageing was conducted on some specimens by heat treatment at temperatures up to 200°C in an air atmosphere, and up to 500°C in an inert gas atmosphere (Ar). Specimens treated to the highest temperatures, that is 500°C for a period of one hour, were destroyed and stripped from the substrate. At lower temperatures between 150°C and 250°C specimens were increased in resistance, the highest values being increased by the largest amount. For example a 6 KΩ/sq. resistor was increased to 120KΩ, and a 10 KΩ/sq. sample increased to 220 KΩ. In both cases the T.C.R. was changed from positive to negative and subsequently the specimens drifted to open circuit. In contrast specimens bombarded in a heated target chamber remained stable provided that the temperature of bombardment was not exceeded in use or testing, for example a specimen bombarded at 300°C remained within 10% of its value after treatment to 250°C.

Ageing at between 100°C and 200°C was found to cause specimens to decrease in value. Since a four-point resistance measurement technique was used this cannot be ascribed to "burning-in" the contacts as carried out by semiconductor manufacturers, and could indicate, for example, the partial annealing of the metallic component. The downward shift represented a greater fractional change for specimens of lower resistance as would be expected from their higher dependence on a metallic component of conduction. Prolonged exposure to these temperatures resulted eventually in an upward change possibly indicating a slow growth of the insulating phase or reduction in the metallic grain size with surface oxide growth, which although small, is nevertheless significant to thin film conduction processes.

These indicative measurements show that while aluminium may be suitable as a test material for the process of ion implantation of resistor films, it does show excessive drift under elevated temperatures unless heat treatment is used during formation. Materials of lower atomic
mobility, for example some refractory metals used for conventional film resistors, could prove more stable.

4.2.6 Electrical Noise

The generation of electrical noise in resistors is important for some applications, particularly those requiring high value resistors of low T.C.R. as in low level and high gain amplifiers. The fundamental source of noise in resistor materials is the result of thermal agitation on the conduction electrons and is termed Johnson Noise. All resistors display Johnson noise, and the mean square noise voltage is given by:

$$\overline{e^2} = 4 k T B R$$

where $k$ = Boltzmann's constant, $B$ is the bandwidth of observation, $T$ is the absolute temperature and $R$ is the resistance value. The noise voltage averages to a constant value at all frequencies within the bandwidth. Metal films that are continuous and have their resistivity increased significantly by impurity scattering or by size effect (surface scattering) display a much lower noise voltage than pure bulk metals owing to the smoothing effect on conduction flow of the increase in the probability of scattering (114).

Resistors that achieve high value by incorporating semiconducting or dielectric material, for example carbon resistors, in the conduction path produce a further noise which only appears and increases as current is drawn through the resistor. Its average amplitude is found to be inversely proportional to the frequency at which it is measured, and so it is termed "current noise" or "$1/f$ noise". Although the phenomenon is well known, it has not yet been explained on a satisfactory physical basis. Bell (114) reviewed many models and showed that none explained satisfactorily the $1/f$ noise spectrum. Bell favoured a model based on a queuing theory of electron transport impeded by potential barriers at gaps between grains. This explained the $1/f$ noise power spectrum in a way no other theory could, and indicated that noise would reduce as the number of parallel paths increase, and would increase...
as the number of series gaps. More recently Offner (115) attempted to explain current noise using a simple random walk model. However Hawkins (116) was able to show that this predicted wrongly that the spectrum became "white" at low frequencies and was identical to the simple trapping model of Burgess (117), thus throwing the field open again.

Ion implanted aluminium films of high value were examined to determine their noise generation. The variation of mean square noise voltage for a 1KHz measuring bandwidth centred on various frequencies is shown in Fig. 4.12 and shows a \( \frac{1}{f} \) spectrum. The variation of mean square noise voltage with the square of the direct current drawn through the resistor was found to be linear as shown in Fig. 4.13, and verifies that the noise present is current-noise. This demonstrates the presence of semiconductor or dielectric phases within the material, even when the T.C.R. was positive and therefore dominated by metallic phases. Table 4.2 summarises data obtained for a range of resistor values. Noise voltage rating is normally expressed in normalized terms as the R.M.S. noise voltage in a decade of frequency centred on 1 KHz, divided by the d.c. voltage bias across the resistor, in \( \mu \text{V/V} \) (118). Thus although the noise voltage was larger for higher value resistors, the noise voltage rating could be smaller than that of low value examples. However the phenomenon of "voltage-bursts", characteristic of semiconductors, was also observed for high value resistors. When this occurred trains of small pulses of voltage a few microvolts in amplitude and several tens of microseconds wide appeared at the resistor terminals when the bias voltage was greater than a volt or so. Prolonged operation at higher voltage removed the burst pulses in precisely the manner described by Bell (114) and indicates a conditioning process typical of the existance of potential barriers in the conduction path.

Annealing at moderate temperatures and ageing were not found to alter noise outputs. When gross changes in resistance were caused by
Fig. 4.12 Frequency Spectrum of Noise Power

Fig. 4.13 Variation of Noise Power with Bias Current
heat treatment or over-voltages, noise voltage became that characteristic of the new resistance value.

4.3 Comparison With Conventional Methods

In an earlier section (Section 1.2) it was shown that a large number of methods exist for the production of thin film resistors having a low temperature coefficient and a relatively high sheet resistance. The most useful way of summarising their properties and comparing them with the ion implanted thin film resistors is by means of the "universal-plot" of temperature coefficient and sheet resistance of the form used by Halaby (72) and Schwartze (92). These are the properties of primary importance, and furthermore are generally found to be interdependent. Stability, noise, and drift can only be compared once the potential of the process is established.

4.3.1 Sheet Resistance and T.C.R.

In Fig. 4.14 several established and experimental resistor materials are plotted together with representative curves for oxygen implanted aluminium film specimens of many different initial thicknesses.

Firstly it can be seen that the ion implanted films follow the same general trend shown by virtually all other methods with a gradual decrease in the T.C.R. value towards higher resistance followed by a change to negative values of the T.C.R. at the highest sheet resistance. Secondly the aluminium films lie very close to many different material "types"; e.g. at low resistance that is below about 100 Ω/sq. the thickest aluminium film is well within the T.C.R. range occupied by Nichrome alloy films, whereas in the high resistance region, that is greater than 1 KΩ/sq. the implanted film comes close to Cr-SiO cermet values. Over some ranges, especially in the 10 KΩ/sq. region, ion implanted resistors show a better combination of sheet resistance and T.C.R. than those of other manufacturing techniques.
Fig. 4.14 Superposition of Measured Properties of Ion Implantated Aluminium Films on Fig. 1.2, for Comparison with Conventional Methods.
4.3.2 Stability and Noise Performance

In addition to providing practical values of resistivity and temperature coefficient, the process of manufacture must ensure that these values remain constant for the life of the circuitry in which they are used. Factors which can change a resistor's performance are excessive temperature, electric field or electric current density and these are normally specified so that limitations in operating conditions may ensure that, for instance, power dissipation does not result in thermal damage, or excessive current cause electromigration in thin film components. A specification for these properties is set out in the H.M.S.O. publication DEF-5115 (118), which also includes test schedules on size, solderability, vibration resistance, fire risk, mould growth etc. These factors are important once the precise nature of use of the components is known, but need not be considered in a preliminary study such as this thesis. The performance specification does consider, in addition to stability and temperature coefficients, tolerance and noise which are of direct importance. Detailed specifications for a range of thin film resistor types are reproduced in Table 4.1.

<table>
<thead>
<tr>
<th>Type</th>
<th>Construction</th>
<th>Tolerance</th>
<th>Stability</th>
<th>TCR p.p.m.deg.C⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>RFG-2</td>
<td>Metal Oxide</td>
<td>± 5%</td>
<td>± 3%</td>
<td>± 500</td>
</tr>
<tr>
<td>RFG-3</td>
<td>Carbon Film</td>
<td>± 2%</td>
<td>± 1%</td>
<td>1200</td>
</tr>
<tr>
<td>RFG-7</td>
<td>Metal Film</td>
<td>± 0.1%</td>
<td>± 0.5%</td>
<td>500</td>
</tr>
<tr>
<td></td>
<td>± 0.5%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RFH-1</td>
<td>Metal or Oxide Film</td>
<td>± 5%</td>
<td>± 2%</td>
<td>± 300</td>
</tr>
<tr>
<td>RFH-2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Stability is measured as the maximum change in resistance value after 2000 hrs. on full load at 70°C.
The performance of various representative specimens of ion implanted aluminium thin film resistors is set out in Table 4.2, below.

TABLE 4.2
REPRESENTATIVE FIGURES FOR PERFORMANCE OF ION IMPLANTED ALUMINIUM FILM RESISTORS

<table>
<thead>
<tr>
<th>Sheet 1 Resistance (Ω/sq)</th>
<th>TCR(^1) (ppm/°C)</th>
<th>Stability(^*) (%/1000hr)</th>
<th>Noise(^+) (μV/V)</th>
<th>Initial Film Thickness (Å)</th>
<th>Ion Dose (mC.cm(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>+1000 to +400</td>
<td>± 10</td>
<td>0.05</td>
<td>100 to 400</td>
<td>1 to 15</td>
</tr>
<tr>
<td>1K</td>
<td>+900 to +200</td>
<td>± 5</td>
<td>0.2</td>
<td>80 to 400</td>
<td>1.5 to 20</td>
</tr>
<tr>
<td>10K</td>
<td>+300 to -400</td>
<td>± 0.5</td>
<td>3.0 to 12.0</td>
<td>80 to 400</td>
<td>1.5+ to 20.0+</td>
</tr>
<tr>
<td>100K</td>
<td>&gt;-3000</td>
<td>&gt;±10</td>
<td>&gt;12.0</td>
<td>80 to 400</td>
<td>&gt;1.5+ to &gt;20.0+</td>
</tr>
</tbody>
</table>

\(^1\) Taken at 20°C

\(^*\) Taken for 2000 hours at normal load and 10 hours at 150°C

\(^+\) Noise figure measured for a one decade bandwidth centred on 1KHz

Thickness of film measured by quartz crystal microbalance at deposition

Ion species: Singly charged Argon or molecular Oxygen at 30KeV
5.1 Introduction

In the previous section many observations of the diverse effects of ion implantation of thin aluminium films were described. In this chapter the electrical effects of implantation are discussed. Interpretations of the mechanisms by which electrical properties are changed are presented so that the formation, performance and structure of implanted resistors may be correlated. The changes caused by implantation of resistors in the initial metallic region will be discussed first. Then a model of the film formation and structure will be derived which permits interpretation of the properties of high resistance region, and can be extrapolated smoothly to the low resistance region. Finally a general computer model will be described, in which the film is represented by a network of resistor elements.

5.2 Low Resistance Region

In this region the film remains metallic in its conduction properties, that is it has a low relative resistivity and a positive T.C.R. with a linear variation of resistance with temperature, with no evidence of current noise generation.

The most significant feature of thin film conduction is that when the dimensions of the film become comparable with the mean free path of conduction electrons, then the scattering effect of the surface raises the resistivity of the film. If the electron mean free path is reduced in a film by implantation of impurities or by lattice damage the behaviour of resistivity becomes complex since the enhancement of resistance by size effect is diminished, while bulk value of resistivity is increased by scattering at defects.

The behaviour of thin film resistivity may be treated as follows:
\[ \rho(t) = F(x) \cdot \rho \]

where \( \rho \) is the bulk resistivity, \( \rho(t) \) the resistivity for a thickness, \( t \),

\[ F(x) = \frac{\rho}{(t/L)^2} \]

where \( (t/L) \) is the electron mean free path.

Now bulk resistivity is also a function of mean free path, given by:

\[ \rho = \frac{m \bar{v}}{n e^2 L} \]

where \( m \) is the effective electron mass

\( \bar{v} \) the mean velocity at the surface of the Fermi sea

\( n \) the number of free electrons per unit volume

\( e \) the electronic charge.

According to Sondheimer (1952) the quantity given by:

\[ \frac{n e}{m \bar{v}} = \left( \frac{8\pi}{3} \right) \frac{z^2 n^{2/3}}{\hbar} \]

is a constant for a given value of \( n \), thus the product, \( \rho \lambda \), is also a constant and so the film resistivity becomes:

\[ \rho(t) = \rho \cdot F(x) = \left( \rho \lambda \right) \frac{F(x)}{\lambda} \]

For \( x > 0.1 \) the simple form of \( F(x) \) may be used and:

\[ \rho(t) \propto \frac{1}{\lambda} \left[ 1 + \frac{3 \lambda}{8 t} \right] = \frac{1}{\lambda} + \frac{3}{8 t} \]

so that whenever the mean free path is reduced, then resistivity is increased, whether the size effect operates or not.

It is known however that the bulk resistivity of a simple metal is limited to approximately 200\( \mu\Omega \) cm when contributions due to all types of defect are summed, and thus for aluminium with an initial resistivity of about 4\( \mu\Omega \) cm (as observed experimentally for samples used) an increase in resistivity by a factor of 50 could be expected by this means, corresponding to a proportionate decrease in electron mean
free path. The most significant contribution to resistivity in a single phase metal is that due to impurities (33). Now Sondheimer (94) states that where the concentration of impurities in a metal is small but significant, the mean free path is of the order of the linear distance between impurity centres. Thus if \( n_1 \) is the concentration of impurities in a metal, \( N \) its atomic population and 'a' the atomic spacing, then the mean free path can be given by:

\[
\lambda \approx \frac{a}{(n_1/N)^3}
\]

Early in the bombardment of a metal film, when the mean free path is long, small changes in the impurity concentration can have a large effect on the mean free path and hence on resistivity. The reduction of the mean free path will also diminish the contribution of size effect to resistivity. As the mean free path becomes shortened, the further introduction of impurities by implantation will have a gradually diminishing effect, with the result that the initially rapid rise of resistance with ion dose will change to slower rate of rise as the bombardment progresses. This is the type of behaviour observed during stage I of the dose-resistance curves and is illustrated in fig. 4.1.

Prolonged bombardment after stage I would cause appreciable changes in film thickness by sputtering, in addition to the steady but slow reduction of mean free path as further impurities are implanted. The sheet resistance of the film would then take the form:

\[
R_s \propto \frac{1}{\lambda \cdot t}
\]

However, as the processes of sputtering and implantation continue, a situation may be reached where enough material has been removed or impurities added that the composition or the structure of the film is no longer that of a single phase material. The assumption of metallic properties for the film ceases to be valid, and resistance and other properties change drastically. This is the behaviour observed as stage III of bombardment, and the three stages of bombardment are shown for films of different thicknesses in figs. 4.5 and 4.6. For the thinnest films, i.e. those below 100Å, stage II was absent owing to the
rapid onset of stage III. The fast rise in resistance in stage III is
typical of mixed phase resistor structures as they approach the critical
conductor-insulator concentration. (95,96,123,124,125) It is in this
region that the characteristics of a transition material are observed
and where high resistance and a low temperature coefficient of resistivity
are obtained. The ion dose necessary to produce a high resistance film,
taken at the vertical asymptote to the curve for proportional increase
in resistance, and therefore close to the maximum usable resistance, is
shown as a function of initial film resistance as in Fig. 4.3. The
process is most efficient, that is, provides the largest increase for
the smallest dose, for the thinnest films. For thicker films, beyond
a thickness of the order of the maximum projected range of ions in the
material, the stage III behaviour was no longer obtained, but instead
the film approached a constant value, and the layered structure
described earlier was formed. (Section 4.2.2).

5.3 High Resistance Region

When a film, thinner than the ion range, increases in
resistivity beyond the metallic conduction zone the conduction path can
be modified in some way. For example some of the metallic content of
the film may be removed by sputtering or oxidation, or the path of the
conduction may be modified by the inclusion in the film of further
insulating phases back sputtered material from the substrate. Evidence
from the electron microscopy studies carried out by other workers (126)
indicates that in this stage (stage III) the aluminium film takes up a
polycrystalline form with a steady increase in the material which
separates the metallic grains as bombardment progresses and resistance
increases. Thus the high values of resistance that are obtained may be
attributed to the high impedance of gaps between conducting crystallites
with the growth of insulating material at the grain boundaries.

If the formation of the insulating layers is perfectly evenly
distributed through the film then the impedance in the film will be
equivalent to a series connection of metallic and insulating components
in parallel with a multitude of identical units. If, however, the gaps
are not identical then at any time a distribution of gap impedances will
exist throughout the film and paths of lower resistance linking low
impedance or thin gaps could be traced out across the film by such
circuitous routes which avoid the highest resistances. With the growth
of all gaps the paths would become even more tortuous and contain
higher and higher impedances. This second case would be represented by
a series connection of low metallic elements, and "gap" elements of
various but increasing resistance, in parallel with other paths of higher
resistance. The substrate is also implanted by the recoil of atoms from
the film so that the surface layer beneath the film is heavily doped
with metal atoms and may therefore possess significant conductivity where
gaps are produced in the film. The different effects of these processes
will be examined at the relevant stage later in the analysis.

5.3.1 Sputter Thinning

The most elementary and direct method by which a film is
raised in resistance is by reducing its thickness and at the doses used
in these investigations simple order-of-magnitude calculations using
accepted values of sputtering rate show that considerable amount of
film material could be removed. Experimentally the films show consider-
able thickening but the accompanying increase in surface roughness
indicates a highly disordered structure. Information on the change in
film resistance with thickness alone was obtained in a series of films
evaporated to given thickness and the sheet resistance measured. The
experiment was conducted using the U.H.V. evaporator to ensure freedom
from contamination and reproducibility of conditions and the results are
shown in Fig. 5.1. The substrates were held at room temperature. The
bulk resistivity was measured as $4 \times 10^{-5}$ ohm cm, and the mean free path for
Fig. 5.1 Sheet Resistance vs Film Thickness for Aluminium Films as deposited in U.H.V.
electrons was estimated as 200 Ω. This agrees well with values published by Mayadas (127) for similar conditions, and correlates with grain size in the polycrystalline films observed by electron microscopy of samples similar to those of the author (126). No annealing procedures were used at this stage. Attempts were made to fit a Fuchs–Sondheimer size effect function to the experimental points using the parameters which were measured for these films, but the striking feature of the observed characteristic is the departure from the size effect in the region below 100 Ω, with a high resistance, tending to infinity, being seen in films approaching 70 Ω in average thickness. At less than about 70 Ω, all films were open circuit and therefore could not be subjected to control by bombardment to normal "electronic circuit" values. Under the conditions of deposition in vacua of from 10⁻⁸ to 10⁻⁹ torr at a rate of greater than 10 Ω/sec, residual gas contamination is unlikely and though exposure to the atmosphere could result in a surface oxide layer, this should only penetrate 15 to 25 Ω in depth at room temperature (36,106,128). The high resistance at so great a thickness as 70 Ω must therefore have another explanation. Now it is known that thin films grow, during deposition, from isolated nucleation sites to form stable, but isolated islands, and only later in the growth sequence is sufficient material built up upon the islands to result in island to island contact (see for example Leaver and Chapman (129)). It has been reported elsewhere that aluminium remains discontinuous until an average thickness of 50 to 100 Ω has been deposited (127,129). This effect is well known in many metals, and it is reasonable on this basis to assume that the films deposited in this study have initially an island structure.

An analysis of films in the just-continuous region has been presented by Namba (131) in which he considers the film to possess a roughened surface. Namba then formulated an equation for resistance as a sum of regions of different thickness and therefore different resistivi-
ties, and showed that very good agreement with measured characteristics was obtained by using just two thickness terms and two length terms to define the film profile as shown in Fig. 5.2. The derivation of the model is reproduced in Appendix B, and its effect is illustrated in fig. 5.3.

A model of the Namba type was fitted to experimental "as evaporated" resistance-thickness characteristic obtained for aluminium and as shown in Fig. 5.4 fitting is possible over a very wide range of values for the thickness and length parameters. However, a critical average thickness, $\bar{t}$ crit, can be defined, at which the film just became continuous and this occurred at $t_1 = 0$ where $t_1$ is the thickness of the thinnest regions in the film, if the associated length term, $l_1$, is significant.

Now $t_2 = h - t_1 + h$ when $t_1 = 0$,

where $t_2$ and $l_2$ refer to the thickest regions and $h$ is the amplitude of the surface undulations of the film, thus:

$$\bar{t}_{\text{crit}} = h \left[ \frac{l_1 / l_2}{1 + l_1 / l_2} \right]$$

and if $\bar{t}$ crit is fixed by experiment at some value, $T_0$, say, then the $h$ term is given by

$$h = T_0 \left[ 1 + \frac{l_1 / l_2}{l_1 / l_2} \right]$$

and the only term that need be adjusted for fit is the length ratio $(l_2 / l_1)$.

The concepts of surface sputtering and the uneven film surface may now be combined so that at some dose per unit area, $q(t_1)$, a film is thinned by sputtering from a certain thickness until its thinnest regions ($t_1$) are removed.

The atomic population of the material removed is then given by

$$\frac{d'}{m} A_n$$

where $d'$ is the material density

$A_n$ is the Avogadro's number

$m$ is the atomic weight.
Fig. 5.2 Illustrating Uneven Film Parameters for Model of Film Resistivity, after Namba (130)

Fig. 5.3 Variation of Resistivity Ratio with Film Thickness and Roughness Amplitude Based on Namba Parameters
Fig. 5.4 Effect of Namba-type Parameters on Fitting Model to Experimental Data
Assigning an arbitrary area, \(a_1\), to the zones of thickness \(t_1\) and a sputtering rate \(S\), then the dose of singly charged ions necessary for removal is:

\[ a \cdot q(t_1) = a_1 \cdot S \cdot e \cdot \left( d' \cdot \frac{A_n}{m} \right) \]

If the film had been instead assumed to be smooth then the dose per unit area required would have been

\[ q(\bar{t}) = S \cdot e \cdot \bar{t} \cdot \left( d' \cdot \frac{A_n}{m} \right) \]

where \(\bar{t}\) is the smooth film thickness and is numerically equal to the rough-film average thickness,

\[ q(t_1)/q(\bar{t}) = t_1/\bar{t} \]

and with this model \(t_1 < \bar{t}\) so that \(q(t_1)\) is less than \(q(\bar{t})\) and the dose required to give this type of uneven film high resistance will always be less than that required by a smooth film.

The term \(\bar{t}\) is the average thickness which would be measured for example, by a quartz microbalance during deposition. The value of \(t_1\) cannot be measured directly, but the limiting value \(\bar{t}_{\text{crit}}\) is known from Fig. 5.4.

Now

\[ t_1 = \bar{t} - h \left( \frac{t_1/\bar{t}}{1 + t_1/\bar{t}} \right) \]

and when \(t_1 \to 0\), \(\bar{t} \to \bar{t}_{\text{crit}}\) for \(l_1\) of significant length,

then \(t_1 = \bar{t} - \bar{t}_{\text{crit}}\), and

\[ q(t_1)/q(\bar{t}) = 1 - \left( \frac{\bar{t}_{\text{crit}}/\bar{t}}{\bar{t}} \right) \]

The dose required to produce an "infinite" resistance value is then

\[ q(t_1) = \left( 1 - \frac{\bar{t}_{\text{crit}}/\bar{t}}{\bar{t}} \right) S \cdot e \cdot \bar{t} \cdot \left( d' \cdot \frac{A_n}{m} \right) \]

and as \(\bar{t}\), the initial average film thickness, becomes closer to \(\bar{t}_{\text{crit}}\), the effect of sputtering on the electrical resistance of the film is enhanced. The dose, \(q(t_1)\), may be calculated using only measured values and known constants, with the sole exception of the sputtering ratio, \(S\).
which may be modified by the thin nature of the film (Section 2.3.2).

The only assumptions made regarding film structure were:

(i) that it was uneven, and

(ii) that the length of the thinnest regions
was sufficient to provide a high impedance.

The curve predicted by this formula is that of dose for an
infinite resistance for different values of average initial film thickness
and may be compared with the experimental curve of "saturation dose"
obtained earlier (Section 4.2.2) as shown in Fig. 5.5. There is
a very good fit for a sputtering coefficient of about 1.5 which is a
reasonable value for aluminium and is close to that which would be
expected from data measured by Perkins (101) in similar bombardments.

The mechanism of sputtering mentioned above was that of surface sputtering,
but this does not preclude the loss of material by forward sputtering
into the substrate. Forward sputtered atoms, however, accumulate close
to the film-substrate interface and tend to a limit of saturation in
concentration owing to the presence also of back sputtering from the
substrate to the film.

It may be concluded therefore that the electrical effect of
bombardment is due to various forms of sputtering and further that these
effects are highly dependent on the initial structure of the film. The
films were deposited at room temperature but if the deposition tempera-
ture were changed this could alter the film structure and change the rate
of resistance change with ion dose, drastically.

The present measurements however permit bombardment character-
istics of dose and resistance to be predicted from the "high resistance"
or saturation dose region down to the low resistance region using the
uneven-film model, provided account is taken at low resistance of changes
in resistivity due to the introduction of damage and impurities.
Fig. 5.5 Comparing Measured Values of Saturation Dose with Those Predicted by Uneven Film Model
5.4 Temperature Coefficient of Resistance

When the sheet resistance of a metal film was changed by bombardment with heavy ions, the temperature coefficient of resistance (TCR) was also changed, as shown in Fig. 4.8. At the initial low resistance prior to bombardment the film possessed a large positive TCR typical of a metal, but below bulk value by virtue of the presence of the size effect, since the film thickness was smaller than the value of electron mean free path calculated from bulk resistivity measurements.

Now, using Matthiessen's Rule (Section 2.3.1), the resistivity of a metal is given by:

$$\rho_o = \rho(T) + \rho_i$$

where $\rho_o$ is the bulk resistivity of the metal

$\rho(T)$ is the resistivity due to the lattice scattering of the conduction electrons and is temperature dependent

$\rho_i$ is the resistivity due to the presence of impurities and is independent of temperature.

The TCR is given by:

$$\alpha_o = \frac{1}{\rho_o} \cdot \frac{\partial \rho(T)}{\partial T}$$

From Section 2.3.2 the TCR of a metal film, $\alpha_f$, is given by the product of $\alpha_o$ and a size effect function, $F_2(x)$, thus:

$$\alpha_f = \frac{F_2(x)}{\rho(T) + \rho_i} \cdot \frac{\partial \rho(T)}{\partial T}$$

Let the TCR of the metal film after an arbitrary dose of ions, less than the critical dose, be:

$$\alpha'_f = \frac{F_2(x')}{{\rho_o}'} \cdot \frac{\partial \rho(T)}{\partial T}$$

then

$$\alpha'_f \frac{\rho_o}{F_2(x')} = \alpha_f \frac{\rho_o}{F_2(x)} = \alpha_o \rho_o$$

When the concentration of impurities in a metal is small but significant as was discussed in Section 5.2, the product of the bulk resistivity and the mean free path is constant. Thus

$$\rho_o \lambda = \rho_o' \lambda'$$

where $\lambda$ and $\lambda'$ are the mean free paths associated with resistivities.
\( \varphi_0 \) and \( \varphi'_0 \) respectively. Further when \( x' > 0.1 \) due to the reduction of the mean free path, then the size effect function \( F_2(x') \) tends to unity. The relationship for the corresponding TCR's may then be written:

\[
\alpha'_T = \alpha_0 \frac{\lambda'}{\lambda} \frac{1}{F_2(x')}
\]

that is, the temperature coefficient of resistance is proportional to the mean free path of conduction electrons, whereas the sheet resistance of a film becomes proportional to \( 1/\lambda t \) (Section 5.2). Thus when the mean free path is dominated by the presence of impurities introduced by implantation, TCR and sheet resistance will be changed simultaneously. The plot of sheet resistance against T.C.R. is shown in Fig. 5.6 and the predicted variations due to size effect alone and impurity scattering alone have been superimposed. The curve for the ion bombarded film fits between these curves, being dominated by size effect initially and then tending toward the impurity scattering curve after an appreciable dose of ions, as indicated by analysis.

Beyond this regime it was observed that the T.C.R. changed very rapidly, and became more negative, first reducing from a low positive value to zero and then becoming rapidly larger but in the negative sense. This cannot be explained in terms of metallic conduction and indicates the introduction of a semiconducting or insulating phase in the metal film. The conduction processes present in a film of material possessing a low near-zero temperature are at once of great importance and difficult to determine experimentally. However, it is possible first to examine those films with a very large negative temperature coefficient, and secondly apply the results of such an investigation to the related conditions of low temperature coefficient from which the material developed, and this will be examined as follows.

Consider the thermal behaviour of a high resistance film.
Fig. 5.6  Sheet Resistance vs TCR for Bombarded and Unbombarded Specimens Showing Limits of Impurity Scattering and Size Effect.
Whereas the T.C.R. is taken as an average change normalised to room temperature to yield a single value, the film resistance at high values varies non-linearly with temperature. When these results are re-interpreted using an Arrenhius plot of current at constant voltage or conductance, against inverse temperature, it is found that an activation energy may be defined for the film conduction at high temperature, but which disappears at low or room temperature in a stable and repeatable manner. This is interpreted here in a model composed of two elements, one metallic, having a low positive temperature coefficient, combined with another element possessing an activated form of conduction.

The simplest combinations of two such elements are straightforward series and parallel connections (Fig. 5.7). The equations for the conductance of each connection are:

Parallel: \[ G_p = \frac{1}{R_m + G_d} \]

Series: \[ G_s = \frac{G_d}{(1 + R_m G_d)} \]

The variations of the combined conduction of each connection with temperature is illustrated schematically in Fig. 5.8. The difference between the two characteristics is quite marked, and only the parallel connection exhibits the characteristics necessary to explain the behaviour observed for the high resistance ion bombarded film.

Experimental curves may now be resolved into two components using the parallel element model, and an example is shown in Fig. 5.9. The positive metallic element was determined at low temperature from the slope of the resistance-temperature plot of the part of the curve showing the zero temperature coefficient region as given in Fig. 4.9. on p.100.

In the resolved components in Fig. 5.9 it can be seen that a straight line over more than two orders of magnitude of conductance was obtained when the metallic element was subtracted, indicating that a single activation energy of about 0.2 eV existed in the negative portion.
Fig. 5.7 Illustrating (a) Series and (b) Parallel Configurations of Two Phase Conductors.

Fig. 5.8 Illustrating Variation of Conductance with Temperature for (a) Series and (b) Parallel Configurations shown in Fig. 5.7
Fig. 5.9 Illustrating Resolution of Components for Parallel Model of Implanted Film
of the temperature variation of resistance. All other near-zero or negative temperature coefficient characteristics treated in this way yielded a component with a single activation energy, normally between 0.05 and 0.2 eV.

It has been shown that an island model satisfactorily explains the observed behaviour in the increase of the resistance of a metal film by a sputtering method. Near to the point at which resistance rises sharply with dose (i.e. when the island structure becomes predominant, in determining the resistance of the film, the temperature coefficient of resistance passes from positive to negative through a point of zero temperature coefficient. This provides a situation in which to test again the validity of the island structure and to postulate the range and types of conduction processes which contribute to the attainment of the low temperature coefficient.

Initially a simple rough surface model will be used, and this will be extended to demonstrate that if a zero temperature coefficient is to be obtained by combining two components, one of which is metallic, then the other component must have a T.C.R. which is not merely negative, as in a semiconductor, but is also very low.

5.4.1 Uneven Film Model of T.C.R.

Now the temperature coefficient of resistivity using the notation of the uneven film model is given by

$$\alpha(t) = \frac{1}{\rho(t)} \cdot \frac{\partial \rho}{\partial T}$$

where $\rho(t)$ is the resistivity for film of thickness $t$

and

$$\alpha(t) = \frac{\alpha(t_1) \rho(t_1) I_1/l_1 + \alpha(t_2) \rho(t_2) I_2/l_2}{\rho(t_1) I_1/l_1 + \rho(t_2) I_2/l_2}$$

or

$$\alpha(t) = \frac{A \cdot \alpha(t_1) + B \cdot \alpha(t_2)}{A + B}$$

where

$$A = \rho(t_1) \cdot I_1/l_1$$

$$B = \rho(t_2) \cdot I_2/l_2$$
Now if one element, $\mathcal{C}(t_1)$, becomes the dielectric or gap impedance with a correspondingly high negative T.C.R. $\alpha(t_1)$, then $\mathcal{C}(t)$ is the T.C.R. of a cermet type film.

If zero temperature coefficient is to be obtained by subtraction of the two component terms of $\alpha(t)$ with one positive and the other negative, then

$$\frac{A}{A + B} \alpha(t_1) + \frac{B}{A + B} \alpha(t_2) = 0$$

and therefore

$$\alpha(t_1) = -\frac{B}{A} \alpha(t_2)$$

$$= -\frac{t_2}{t_1} \frac{\mathcal{C}(t_2)}{\mathcal{C}(t_1)} \alpha(t_2)$$

that is

$$\alpha(t_1) \frac{\mathcal{C}(t_1)}{t_1} = -\left(\frac{t_2}{t_1}\right) \alpha(t_2) \frac{\mathcal{C}(t_2)}{t_2}$$

Note that the above expression is formulated in terms of the products of resistivity and temperature coefficient of the two components.

Now it is known that the trend of temperature coefficient with resistivity in general terms follows the characteristic shown in Fig. 1.1, due to Halaby (72). When this characteristic is interpreted in the form of the product term $\alpha \mathcal{C}$, the curvature of graph towards high resistivity is greatly accentuated so as to provide very high negative values, and very small positive values. Thus $\alpha(t_1) \mathcal{C}(t)$ will be much greater than the term:

$$|\alpha(t_2) \mathcal{C}(t_2)|$$

Therefore

$$\frac{\alpha(t_1) \mathcal{C}(t_1)}{\alpha(t_2) \mathcal{C}(t_2)} = \left(\frac{t_2}{t_1}\right) \left(\frac{t_1}{t_2}\right) \gg 1$$

Normally $t_1 > t_2$ so that $|\mathcal{C}(t)|$ and the lengths of the very high resistivity regions of the film must be very small.

If a limit of a few hundred Angstroms were to be put upon the lengths of the thick zones then the length of the thin zones would be less than interatomic distances and thus ineffective. However, near to such a value different forms of conduction mechanisms may come into play. Nothing has yet been said about the type of conduction that would be
expected in the region left by the removal of the very thin zones, save
that it must be of negative T.C.R. to compensate for the positive
temperature coefficient of the remaining metallic islands. When no
metallic regions exist the compensation technique becomes impossible as,
in general, dielectric conduction is characterised by negative tempera-
ture coefficient.

Taking typical values for materials:

for an impure metal \( \rho (t_2) \approx 100 \, \mu \Omega \cdot \text{cm} \), \( \alpha (t_2) \approx -400 \text{ppm/}^\circ \text{C} \)
for an impure semiconductor \( \rho (t_1) \approx 1 \, \mu \Omega \cdot \text{cm} \), \( \alpha (t_1) \approx -1000 \text{ppm/}^\circ \text{C} \)
hence \( \frac{\rho (t_1)}{-\rho (t_2)} = 10^4 \)
and therefore \( \left( \frac{l_2}{l_1} \right) \cdot \left( \frac{t_2}{t_1} \right) \approx 10^4 \)
if \( t_1 \ll t_2 \) by a factor \( 10^2 \), say, then \( l_2 / l_1 = 10^6 \)

The resistivity of such a substance would then be given by

\[
\rho (\bar{t}) \cdot \left( \frac{l_1 + l_2}{\bar{t}} \right) = \frac{l_1}{t_1} \cdot \rho (t_1) + \frac{l_2}{t_2} \cdot \rho (t_2)
\]
rearranging:-

\[
\rho (\bar{t}) = \frac{\bar{t}}{l_1 + l_2} \left\{ \rho (t_1) \frac{l_1}{t_1} + \rho (t_2) \frac{l_2}{t_2} \right\}
\]
but for the numerical example \( \bar{t} \approx t_2 \) and \( (l_2 + l_1) \approx l_2 \)
therefore

\[
\rho (\bar{t}) = \frac{t_2}{l_1 + l_2} \left\{ \rho (t_1) \frac{l_1}{t_1} + \rho (t_2) \frac{l_2}{t_2} \right\}
\]
simplifying:-

\[
\rho (\bar{t}) \approx \rho (t_2) + \rho (t_1) \cdot \frac{t_1}{t_2} \cdot \frac{t_2}{t_1}
\]
and since \( \left( \frac{l_2}{l_1} \right) \left( \frac{t_1}{t_2} \right) \approx 10^4 \) for this example,
then

\[
\rho (\bar{t}) \approx 2 \, \rho (t_2)
\]

Thus this method of providing a low temperature coefficient by
adding together two bulk-like zones of metal and semiconductor appears
to result in an improvement in resistivity over the simple thin film
case, of only a factor of 2, e.g. if \( \varrho(t_2) \) is of the order of 100 \( \mu \Omega \text{cm} \) and \( t_2 \) is of the order of 100 Å then the sheet resistance is given by

\[
\varrho(t_2) / t_2 \approx 100 \mu \Omega / \text{sq}
\]

And yet specimens of \( 10^4 \) and \( 10^5 \Omega \text{sq} \) were obtained with zero
temperature coefficient.

On examination of the expression for resistivity the following
is observed:

\[
\varrho(\bar{t}) = \left( \varrho(t_1) / (t_1 \cdot t_2) \right) \cdot \varrho(t_1) + \varrho(t_2)
\]

and at zero temperature coefficient this simplifies to

\[
\varrho(\bar{t}) = \varrho(t_2) \left\{ 1 - \alpha(t_2) \right\}
\]

where \( \alpha(t) \) is itself negative, and this expression represents a criterion
for zero temperature coefficient obtained by summing the impedances of
a metal and semiconducting material in series. Immediately it is seen
that if \( |\alpha(t_1)| \gg |\alpha(t_2)| \), as is the case for normal bulk materials, then

\[
\varrho(\bar{t}) \to \varrho(t_2)
\]

if a zero temperature coefficient is to be obtained.

This result shows that for a zero temperature coefficient,
using the structure suggested, for the highest resistivity the
temperature coefficient of the dielectric material must be

a) negative and

b) itself as near to zero as possible.

In the limit the entire structure becomes composed of this
dielectric material with zero temperature coefficient. This requires
the interspersing insulator to have the properties it was hoped to
achieve by mixing dielectric with metal. This implies therefore that
for the material obtained experimentally the interspersed insulator was
of the "transition material" type and itself therefore a mixture.
Furthermore, observations show that a parallel arrangement of metallic and dielectric components rather than a series connection is required to explain the variation of resistance with temperature for the practical case.

Now the material sputtered from the film may be ejected in any available direction when the collision sequences are random, as in the case of an amorphous material. Thus the metal may be driven into the underlying substrate as well as the surface vacuum environment, and indeed other studies have demonstrated that an interchange of material occurs across the film substrate boundary,(101) and may be used to enhance the adhesion of the film to the substrate (132). As the bombarded zone disappears from the surface of the substrate, then due to the accompanying forward sputtering of the film, the metallic concentration in the substrate immediately below the film may be high. Thus towards the final stages of removal of the film by bombardment there may exist the combination of an extremely thin metallic layer in the film in parallel with a metal rich insulator in the substrate. This combination in itself may provide conduction mechanisms displaying mixtures of both positive and negative temperature coefficient acting in such a way as to provide compensation and near zero temperature coefficients over a certain range of temperature.

Let the material be composed of a thin metallic zone in parallel with a thin zone of highly doped insulator, in the inter-island gap. The effective resistivity of the combination is given by \( \rho_c \) where

\[
\frac{\rho_c}{\ell} = \rho_a\left(\frac{\ell_a}{\ell_c}\right) \cdot \rho_b\left(\frac{\ell_b}{\ell_c}\right) / \left( \rho_a\left(\frac{\ell_a}{\ell_c}\right) + \rho_b\left(\frac{\ell_b}{\ell_c}\right) \right)
\]

Here \( \ell = \ell_a = \ell_b \), \( t = t_a + t_b \)

\[
\frac{\rho_c}{\ell} = \left\{ \frac{\rho_a//t_a, \rho_b//t_b}{\rho_a//t_a + \rho_b//t_b} \right\}
\]
Now let a small temperature difference $\Delta T$ cause changes $\Delta \rho_a$, $\Delta \rho_b$ and $\Delta \rho_c$ in $\rho_a$, $\rho_b$ and $\rho_c$ respectively.

Then

$$\frac{\rho_c + \Delta \rho_c}{t} = \frac{(\rho_a + \Delta \rho_a)/t_a - (\rho_b + \Delta \rho_b)/t_b}{(\rho_a + \Delta \rho_a)/t_a + (\rho_b + \Delta \rho_b)/t_b}$$

Therefore

$$\frac{\Delta \rho_c}{t} = \frac{(\rho_a + \Delta \rho_a) (\rho_b + \Delta \rho_b)}{t_a t_b} - \frac{\rho_a + \rho_b}{t_a + t_b}$$

which becomes

$$\frac{1}{\rho_c} \frac{\Delta \rho_c}{\Delta T} = \left[ \frac{\frac{\rho_a}{t_a} \frac{\Delta \rho_a}{\Delta T} + \frac{\rho_b}{t_b} \frac{\Delta \rho_b}{\Delta T}}{t_a \rho_a + t_b \rho_b} \right]$$

Therefore $\alpha_c = \text{temperature coefficient of resistivity of the combination as given by:}$

$$\alpha_c = \frac{\alpha_b \cdot \rho_a (t/t_a) + \alpha_a \cdot \rho_b (t/t_b)}{\rho_a (t/t_a) + \rho_b (t/t_b)}$$

where $\alpha_a$ is the T.C.R. of $\rho_a$

$\alpha_b$ is the T.C.R. of $\rho_b$

Hence for $\alpha_c$ to become zero or negative, $\alpha_a$ or $\alpha_b$ must become negative. In this case the $\rho_b$ component is more likely to possess a negative temperature coefficient as it is gradually becoming conductive from an initial dielectric state. The $\rho_a$ component, which a metallic layer, can contribute the positive temperature coefficient term necessary for a low combined T.C.R.

For $\alpha_c$ to be near zero:

$$\alpha_b \cdot \rho_a (t/t_a) + \alpha_a \cdot \rho_b (t/t_b) \to 0$$

and therefore

$$\frac{\rho_a}{t_a} \alpha_b = - \frac{\rho_b}{t_b} \alpha_a$$

and

$$\frac{\rho_a}{\rho_b} = - \frac{\alpha_a}{\alpha_b} \left( \frac{t_a}{t_b} \right)$$

or

$$\rho_b = \rho_a \left( - \frac{\alpha_b}{\alpha_a} \frac{t_a}{t_b} \right)$$

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substituting into \( \rho_c \) for \( \rho_b \)

\[
\frac{\rho_c}{t} = \frac{\rho_a/t_a}{1 - \alpha_b/\alpha_a}
\]

However it is seen that in the likely event of \( |\alpha_b| \gg |\alpha_a| \) the combined resistivities provide:

\[
\rho_c = \frac{t}{t_a} \cdot \rho_a
\]

and unless \( t_b \gg t_a \), then once again the improvement in \( \rho_c \) over the metallic component may be negligible. In this case, though, \( \rho_a \) has a high resistivity as it is an ultra thin layer of metal and therefore a very much higher resistivity than pertained for the series combination.

For the trial calculation let \( t_a = 10 \mu \), \( \rho_a = 10^3 \Omega \text{cm} \)

then the sheet resistivity is given by

\[
\frac{\rho_c}{t} = \frac{\rho_a}{t_a} = 10^{-3} \div (10 \times 10^{-6}) = 10^4 \Omega/\text{sq}
\]

If this resistivity is driven higher in value, e.g. by reducing \( t_a \), then \( \alpha_c \), the temperature coefficient of the combination, may be made negative and may be used in conjunction with the series metallic element to provide overall zero temperature coefficient.

Referring once again to the zero temperature coefficient case for the overall combination treated earlier,

\[
\rho(t) = \rho(t_1) \left( 1 - \frac{\alpha(t_1)}{\alpha(t)} \right)
\]

If \( \rho(t) \) is to be very high, then since \( \rho(t_1) \) has a low metallic value then \( \alpha(t_1) \), which is itself negative, must be low. For an improvement of two orders of magnitude in \( \rho(t) \) over \( \rho(t_1) \) the term \( \frac{\alpha(t_1)}{\alpha(t)} \) must be of the order of \( 10^2 \), i.e. \( -\alpha(t_1) \gg 10^2 \alpha(t_1) \)

for example: if \( \alpha(t_1) = 400 \text{ ppm/}^\circ\text{C} \)

then \( \alpha(t) = -4 \text{ ppm/}^\circ\text{C} \) for \( \alpha(t) \) to be zero.

Thus by combining only three components with properties of
a feasible nature it is seen that a high resistance with a zero
temperature coefficient is feasible, and this provides a possible,
though by no means conclusive, explanation of the observed phenomenon.

5.5 Discussion of Electrical Effects of Ion Bombardment

In Section 5.3 the electrical effects of ion bombardment on
thin aluminium films in the range 70 Å to 1000 Å was explained in terms
of sputtering. It was argued that since the early phases of film
nucleation and deposition produce an island-like structure which, when
continuous, has an uneven surface with thick polycrystalline islands
connected by thinner regions then under the influence of ion bombarment
which sputters away the film, the thinnest parts are removed first, thus
tending back to a discontinuous island structure. Calculations of the
dose necessary to make the film discontinuous and hence provide a very
high resistance were made requiring only two film parameters:
sputtering rate, S, and critical thickness for discontinuity, \( t_{crit} \).
The critical thickness \( t_{crit} \) was obtained by a separate experiment to
obtain the variation of resistance with film thickness. However,
sputtering rate, S, could not be measured directly but published data
indicates values between 1 and 2, and the calculations of the open
circuit or saturation dose were in close agreement for \( S = 1.5 \).

Island structures are generally considered as possessing two
electrical impedance elements arranged in series which are the low
resistance metal islands with a low positive T.C.R. in series with a
small "gap" of dielectric possessing a very high impedance and a high
negative T.C.R. When these balance in some way, a high resistance
material with a low T.C.R. is obtained. However, measurements of the
variation of resistance with temperature for films with a T.C.R. near
to zero showed a simple series connection of two elements to be
inadequate. Instead a three element connection was shown to be in
better accord with measurements and that the film impedance was
dominated by two parallel elements, one resistive, the other
dielectric, replacing the single gap element, placed in series with
the original metal "island".

Processes by which ion bombardment could produce the structure
necessary to accord with sheet resistance and temperature coefficient
measurements will now be discussed.

5.5.1 Effect of Recoil Implantation

The concentration of impurities from recoil implantation in
the film and substrate may be calculated as follows. According to
Stroud (100) using simple and approximate considerations the flux of
atoms sputtered forwards across an interface is given by:

$$\Phi_f = \frac{x_f N_f \sigma_f}{\kappa \sigma_b} \left\{ 1 - \exp \left( - \frac{\kappa \sigma_b \rho}{t} \right) \right\}$$

and the flux sputtered backwards from the substrate by:

$$\Phi_s = \frac{\kappa x_s' N_s \sigma_b'}{\sigma_b' x_s' \kappa} \left\{ 1 - \exp \left( - \frac{\kappa \sigma_b' \rho}{t} \right) \right\}$$

where it is assumed that only laminae of $x_s$ and $x_f$ each side of the
interface take part in the process, with $x_s$ less than the film thick-
ness $t$.

$\sigma_n$ and $\sigma_b$ are total scattering cross sections

$\kappa$, is the fraction of projectile penetrating to
the substrate ($\gtrsim 0.95$ for most films)

$N_f$ and $N_s$ are volume atomic densities

primed values relate to collisions between projectiles
and substrate atoms.

Values of cross sections for argon ions of 30 KeV were quoted
as:

$$\sigma_f' = 6.5 \times 10^{-17} \text{cm}^2$$

$$\sigma_s' = 2.5 \times 10^{-17} \text{cm}^2$$

which would be expected for
very thin film areas bombarded with a primary beam of 30 KeV. The
lengths $x_s$ and $x_f$ were estimated at about 200 $\AA$ and measurements
indicated saturation implantation at between $10^{16}$ and $10^{17}$ aluminium atoms per cm$^2$ into SiO$_2$, for doses greater than $10^{16}$ ions cm$^{-2}$. It is difficult to apply these figures directly to the experimental data of this study because of the uncertain nature of the film profile. However for the thinnest films a "saturation" dose of about 2 mC/cm$^2$ was observed resulting in a low near zero temperature coefficient. The flux of film atoms implanted into the substrate could therefore approach between $10^{16}$ and $10^{17}$ atoms. The profile predicted by Nelson (81) for this process takes the form of an inverse square function, so that the majority of the implanted atoms would reside near to the interface at some fraction of length $x'$. For a value of $x'$ of about 200 Å, and assuming that 50% of the implanted atoms lie within 50 Å of the surface, a doping density of $3 \times 10^{22}$ atoms cm$^{-3}$ could be expected. This would approach the normal atomic concentration of the substrate and could therefore contribute to electrical conduction.

Similarly the reduction in conductivity of the aluminium film would be appreciably influenced by (i) the loss of metal atoms to the substrate, (ii) the implantation of substrate atoms by recoil in addition to (iii) the loss of atoms to vacuum by surface sputtering. Measurements by Perkins (101) indicate that contributions to sputtering from surfaces and interfaces are roughly equal for the same ion energy at the point of impact. Thus sputtering rates for the films observed in this study of about 0.75 would seem reasonable, assuming the influence of an uneven film structure discussed earlier.

The maximum value of conductivity would be expected at the saturation concentration of recoil implanted atoms. This would occur at ion doses approaching $10^{17}$ ions, cm$^{-2}$ or about 16 mC.cm$^{-2}$, and, for films of thicknesses greater than 250 to 300 Å, would provide the most favourable conditions for a balance of positive and negative temperature coefficients at a low sheet resistance. The initially
thinner resistors would have their metal content removed before the saturation concentration was reached in the substrate, and would require a higher value of film resistance for zero T.C.R. This would accord well with the observed behaviour of the film resistors. Once the thin metal regions were removed by surface sputtering the impurity concentration in the underlying substrate areas would be diluted by continued bombardment and increase rapidly in resistance.

5.6 Numerical Matrix Solution For a Resistor Mesh Model

5.6.1 Introduction

Cermet materials or ultra thin films composed of metallic islands or grains connected by dielectric or semiconducting material may be represented by a mesh of interconnected impedances. At low concentrations of dielectric material the film resistance is low since the metal islands touch. As the concentration of dielectric is increased some of the grains become separated and at some critical concentration the resistance of the film increases abruptly to a high value. This behaviour is similar to that observed during the bombardment of a thin metal film with energetic ions and the object of this exercise was to investigate methods of modelling the process, by means of a simple resistor mesh using an automated numerical solution technique, to assist in interpretation of the effect of conduction and bombardment mechanisms relevant to this study.

5.6.2 The Mesh Model

A simple two dimensional model was used with, initially, a square mesh (Fig. 5.10). The contacts to the film were modelled by putting the end rows to zero resistance. The nodes represented the array of metallic islands, and the linking arms the contact areas. The linking arms were increased in a random sequence to simulate the gradual introduction of dielectric material and the increase in value of the impedance of the entire mesh was found at each step by a matrix
Fig. 5.10 **Simple 2-Dimensional Square Mesh**

Fig. 5.11 **General Section of Mesh, Illustrating Notation Convention**
solution technique devised by the author. The new value of each linking arm impedance could be achieved in a single jump or follow a sequence of steps to the final value so that abrupt or gradual changes in "dielectric" impedance could be modelled, and the effect on the film resistance investigated.

5.6.3 Matrix Solution

A generalised section of the mesh is shown in Fig. 5.11. The convention to be observed is that currents are considered to circulate clockwise in each mesh cell or loop, that the loops are numbered in sequence from left to right and downwards, and that the impedance, for example, $Z_{jk}$ is that which is common to the $j$.th and $k$.th loop. In a loop, for example the $j$.th, the loop voltage is given by,

$$V_j = I_j (Z_{bj} + Z_{jk} + Z_{jy} + Z_{ij}) - I_b Z_{bj} - I_k Z_{jk} - I_y Z_{jy} - I_i Z_{ij}$$

For a closed loop the loop voltage is zero, for an open loop the voltage is determined by a forcing or input potential. Using matrix notation the loop voltage equations for the entire mesh are given for a mesh of $n \times n$ cells by:

$$\begin{bmatrix}
V_a \\
V_b \\
V_c \\
\vdots \\
V_n
\end{bmatrix} = \begin{bmatrix}
Z_{aa} & -Z_{ab} & -Z_{ac} & \cdots & \cdots & -Z_{an} \\
-Z_{ba} & Z_{bb} & -Z_{bc} & \cdots & \cdots & \cdots \\
-Z_{ca} & -Z_{cb} & Z_{cc} & \cdots & \cdots & \cdots \\
\vdots & \vdots & \vdots & \ddots & \vdots & \vdots \\
-Z_{na} & \cdots & \cdots & \cdots & Z_{nn}
\end{bmatrix} \begin{bmatrix}
I_a \\
I_b \\
I_c \\
\vdots \\
I_n
\end{bmatrix}$$
Note that only the elements of the diagonal, \( Z_{aa} \) to \( Z_{nn} \), are positive; all other terms in the \( Z \)-matrix are negative. An external forcing voltage is introduced as the first potential in the \( V \)-column matrix.

Reduction to a single value is achieved in stages by considering in turn each last potential in the \( V \)-column matrix. Only \( V_a \), the forcing function, is non-zero, all others are closed loop potentials.

Thus \( V_b = V_c = V_d = V_e = \ldots = V_n = 0 \)

and \( -Z_{na}I_a -Z_{nb}I_b \ldots = Z_{nn}I_n = 0 \)

hence

\[
I_n = \frac{I_aZ_{na}}{Z_{nn}} + \frac{I_bZ_{nb}}{Z_{nn}} + \frac{I_cZ_{nc}}{Z_{nn}} + \ldots
\]

and in, for example, row 'a' the resistance value becomes:

\[
Z_{aa} - \frac{Z_{an}Z_{na}}{Z_{nn}} - \frac{Z_{ab}Z_{nb}}{Z_{nn}} \ldots
\]

so that the last row and column in the \( Z \)-matrix and the last terms in the \( V \) and \( I \) column matrices are eliminated. This procedure is easily implemented by automatic computation and repeated until only a single term remains in the \( R \) matrix. This term then gives the impedance of the mesh.

The new mesh is then re-written with one change in the resistance of one link and the mesh impedance recalculated by the above procedure. This is repeated until every link except the end connection is at the new value, and at each point a new mesh impedance is obtained so that the change of impedance with a steadily changing "concentration" of high resistance or dielectric links is obtained.

5.6.4 Programme Notes

The link to be changed for each matrix reduction is chosen according to a random number sequence drawn from a pseudo-random generation subroutine. In order to prevent more than one change (or
the required number $x$ if more than one change is needed) in each resistor, an integer array is used to record when each resistor is changed. Should the same resistor be picked by the random number generator more than the once (or $x$ more than $x$ times) further change is inhibited and another random number called until all resistors show the required change. This procedure may be likened to "pulling numbers from a hat" rather than simply calling a sequence of numbers at random.

The matrix reduction is achieved in an elegant manner by exploiting three nested "DO-loops" and the simple reduction equation:

$$Z(I,J) = Z(I,J) - Z(I,L) * Z(L,J) / Z(L,L)$$

where $Z(I,J)$ is the matrix element of the $I$th row and $J$th column and is calculated for $J$ going from 1 to $K$ for each value of $I$ from 1 to $K$ where $K = L-1$ and $L$ goes from $n$ to 2 to reduce an $n \times n$ matrix to a single value. A large number of $Z(I,L)$ and $Z(L,J)$ terms were zero at first, because each loop only linked with a maximum of four others, and considerable savings in computing time could be made by testing these terms and skipping the reduction calculation for zero values.

5.6.5 Results for Simple Square Resistor Mesh

The effect of changing the mesh elemental resistors from an initial value of 1 Ω to a final value of $10^4$ Ω is shown in Fig. 5.12. At first the changes in the resistor values have only a little effect, and the overall resistance raised in a slow and steady manner. When roughly half the mesh resistors have been changed and the increase in mesh resistance is roughly half an order of magnitude, there is a sudden jump by about 3 orders of magnitude. Following the jump the mesh resistance continued to rise at a slow rate, to the final value. Repetition with sequences of random numbers moved the point of the upward jump over a wide range, that is as low as 40% to as high as 75% of the total number of changes executed.

Changes in the final value of resistance were found to have
Fig. 5.12 Results for Several Runs with an Increase Factor of $10^4$.

Fig. 5.13 Results for the Same Run taken with Various Values of Increase Factor.
Fig. 5.14 Results when each resistor is given two steps, at random intervals. (In this example each step was $x10^2$, and two separate runs are shown.)
Fig. 5.15 Result when each resistor is given three steps, at random intervals; each step was $x10^2$. 

1MΩ

Mesh Value

100kΩ

10kΩ

1kΩ

100Ω

10Ω

Ω

33 65 92

Change Number
little effect upon the form of the regions of slow change, as shown in Fig. 5.13. Increases of only a factor 10 in resistor elements showed no significant jump since the changes in the two slow regions were about half an order of magnitude each.

5.6.6 **Effect of Multiple Steps in Element Resistors**

If the element resistors were made to change more than once to attain their final value, then, even though the sequences of the first and subsequent changes were completely random, the curve of the rise in mesh resistance showed distinct "Bands" between the large jumps each centred on a resistance value associated with the values through which the individual resistors should pass. This is shown, for example, in Fig. 5.14 where each resistor was given two changes. Here two jumps appear, the slow-half-order-of-magnitude region is clearly apparent either side of the middle value and at the two extremes.

Similarly three steps in element resistor value produced three jumps, (Fig. 5.15) still retaining the slow-half-order-of-magnitude regions, whereas five steps showed an almost continuous curve since the slow regions were sufficiently closely spaced to mask any jumps, and produced a logarithmic increase in resistance when the resistor steps were logarithmically related, i.e. a sequence \(1, 10, 10^2, 10^3, 10^4, 10^5\) was used.

5.6.7 **Probability of Jump Point**

For a large number of runs the stage at which the jump occurs, the jump point varies. The frequency of each point is taken over a series of 100 runs with different random sequences is shown in the histogram in Fig. 5.16. The most probable jump point, about one quarter of all jumps, came near to the 18th change out of a total of 32, i.e. close to 56% with a spread from about 27% to 84%, while more than 50% of jumps came between 54% and 66% changed points. Thus if a much larger array were considered with each mesh component made up
Fig. 5.16 Histogram showing the Frequency of Jump as a Function of Change Number

Mesh Constant \( n = 4 \)
Single Step
Sample of 100 runs

Frequency of Event

Change Number at which Jump Occurred
of a simple mesh then sufficient numbers of elementary meshes would have changed at the 50% mark to cause the major mesh to jump.

5.6.8 Changes in Configuration and Size of Mesh

Several different configurations of mesh were tested in a similar way to that used for the simple square mesh, without significant differences emerging. Also a much larger mesh (16 x 16) was investigated by making use of a large computer and, once again without significant differences emerging. Further, it may be argued by symmetry that if an inverse of the mesh were considered, i.e. all high value elements made low and all low values high, then as many jumps below the mean would occur as above. Thus the most probable jump point should always occur near to 50% of elements changed, and no evidence to contradict this supposition has yet emerged.

5.6.9 Limit of Matrix Size

The maximum size of mesh that could be reduced to a single value by the above procedure was determined by the computer storage capacity. An estimate of the storage requirement was made as follows:

For a single square mesh of n x n cells there are \( n^2 + 3n \) loop currents. The impedance matrix will therefore require \( (n^2 + 1)^2 \) non-integer terms. The mesh will contain \( (2n^2 + 2n) \) resistors and the column matrix which registers the resistor changes will require \( 2n(n + 1) \) integer terms. Little extra storage is needed excepting that for the programme and subroutines, and since non-integer numbers require three times as much storage space as integers the total data storage requirement is,

\[
3(n^2 + 1)^2 + (2n^2 + 2n) \text{ words}
\]

and this is plotted in Fig. 5.17 and for a store of 4K words, e.g. PDP7, the maximum mesh size \( n = 4 \), with 40 resistors at 28 currents, whereas for a large machine with an 82K word store, e.g. STRETCH, \( n = 16 \) is the largest mesh size with 544 resistors.
Fig. 5.17 Estimated Computer Storage Requirement as a Function of Mesh Constant
5.6.10 Conclusions on Mesh Model

From the investigation of the use of a simple resistor-mesh to simulate a mixed phase conductor material the following tentative conclusions were drawn.

(i) The occurrence of a jump in resistor value is predicted which occurs near to a 50% population of high resistance value elements. The number of elements, however, was small in comparison with that to be expected in a typical cermet structure, i.e., the model contained a maximum of $5.5 \times 10^2$ elements even using the largest available computer, whereas a typical cermet resistor $100 \Omega$/square could contain more than $10^8$ islands of $100 \Omega$ diameter. For such large numbers some smoothing would be expected, but since a change in resistance value of each element could be of the order of $10^{12} : 1$ a jump would still be expected.

(ii) The variation of resistance prior to the jump is not dependent on the actual value of the resistance change, as long as it is significantly large, i.e. $10^2 : 1$.

(iii) If the element resistance change is achieved in stages, then the overall change in mesh resistance will show as many jumps as there are stages. This would explain such characteristics as shown in the work of Millgram and Lu (95) and Perkins and Stroud (126) where resistance of a cermet was found to vary in a step-like manner with changes in the metallic concentrations of the metal-silicon oxide mixture.

(iv) The mesh model provides some basis for discussion and comparison with observations, but is at an early stage and would require considerable development before general
application and use.

(v) The matrix reduction technique was fast and efficient but limited by the storage capacity of the computer. There is scope for development, however, since by its nature the matrix reduction progressively reduces the storage requirement significantly during computation and use could be made of this occurrence to increase the size of mesh considered, but computation time could then prove excessive for a realistically large mesh.
6.1 Introduction

The process of ion implantation of thin metal films has been investigated to discover the potential properties and advantages that it may bring to the manufacture of thin film resistors, and to determine the main factors in the process of thin film resistor formation by bombardment.

A wide range of physical properties are modified extensively by ion bombardment by means of radiation damage, implantation by direct and recoil methods and sputtering. The conduction properties of thin films are highly dependent upon the film structure and it is by altering the film structure that ion bombardment modifies the electrical characteristics of thin films.

Aluminium was used as a test material and demonstrated that electrical properties typical of a wide range of well known materials and structures could be produced by the single technique of ion bombardment. Tests on other metals have shown similar changes confirming that electrical effects are influenced by structure more than by the actual material species, and are described briefly in Appendix A.

The resistance of films could be increased from an initial value of a few ohms up to near insulating values of the order of $10^{12}$ ohms traversing the entire range of electrically useful resistance materials and providing a capability of producing insulating regions for isolation. The temperature coefficient of resistance (TCR) was found to vary at the same time changing from an initially high positive value typical of a metal, to a very high negative value typical of an insulator. Thus resistance and TCR were related in the general manner summarised in Fig. 1.1 due to Halaby (72) which would be expected for normal conduction processes. The sheet resistance of the bombarded
films was sufficiently high, of the order of $10 \, \text{k\Omega}/\text{sq}$, near to zero temperature coefficient to represent a technologically useful material fitting between conventional cermets and single-metal systems. A feature of conduction processes in resistance material is that generally impurities, disorder and damage to the crystalline structure improve the electrical properties, that is increase resistivity and reduce temperature coefficient. One of the objectives of this study was to investigate how far heat treatment of the type essential to restoring order to ion implanted semiconductors could be avoided. The stability of aluminium resistors, however, proved disappointing at high temperatures ($\sim 200 \rightarrow 300^\circ C$) unless elevated temperatures were applied during bombardment, so that some form of heat treatment or annealing is necessary even with this form of manufacturing process. However it is known that refractory materials, e.g. Ta, Hf, Re, have a low atomic mobility so that their use together with the correct choice of film thickness, ion and energy could produce a highly stable product.

6.2 Resistor Structure

The resistor structures investigated were all of the planar form. This is normally used in thin film microcircuits because it provides good contact with the substrate for lower dissipation, possesses low inductance and stray capacitance and is conveniently and accurately defined in area and geometry by masking and photolithographic techniques. Additionally the planar geometry restricts the working voltage range to the low field region which provides linear and ohmic characteristics even when thermally activated and field dependent conduction processes are used to enhance the sheet resistivity. This has the disadvantage of making the interpretation of conduction properties difficult. However by careful observation of the thermal behaviour of the film resistance near to zero TCR it was shown that the resistance could be resolved into two components, one metallic with a positive and linear TCR, the other of an activated type with a negative and non-
linear TCR which compensated by acting in parallel to provide the zero TCR condition. This contrasts with the normally accepted concept of components of positive and negative TCR activating in a series connection.

Electron photomicrographs indeed show the film structure to be composed of metallic islands dispersed in an amorphous matrix but, in summary, the resistance of the film may be expressed as

\[ R = r_m + r_c \]

where \( r_m \) is the component due to the metallic islands and \( r_c \) that due to the composition of the intervening matrix. When the temperature coefficients of these components, and respectively balance the value of film resistance is given by

\[ R = r_m \left( 1 + \left| \frac{\alpha_m}{\alpha_c} \right| \right) \]

and for realistic values of \( \alpha_m \) and \( \alpha_c \) the value of \( r_m \) must be very low.

Models of the film formation under bombardment indicated that the film was in fact of an uneven thickness and was adequately described by a conduction model due to Namba. Thus the component \( r_c \) could be more realistically described by a region of very thin film reduced in thickness by surface sputtering, tightly bonded to the substrate by recoil implantation and providing a significant doping concentration in the underlying substrate by the same recoil bombardment mechanisms. The resistance of such a structure is given by

\[ r_c = r_f \cdot r_s / (r_f + r_c) \]

where \( r_f \) is the film resistance and \( r_c \) the resistance of the underlying substrate. When \( \alpha_c \) approaches zero, the condition required above then the expression simplifies to

\[ r_c = r_f / (1 + |\alpha_f / \alpha_s|) \]

where \( \alpha_f \) and \( \alpha_s \) are respectively
the temperature coefficients of \( r_f \) and \( r_c \). The substrate resistance would then be a doped glass of the type investigated by Perkins (101) formed by recoil implantation in related work which he reported as possessing an activated tunnelling conduction characteristic, and therefore displaying a high negative TCR. Whereas \( r_f \) has the form of a very thin metal film having a very small and positive value of TCR.

Thus

\[
\frac{\alpha_s}{\alpha_f} = \frac{r_c}{r_f}
\]

Rewriting the expression for total sheet resistance:

\[
R = r_c \left(1 + \frac{\alpha_c}{\alpha_m}\right)
\]

so that

\[
R \rightarrow r_c = r_f
\]

It can be seen therefore that using this model the very thin regions of film between the islands dominate the sheet resistance and the presence of a parallel path in the substrate compensates the temperature coefficient to provide a zero TCR, which agrees very well with the observed changes in resistance with temperature.

This structure could be described as a "not-quite-discontinuous" film and since the achievement of low TCR requires that the substrate is doped while the film is made thin enough for high sheet resistance values the structure is unique to the ion bombardment process. The use of very thin conducting layers however implies high current densities and it is well known that aluminium, the material used in these investigations is notorious for electromigration at high current densities. Stroud has conducted tests on high resistance ion implanted aluminium films in which he pulsed the film at high current and observed drastic changes in resistance. Some films could be seen to fuse across the film normal to the current flow, as would be expected as any weak point would immediately increase the current density across the film at that point, and weaken it to fail under further pulsing.

A better choice of resistor material would be a more refractory metal, for although the resistance of aluminium to elec-
migration can be improved by incorporating impurities such as oxides or copper; refractories such as tungsten and molybdenum have limiting current densities over an order of magnitude higher.

6.3 Mechanism of Formation

The main mechanism by which ions acted upon the films to change electrical properties was found to be sputtering. The surface of the film is etched away by sputtering, and ions which penetrate to the back of the film can cause internal sputtering or "recoil implantation" at the metal-substrate interface. The effect on conduction is twofold; forward sputtered atoms of the film produce a metallic doping concentration in the insulating substrate which leads to an increase in conductivity, and atoms are sputtered back from the substrate into the metal film to add impurities which increase the film resistance. When the film has a granular structure and an uneven surface, very thin regions can be produced between the surface metallic grains and these regions then dominate the film resistance and produce the useful conduction properties.

The granular structure of the film arises during the initial deposition phase of the film and is therefore a function of the nucleation and growth process. Control, or variation of these processes could also be a means of modifying the effects caused by bombardment.

6.4 Ion Doping Procedures

In the formation of a mixed phase or cermet material the relative quantities of metal and insulator are of the same order, and their precise value determines the resistivity and conduction properties when pre-mix or co-evaporation techniques are used. With ion bombardment, however, the material chosen is of single phase and the impurity phase added by implantation until, at relatively high doses, roughly equal proportions of the phases are achieved and then fine adjustment of dose can provide a wide range of resistivities in a transition
A choice is therefore available to the manufacturer; whether to implant the conductor phase into insulator targets and so reduce the resistivity to form conductor tracks, or to implant the insulator phase into the conductor to form high resistance regions, and possibly to isolate conductor tracks by producing very high resistance outlines and bands. The advantages of starting with a conducting film is that the electrically active material is already present and may be modified using gaseous ions which are easily obtained at high beam current. Almost any thin film metal could be used and with adequate precautions adverse effects of charge build up can be avoided. Further, the range of thin film sheet resistance values normally used in electronic circuitry is covered by the ion implanted metal film during its change from the initial unbombarded value to that near to zero temperature coefficient. If the alternative procedure of starting with a dielectric target were adopted, problems would arise in obtaining suitable metal ions at sufficiently high current densities. Difficulties with charge build up could also become serious since the conducting track could be fused to high resistance even as it formed. The use of sandwich structures for high resistors as used by Perkins (101) would be precluded by its high parasitic capacitance, and the range of ions could prove embarrassingly large unless very low energies, e.g. a few KeV, were employed. The process would then merely represent an ion beam depositior technique equivalent to D.C. or R.F. sputter deposition but possessing the potential advantage of writing a circuit by means of a controlled and programmed "pencil" beam.

The writing of circuits using an ion beam is known, by calculation, to be feasible but suitable ion optic techniques have yet to be developed. The location and control of such a beam would present a fearsome problem in manufacturing resistors on, for example, a
microcircuit slice with some 200 circuits each requiring, say, 20 implanted resistors since 4000 separate and accurately located high dose implantations would be required. Methods taking advantage of the highly developed photolithographic techniques that are available at present could represent a more economical prospect, since normal production would require their application for device fabrication. Then the entire slice could be implanted at once with a uniform beam. Typically a 1.25 inch diameter slice implanted to a dose of $10^{17}$ ions/cm$^{-2}$ would require about 0.23 coulombs, and this could be provided by a 1 mA ion beam in less than four minutes, without the need for alignment. In addition the resistance change could be monitored and stopped at the precise value required.

6.5 Range and Energy Considerations

It is instructive to examine the different effects of ion bombardment which are obtained over the spectrum of presently available energies, that is up to a few MeV, to place the present study in its context and illustrate potential uses of ion beam technology. The lowest energy of significant interest is that necessary to displace target atoms from their lattice sites, normally about 25 eV, and the smallest distance of significance in surface studies for instance is about one atomic diameter. In Fig. 6.1 data for range, straggling and sputtering are summarised diagrammatically using as an example aluminium as target and mono-atomic oxygen as the ion. At very low energies, i.e. below 1 KeV, the penetration distance of ions is very small, while sputtering is also small. In this region the main effects are modifications to the surface by local damage and ultra shallow implantation, which may be used in surface sensitive investigations such as nucleation studies for preferential deposition (100). At higher energies, that is 1 KeV to 100 KeV the ion ranges become comparable with normal thin film depths, and sputtering rises to a
Fig. 6.1 Summary Chart of Ion Effects: Illustrating Relationship between Ion Energy and Depth of Penetration for Ion Beam Applications. (Shown for Oxygen Ions in Aluminium)
maximum. This is the region in which the work described in this thesis was conducted and it has been shown that highly significant changes may be made to thin metal films and to surface layers by oxidation, and to dielectric films (101), which have potential uses in the field of microelectronics and passive component fabrication.

Beyond 100 KeV the incident ions are slowed initially by inelastic or ionising collisions and surface sputtering is no longer significant. The ions penetrate to fairly large depths before stopping to form a layer, that is a buried layer. The material penetrated by the ions above the layer is normally undamaged and the formation of, for example, buried Silicon Nitrate layers by 1.5 MeV Nitrogen ions in a Silicon target has been reported elsewhere. This would have potential in the manufacture of capacitor devices if the material could be made thermally stable.

6.6 Future Work

During the course of this research a large number of interesting effects emerged and have been described earlier, while some through necessity were left unpursued. One of the most important results found by the detailed analysis of aluminium films was the very strong dependence of the formation of resistance by the ion beam method upon the initial structure of the film. For example films initially close to the discontinuous conditions (about 70 Å average thickness) required only a very small dose of ions to increase to a given sheet resistance but displayed different conduction characteristics and TCR from initially thicker films raised to the same resistance by a larger ion dose.

In these experiments a standardised deposition schedule was adopted to obtain reproducible specimens. These were not necessarily optimum for producing, by ion bombardment, high quality resistor material but permitted a thorough and accurate investigation of the material's
properties, and were shown to provide a material which could rival the
cermet and silicide compounds in all but stability. Controlled
changes in deposition conditions could however be used to extend the
scope and flexibility of ion beam processing by, for instance, increas-
ing the nucleation density. This would produce a film of smaller initial
grain size and a lower average thickness for film continuity. The
resulting material would be more uniform when bombarded and could hold
promise for greater stability than at present.

The nucleation process could be controlled by reducing the
substrate temperature, by charging the surface electrically or by
sensitizing the substrate by ion or electron bombardment in the manner
described by Stroud (100). Heating and thoroughly out-gassing the
substrate could reduce the nucleation density and increase the critical
average film thickness for nucleation. A combination of these
processes could be used in place of masking to delineate areas for
resistors and insulating tracks. A charge-sensitising and optically
patterned discharge process akin to the Xerox process could be employed
to avoid masking. Film deposition under normal vacuum at U.H.V.
conditions were not found to produce significantly different material
after ion bombardment. Gas absorption in a poor vacuum introduced
impurities and hence increased the initial sheet resistance exactly as
that achieved by recoil or direct implantation early in bombardment.
Low pressures were not essential during ion bombardment but the presence
of hydrocarbon vapours gave rise to contamination. Clean vacua rather
than ultra low pressures are required.

The logical extension of this work is to further materials
more suitable to high stability applications. Some tests have been
performed (Appendix A) which show that other materials, in common with
aluminium, can be increased in resistance by ion beam processing, and
because the conduction processes were structure dependent, exhibited
similar conduction and temperature dependent characteristics. The different atomic mass and density would however require higher ion energies to ensure penetration but careful choice of film thickness, ion and energy would be required to ensure that sputtering conditions were not affected adversely for the process.

The high optical transmission obtained for conductive specimens could find application in liquid crystal display electrodes, but aluminium has not proved satisfactory (Stroud private communication) and a suitable choice may lie in other materials.

At high resistivity non-linear characteristics of conduction emerge with high electric-field and temperature dependence. In this region the TCR becomes very large and negative and could be employed as a thermal-sensing element, but with the disadvantage of having a non-linear temperature coefficient. The electric field dependence of resistance in this non-linear region does not appear to have received any exploitation in the field of electronic devices. When the conduction is space charge limited, current becomes a function of the square of the applied voltage and such square law characteristics could have application in passive mixer circuits in place of diodes or transistors. Other forms of conduction exhibit exponential and square root dependence of current upon voltage and applications in function generation, non-linear feedback, signal processing e.g. companding, and in logarithmic amplification suggest themselves. A not inconsiderable difficulty is the achievement of stability, particularly with temperature, and current noise and burst phenomena which are present whenever potential barriers are used as a means of impeding current flow.

Implantation by ion beams and the associated phenomena are in use commercially but in restricted and specialised areas enumerated in the introduction. The great advantage of the process is the extremely high degree of control that it confers upon doping concentration,
sputtering and spacial location. It has proved a valuable research tool especially in the field of solid-state physics, and may yet see a further development in exotic manufacturing technologies in outer space where clean high vacuum is readily available. It has been shown in this and associated research that many types of passive component can be successfully fabricated by ion beam implantation processes, for example high quality resistor materials, capacitors, functional passive networks, strain gauges, thermal sensors, transparent electrodes, are all feasible at the present state of the art. Doubtless many more phenomena and applications await discovery and should make this field of research a fruitful and rewarding topic for some time to come.
APPENDIX A

SOME EXPERIMENT ON OTHER MATERIALS

A.1 Introduction

In addition to measurements of aluminium films, several subsidiary experiments were conducted on other materials in order to:-

(i) confirm that the ion bombardment process was applicable to materials other than aluminium

(ii) to explore effect of variations in material parameters which influence formation and behaviour of resistors.

The materials chosen (Ta, Ti, Au, Cu) were those which already have some application in electronics in addition to the special features which were to be evaluated. Tantalum has proved to be an extremely useful material in thin film electronics both as a resistor metal and as a capacitor dielectric. Its high stability and refractory nature are well known. Titanium has also been used for very high value resistors, but because it forms an oxide with semiconducting properties it cannot be considered in the context of high stability. Its main virtue is its exceedingly high dielectric constant.

Gold has been used with SiO to form a cermet material and since it has a very high sputtering rate, formation by ion bombardment could be expected to be very rapid. Similarly copper has a high sputtering rate, but since it can form a semiconducting oxide, copper could provide characteristics different from gold.

A.2 Tantalum

In the early stages of this research the technique of tantalum evaporation deposition was developed and used to produce thin films. It was thought that tantalum would prove a superior material to aluminium for both resistor and dielectric devices, being a more stable metal and having a better dielectric constant as an oxide.
However the comparative ease of aluminium film production, and the difficulty of achieving adequate ion range in tantalum caused work to be concentrated on aluminium. 

\((0_2^+ \text{ was used - if } 0_1^+ \text{ were used the range would be doubled, i.e. at } 35 \text{ KeV } \bar{R}_p \text{ would be } 200 \text{ A})\)

A.2.1 Tantalum Capacitor

A Tantalum film, prepared by vacuum evaporation on to a glass substrate, was bombarded with 30 KeV molecular oxygen ions to form an 'oxide' layer. Owing to the high density and large atomic mass of Tantalum the range of penetration of the oxygen ions was confined to a thin surface layer. A capacitive device was then formed by evaporating a Tantalum counter-electrode on to the centre of the bombarded area. A capacitance of about 10 nF was obtained and no rectifying action was found, but the electrical properties of the device as a pure capacitor were poor. A high d.c. leakage equivalent to about 10 KΩ shunt resistance, voltage variable a.c. shunt conductance and a breakdown voltage of just under 1.5 volts were measured. After breakdown the leakage and shunt conductance doubled, and the capacitance dropped slightly. The capacitance was also found to vary with applied voltage, but this can be explained solely in terms of series lead resistance and shunt conductance variations.

The counter electrode was 2 mm in diameter and the dielectric thickness estimated as 250 Å, which indicate a dielectric constant of 10 and a breakdown field strength of \(2\text{MV/cm}\). These values are lower than those for bulk tantalum oxide and this is thought to show that the oxide was either impure, or incomplete, or both. (For Ta_2O_5 the dielectric constant is 26 and the dielectric breakdown field strength 0.7MV/cm.) When used as a three terminal device the capacitor was found to display distributed resistance-capacitance characteristics.

The accommodation of the bombarding ions may be estimated as
The specimen dose was 40 mC/cm$^2$ and the resistance increased from 25 to 60Ω probably halving the thickness of the conducting layer. 40mC/cm$^2$ corresponds roughly to $4.5 \times 10^{17} \text{O}^+_{1}$ atoms per cm$^2$, and if impact dissociation is assumed then the maximum range is that for 15 KeV O$^+_{1}$ ions, i.e. $\sim 250 \, \AA$. Now in 250 \, \AA of Ta there are roughly $1.3 \times 10^{17}$ Atoms/cm$^2$. Thus it can be seen that orders of magnitude are correct for conversion of the 250 \, \AA layer estimated by capacitance measurements. This also indicates that spreading of the implanted material occurs, otherwise the profile would cause super-saturated oxide to occur in a thin layer about 28 \, \AA thick at mean range, and little elsewhere. Spreading and distribution would be expected in the presence of internal sputtering and since all implanted material at rest is effectively target material the oxide can be distributed throughout the bombardment affected zone.

Later electron beam evaporation equipment was re-furbished and thin Ta films were made and bombarded. A fairly typical characteristic of resistance rise against dose was obtained using very impure initial material, thereby verifying the applicability of the process to tantalum. Since this work the bombardment of Ta with ions of oxygen, argon and nitrogen has been studied in depth by a group at Surrey University (133, 134, 135).

A.3 Chromium

Chromium films proved difficult to produce and only one thick film was bombarded. A characteristic typical of a film thicker than total ion range was obtained, demonstrating the possibility of using chromium films.

A.4 Titanium

Titanium can be evaporated with relative ease from a tungsten spiral, but owing to its extremely reactive nature tends readily to
trap gas to form an impure film. Thus a U.H.V. technique is required for pure films. A bombardment characteristic for Ti appears to have a form initially identical to aluminium showing regions I and II, but the resistance increase thereafter did not tend directly to an asymptote. A significant contrast with aluminium is the large drift of more than 20% on the cessation of irradiation. This is thought to be due to absorption of reactive gas which it is known to do readily. A method of preventing this may lie in the use of overlaying the metal with a dielectric such as Si0 prior to bombardment. To test this technique under known conditions, aluminium samples were so treated.

A.5 Dielectric Overlayer

To test the feasibility of bombarding through a dielectric layer a 100Å aluminium film was coated with a 200Å layer of silicon monoxide and irradiated with 35 KeV O$_2^+$ ions.

The characteristic obtained by this technique demonstrated all the typical features of normal aluminium bombardment, but a higher dose was required - sufficient (by calculation) to remove the silicon monoxide overlayer by sputtering.

A.6 Gold

It is known that gold is chemically a highly stable material, but possesses a high sputtering coefficient ($4-8 \frac{\text{Atoms}}{\text{Ion}}$). In order to explore the effect of predominant sputtering a gold film of about 100Å was bombarded with 35 KeV O$_2^+$ ions. The characteristic obtained was similar in some respects to aluminium and a sheet resistance of 10 KΩ/sq. was obtained at a dose of 2.7mC/cm², with a rapid final rise in resistance.

The initial section of the characteristic was however entirely different, in that it displayed an initial drop in resistance of about 20%. This is similar to observations by Navinsek and Carter (20). They attribute this to desorption, but the topic was
left open to alternative explanations e.g. boundary smoothing, restructuring etc.

As a complementary experiment a gold film was overlaid with a SiO film of about 100 Å and similarly bombarded. An entirely different characteristic was produced: - The initial drop in resistance was reduced to negligible proportions and the resistance rise was reduced to a very slow rate. This is thought to demonstrate the following:

1) initial drop may indeed be due to desorption since the initial resistance of the two films was similar and the overlayer maintained approximately stationary condition at the boundary

2) the vacuum sputtering rate was suppressed by immediate capture in the overlayer, (in a solid the range of such sputtered particles is small)

3) the slow resistance rise may be due to the introduction of impurities into the gold allied to the gradual boundary spreading due to back sputtering to produce a gold-glass cermet.

A.7 Copper

A thin copper film was bombarded with 35 KeV $O_2^+$ ions and its resistance characteristic was measured. The initial resistance change was similar to that obtained with gold film i.e. showing a drop followed by a normal rise, (the common factor being high sputtering ratio). A considerable upward drift was observed upon the cessation of bombardment, similar to Ti, and again is thought to be chemisorption.

A.8 Conclusions

Although the tests on metals other than aluminium were of a brief nature they demonstrated the general applicability of the ion
implantation technique to thin film resistors. The characteristic change in sheet resistivity with ion dose was in most cases similar to that observed for aluminium, showing that high resistance films could be formed for films thinner than the ion range. Some metals, e.g. Au, Cu and Ti, showed considerable drift following bombardment indicating instability in the phases and structure.

Low temperature coefficients were also obtained and when the variation of resistance with temperature was examined close to zero TCR it was found that resistance could be resolved into two parallel components as in the case of aluminium. This once again demonstrates that the structure of the film is more important than the actual material species in producing the desirable conduction characteristics, whereas the parameters of deposition, growth and response to bombardment create the conditions in which such a structure occurs. Thus the final characteristics of the ion implanted resistor could be altered considerably by, for instance, depositing the film at a much higher or lower temperature to alter the nucleation and agglomeration phases of film growth, or by increasing the nucleation density and hence island size by implanting the substrate with impurities or charging its surface prior to deposition.
APPENDIX B
ELECTRICAL CONDUCTION OF THIN METALLIC FILMS
WITH ROUGH SURFACE

B.1 Introduction

It is known that the resistivity of thin metallic films increases as the thickness is decreased. The variation of resistivity with film thickness has been explained as the increase in the scattering effect of the film surfaces upon the mean free path of the conduction electrons. Fuchs (93) and Sondheimer (94) have derived analytical expressions for this effect, the "size-effect", by assuming a uniform film thickness, and diffuse scattering of conduction electrons at the film surface. The effects of variations in the specularity of scattering for each surface (136) and angular dependence for rough surfaces (137, 138) have shown good agreement with measurements on thick films but show significant deviations for very much thinner films.

B.2 Rough Surface Model

More recently Namba (131) has shown that a treatment of rough films, in which the film is approximated by a simplified model with two regions differing in thickness and length, shows very good agreement with measurements of very thin films.

The rigorous treatment of a rough film is very difficult and for simplicity the surface is averaged and replaced by the model shown by the dotted line (Fig. B.1).

The roughness parameter, h, is assumed small in comparison with the length parameters $l_1$ and $l_2$, and the resistance is given by

$$R = \left[ \frac{\varphi(t_1) \cdot l_1}{\ell - h \cdot l_1 / (l_1 + l_2)} + \frac{\varphi(t_2) \cdot l_1}{\ell + h \cdot l_1 / (l_1 + l_2)} \right] \times \frac{1}{W}$$

where W is the width of the film

$\varphi(t_1)$ is the resistivity for thickness $t_1$ due to size effect

$\varphi(t_2)$ is " " " " $t_2$ " " " "

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\( \bar{t} \) is the average film thickness

and therefore \( R = \rho'(\bar{t}) \left( \frac{l_1 + l_2}{\bar{t}} \right) \)

where \( \rho'(\bar{t}) \) is the resistivity for thickness \( \bar{t} \) due to the effects of rough surface and size effect.

thus

\[
\rho'(\bar{t}) = \frac{\bar{t}}{(l_1 + l_2)} \left\{ \frac{\rho(t_1)}{l_1} \left( \frac{1}{\bar{t} - \frac{h}{l_1}} \right) + \frac{\rho(t_2)}{l_2} \left( \frac{1}{\bar{t} - \frac{h}{l_2}} \right) \right\}
\]

The resistivity terms \( \rho(t_1) \) and \( \rho(t_2) \) may be calculated from the size effect function, \( F(x) = \frac{\rho(t)}{\rho_o} \) where \( x = \frac{t}{\lambda} \)

and \( \lambda \) is the mean free path of conduction electrons.

From Lucas (136):

\[
\frac{1}{F(x)} = \left( 1 - \frac{3}{4x} \right) \left( T - T^{-3} \right) \left( 1 - \exp(-x|T|) \right) \cdot 2 - P - Q + (P + Q - 2PQ) \exp(-x/T)\left( \frac{x}{T} \right) \exp(-x/T)\left( \frac{x}{T} \right)
\]

where \( P \) and \( Q \) are parameters related to the specularity of scattering of conduction electrons at the surfaces. The equation for \( \rho'(\bar{t}) \) may be re-written in terms of bulk resistivity \( \rho_o \) and mean free path \( \lambda \) thus:

\[
\frac{\rho'(\bar{t})}{\rho_o} = \frac{\bar{t}/\lambda}{(1 + (l_2/l_1))} \left\{ \frac{\rho(t_1)}{\rho_o} \left( \frac{1}{l_1/\lambda} \right) + \frac{l_2}{l_1} \left( \frac{\rho(t_2)}{\rho_o} \left( \frac{1}{l_2/\lambda} \right) \right) \right\}
\]

where

\[
\frac{t_1}{\lambda} = \frac{\bar{t}}{\lambda} - \frac{h}{\lambda} \left[ \frac{l_2/l_1}{1 + l_2/l_1} \right] \quad \text{and} \quad \frac{t_2}{\lambda} = \frac{\bar{t}}{\lambda} + \frac{h}{\lambda} \left[ \frac{l_2/l_1}{1 + l_2/l_1} \right]
\]

and the major parameters, \( P, Q, \bar{t}/\lambda, h/\lambda, l_2/l_1 \) and \( \rho_o \) describe the rough films completely.

Namba has shown good agreement between the model and results.
for gold films. These were evaporated on mica at two different temperatures to obtain different structural dimensions. The mean free path of conduction electrons, $\lambda$, was calculated from the resistivity of thick gold films. By assuming $P = Q = 0$, Namba was able to fit appropriate values to the ratios $h/\lambda$ and $l_2/l_1$, which gave an excellent fit between predicted and measured values of resistivity over a wide range.

Fig. B.1 Illustrating a Rough Film Surface and the Parameters of the Namba Model
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