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Title: Ion Implantation of Tantalum Thin Films
UNIVERSITY OF SURREY

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ION IMPLANTATION
OF
TANTALUM THIN FILMS

BY

K.H. GOH

Thesis prepared for the Degree of Doctor of Philosophy
submitted to the Department of Electronic and Electrical
Engineering, of the University of Surrey.

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ACKNOWLEDGEMENTS

I would like to take this opportunity to thank Dr. K.G. Stephens and Dr. I.H. Wilson for having encouraged and supervised this work in its entirety. I am also indebted to Professor D.R. Chick for the use of the facilities in the Electronic and Electrical Engineering Department.

Many thanks are also due to Mr. J. Smith and Mr. J. Mynard for assisting in the practical experiments, and also to Mr. F. Keitch and his associates for manufacturing numerous hardware during the course of the project.

I am grateful to Mr. R. Duckworth of Ultra Electronics for supplying some of the tantalum films and helpful suggestions, and to Mr. I. Sheikh for some of the films grown at the University of Surrey.

Assistance from the Metallurgy Department of the University of Surrey, in particular Mr. M. Hepburn for operating the electron microscope is gratefully appreciated.

Finally, I would like to thank Miss Jill Jones for patiently typing this thesis.
ABSTRACT

Tantalum thin films have been implanted with argon, nitrogen or oxygen to change their physical, chemical and electrical properties.

The films were deposited either by electron beam evaporation or by D.C. diode sputtering in an atmosphere or argon.

Physical and chemical changes of the films were examined with the aid of the transmission electron microscope (TEM). Some X-ray diffraction techniques and Electron Spectrum for Chemical Analysis (ESCA) were also undertaken in conjunction with the above.

Present results show that the electrical characteristics, viz. sheet resistance, resistivity and temperature coefficient of resistance (TCR) of the thin films before and after irradiation are very dependent on the growth history of the films. In general for a film of given thickness, resistivity increases with impurity content with the TCR becoming more negative.

When the films were implanted with energetic ions, resistivity and TCR change according to the type of ions used.
Films irradiated with argon showed a gradual, almost linear rise in resistivity initially, after which a non-linear region was observed, followed by a very rapid change for a small increase in dose. The TCR remained almost constant throughout. Electron diffraction analysis of the films at increasing doses showed the presence of the lower oxide of tantalum (Ta₂O).

When the films were implanted with oxygen, resistivity versus dose plots similar to the argon treated films were obtained but with a distinct difference in the middle dose region. The TCR for the films changed sign from negative initially, to positive and back to negative again with increasing doses. At light doses, highly crystallised b.c.c. tantalum was precipitated out from the films. This was quickly replaced by less crystalline Ta₂O as the dose increased. The crystal structure of the Ta₂O became more ordered with increasing dose but deteriorated at very high doses, the films becoming amorphous.

When the films were implanted with nitrogen two peaks were observed in the resistivity versus dose plots with correspondingly large negative excursions in their TCR. The compound Ta₄N₅ has been identified in these films. It was observed that the films were very resistant to radiation damage, up to very high doses.
Finally, where possible we have attempted to correlate the physical and chemical effects of implantation to the measured electrical behaviour of the films.
1. INTRODUCTION

1.1 Introduction

With the advent of the ion implanter being accepted as an important research and manufacturing tool in material physics, the initial area of great interest was the doping of Semiconductors\(^{(1)}\), e.g. silicon and gallium arsenide where user benefits were realised quickly, especially in those fields where conventional diffusion doping was at a disadvantage.

However, at the University, interest has grown in the possible application of ion implantation in the fabrication of passive thin films devices, i.e. interconnections, resistors, capacitors and packaged CR filters to complement the rapid strides made in the active devices programme. This is especially true with the increasing use of precision hybrid and linear integrated circuits where passive components play an important part in their circuit operation as opposed to digital circuits where passive component stability and precision are not of prime importance.

At present, the majority of the passive devices are prepared using either conductive inks or sputter deposition of a suitable resistive material, followed by some form of
trimming to obtain the desired resistance values. Heavily doped semiconductors have also been used for resistors but these are normally only suitable for digital circuitry due to their wide tolerances.

We believe that using ion implantation, a potentially advantageous technique may exist for the preparation of accurate resistors and other passive devices, especially in those areas of integrated circuit work where ion implantation can, or is already employed to manufacture the active components.
1.2 **Aim**

It is the aim of the work of this thesis to gain some understanding that can in the future lead to a technique whereby resistor elements can be fabricated in a predictable and controllable manner using ion implantation of a suitable dopant into a metal film.

This thesis is based on a first attempt to determine the physical, chemical and electrical effects of ion implantation on thin metal films and to try and obtain some knowledge of the processes involved. As such, this initial study will unavoidably embrace a wide field, very often requiring expertise and knowledge in different disciplines and for this reason it is difficult to cover any one field comprehensively. However, it is hoped that from this study, areas deserving more concentrated examination will be forthcoming.
1.3 Metal Thin Films

In general, metals which are not easily oxidised in their bulk forms have low resistivities and positive TCR\((^2)\), but when these metals are deposited as thin films, they do not normally exhibit their bulk properties. If the films are extremely thin, very high resistivities combined with large negative TCR are common. However, such films are unstable due to their discontinuous nature\(^3\) and have little practical use. When thicker films are deposited, continuous films are formed but they still as a rule exhibit higher resistivities and less positive TCR as compared to their bulk values. This is usually the result of impurities incorporated in these films during deposition\(^4\), formation of defect centres and the scattering of electrons at the film boundary if the mean free path of the electrons is greater than the film thickness. Unlike the very thin films, these thicker films are usually stable. With the realisation that impure films tend to possess high resistivities and small TCR, ideal device characteristics, thin films have been deliberately doped to achieve this end.

Doping may be carried out either by adding a suitable reactive gas to the system during sputtering or by adding the dopant, such as another metal or its oxide to the sputtering target.
In general, there are two main methods for laying down metal films:

(i) by evaporation using resistive heating or, by electron beam heating\(^{(5,6)}\) in the case of metals with very high melting points.

(ii) by sputtering. Normally, metals with high melting points are prepared in this manner and the ability to dope the films as they are being deposited has led to the adoption of sputtering systems for most thin film work.
Electrical Conduction in Thin Metal Films

Generally, in thin metal films, the electrical conduction processes depend on the physical character of the films\(^2\), i.e. thickness and continuity.

When the film thickness is greater than the mean free path (m.f.p.) of the conduction electrons, and provided it is continuous, the film will tend to exhibit the bulk electrical properties of the metal, with a low resistivity and a positive TCR. However, due to impurities incorporated into the film during deposition, the bulk properties are not usually achieved and furthermore it is possible for the resistivity to be high due to size effect, i.e. the size of the individual metal islands forming the continuous film is less than the m.f.p. of the electrons. If the film is thinner than the m.f.p. of the conduction electrons, scattering at the film surfaces will occur causing its resistivity to be higher than the bulk metal, with a less positive TCR.

For a film consisting of metal islands surrounded by some insulating phase an activation type conduction process occurs. This can be represented by an expression of the kind:-

\[
\sigma = \sigma_0 e^{-E/kT}
\]

where \(\sigma\) = conductivity
\(\sigma_0\) = Constant
\(E\) = activation energy
\(k\) = Boltzmann's constant
\(T\) = temp. in Degrees Kelvin
E, the activation energy, is that energy that must be given to a conduction electron to transfer it from one metal island to its neighbour in order to overcome the energy barrier of the insulating phase and is dependent on island size and spacings between the islands and these parameters are in turn dependent on the film thickness. From the above expression, by plotting \( \sigma \) vs. \( 1/T^0K \) it is possible to calculate (from its slope) a unique activation energy for a given film. This activation energy also causes the film to exhibit a negative TCR. We can show this by rearranging the conductivity relationship in terms of resistance:

\[
R = R_o e^{E/kT}
\]

where \( R = \) resistance

\( R_o = \) constant

Differentiating we have:

\[
\frac{dR}{dT} = -R_o \frac{E}{kT^2} e^{E/kT}
\]

Now TCR is defined as \( \frac{dR}{dT} \times \frac{1}{R} \), therefore we have TCR = \( -E/kT^2 \).

However, in practice thin films are not totally continuous or discontinuous and this results in a combination of the metallic/activation type conduction processes acting in parallel, with the positive TCR of the metallic conduction opposing the negative TCR due to the activated component. It is interesting to note that by balancing these two components, perhaps during deposition or other post treatment like ion-implantation, it should theoretically be possible to produce films with zero TCRs.
1.4 Properties of Tantalum

In this thesis, tantalum has been chosen for the preparation of thin film resistors for several reasons. Briefly, tantalum has been found to possess both, good resistor (high resistivity coupled to low TCR) and capacitor properties (high dielectric constant and good dielectric strength).

Tantalum is a refractory metal with a bulk density of 16.6 gm/cm$^3$ and crystallises in the b.c.c. structure with a lattice constant, $a_0 = 3.3508 \, \text{Å}$ (ASTM X-ray diff. file 4-0788). It has a very high melting point (3000°C), is not readily attacked by most common acids and alkalis and is very abrasive-resistant, all of which are very desirable properties for the fabrication of electronic components. However, like titanium, it is a very good gettering metal and interacts strongly with oxygen, nitrogen, water, carbon dioxide, carbon monoxide and the lighter hydrocarbons. The bulk specific resistivity of tantalum is 13.6 micro.ohm.cm. and it has a TCR of about +25ppm/°C, depending on the purity of the metal.

On account of its high melting point, tantalum thin films are not normally deposited by resistance heating in vacuo. The most popular method is by cathode sputtering in the presence of a glow discharge using inert argon as the
source of ions.

At the University of Surrey, tantalum thin films have been grown by electron beam evaporation in an ultra high vacuum station. As tantalum is such a powerful gettering agent, it is desirable to grow the films in a clean, high quality vacuum to achieve reproducible results. It is known that tantalum films grown using exactly the same vacuum stations and 'similar' vacuum pressures have produced very different films. As a rule it is best to avoid pumping systems where oils of any kind are used unless efficient traps to prevent backstreaming of hydrocarbons are used. Contrary to popular belief, the 'cleanliness' of a vacuum system is not governed solely by the pressure; backstreaming of oils from the pumps may be worse in a system with a low pressure and high gas output than in one with a high pressure and a low gas throughput.
2. LITERATURE SURVEY

2.1 Undoped Tantalum Thin Films

Published literature \(^{(18-21)}\) on tantalum films grown without doping suggests the possible existence of two forms of tantalum, a b.c.c. type which is the bulk form (resistivity = 13.6 micro.ohm.cm., TCR = +25ppm/°C) and a β-type with a higher resistivity of about 200-300 micro.ohm.cm. and a negative TCR, the actual values depending on the purity of the films.

β-tantalum was first identified by Read and Altman\(^{(22)}\) using sputter deposition and they claimed that their films exhibited resistivities of about 200 micro.ohm.cm. with a near zero TCR, and crystallised in the tetragonal structure with lattice constants (a and c) of 5.34 and 9.94 Å. However, they were undecided as to whether it was an allotrope of b.c.c. tantalum or an impurity stabilised phase. On heating their films to 755-775°C in vacuum, they reported that their films reverted to the b.c.c. type.

As oxygen incorporated in the films was widely suspected as the cause for the β-tantalum, Wilcox and Westwood\(^{(23)}\) measured the amounts of oxygen in their b.c.c. and β-tantalum films. They found that the b.c.c. films contained less than 5 atomic % oxygen whereas the β-type contained at least 7 atomic %. Waterhouse et. al.\(^{(24)}\) and
Westwood et al. (25) have reported similar findings. However, Velasco (26) using nuclear micro-analysis could not detect any measurable difference between his b.c.c. and $\beta$-tantalum and concluded that oxygen was not responsible for the $\beta$-tantalum.

Earlier, Fujimoro et al. (27) obtained b.c.c. tantalum with a resistivity of about 30 micro.ohm.cm. at low pressures in their triode system but they observed that as the vacuum pressure increased, the resistivity also increased and the b.c.c. tantalum reverted to the $\beta$-type.

The reason for the formation of $\beta$-tantalum in sputtered films has been the subject of much investigation and controversy and is still unresolved. Oxygen content has been the main contender, but others such as substrate composition (28), water vapour in the vacuum station (29), arrival rates of impurities (30,31), substrate biasing and many others (32) have also been proposed.

The small amounts of material generally available make measurements of impurity concentrations exceedingly difficult. Several methods have been attempted (33-37) but so far with very limited success. Very often, the task of differentiating between the b.c.c. and $\beta$-type has proved difficult and confusing.
The interplanar spacings for a number of reflections in the b.c.c. and β-tantalum phases are quite similar and this, combined with small changes in the lattice parameters, which are often present in thin films, and preferred orientations\(^{38,39,40}\) can make identification difficult. For example, Fujimori et. al.\(^{(41)}\) observed only one weak X-ray reflection, \(\alpha = 2.386 \text{ Å}\); they assigned this to the (110) b.c.c. plane, but it could be due to the (202) β-tantalum plane.
2.2 Ion Implantation

In ion implantation, the dopant ions are produced in an ion source\(^{(42)}\), mass analysed and then accelerated down a beam line into the target. By choosing the appropriate accelerating voltage\(^{(43)}\) we can control the dopant profile in the target. Also, by monitoring the ion current we can control the doping level in the target precisely as the doping process is essentially a discrete one.

These two striking advantages of ion implantation make the method highly suitable for doping metal films as compared with sputtering.

In conventional sputtering, metal films are doped either by using a reactive gas (i.e. one that reacts with the metal being sputtered) or by bombarding a target which already contains the dopant, e.g. an alloy. If the dopant is a gas, this is usually bled in continuously during deposition\(^{(44-47)}\) or a static level is first established before sputtering. Both these methods suffer from the disadvantage that once sputtering is initiated there is no proper control of the reactive gas within the system\(^{(48)}\).

Gersternberg and Calbick\(^{(49)}\) have doped tantalum films with oxygen in their sputtering rig and obtained resistivity variations of at least two orders of magnitude.
(from about 60 micro.ohm.cm. to 2000 micro.ohm.cm.) for oxygen content from 5-40 atomic %. Their TCR changed from positive to negative values for increasing oxygen levels. Since then, other workers\(^{(50,51,52)}\) have published similar findings. Figs. 1(a) and (b) show resistivities and TCR as a function of partial pressures of oxygen. Figs. 2(a) and (b) show the same variables but for films doped with nitrogen.

Referring to Figs. 1 and 2 we see that relatively small changes in doping levels in the films can cause quite large variations in resistivities and TCR. This is especially true for the TCR. In practice it might prove impossible to achieve the exact doping levels to obtain the desired resistivity and TCR combinations. Waterhouse and Wilcox\(^{(53)}\) have pointed out that the doping levels in the films are not necessarily governed by the partial pressures of the dopant gases during sputtering.

Theoretically, with ion implantation, once a relationship between resistivity and TCR has been established, the required resistivity and TCR combination can be easily attained as the doping process is now essentially a discrete one. Furthermore, the possibility of controlling the impurity profile within the film gives us an additional parameter which we can use to modify the electrical characteristics of our films. An added degree of flexibility which is not available with normal reactive
Fig. 1(a)

Oxygen

\[ \rho (\mu \Omega \text{cm}) \]


Fig. 1(b)

(atomic\%)

\( -0.01 \)

Fig. 2(a)

Nitrogen

\[ \rho (\mu \Omega \text{cm}) \]

Waterhouse

Fig. 2(b)

(atomic\%)

\( 0.05 \)

McLean
sputtering is that by using ion implantation we can introduce almost any impurity as a dopant into a metal film, subject only to the ion source capability of the implanter.

Of course, ion implantation is not the answer to all the above problems encountered in reactive sputtering, and like any system has its limitations. During implantation, sputtering of the target film always occurs. This places an upper limit on the dopant concentration we can put into the film. Also, radiation damage and radiation enhanced diffusion may occur creating further problems.

Recently, Perkins (54), O'Connell (55) and Collins (56) have doped metal films using ion implantation as an alternative to conventional reactive sputtering. O'Connell doped thin aluminium films with argon and oxygen using this technique and reported resistivity spanning at least five orders of magnitude. His results for an aluminium film implanted with oxygen are reproduced in Fig. 3.
Fig. 3. Variation of sheet resistance and TCR with ion dose (O'Connell).
3. APPARATUS AND EXPERIMENTAL TECHNIQUES

3.1 Deposition of Tantalum Films

The films were grown on alkali-free alumina borosilicate Corning glass, type 7059 of physical dimensions 1" × 1". Manufacturer's figures quoted for the micro-roughness of the glass substrates is about 250 Å peak to valley distance.

Prior to loading the substrates into the vacuum evaporation station, the substrates were first washed in hot teepol solution, rinsed in hot distilled water, ultrasonically agitated in methanol, rinsed again in distilled water and finally washed in running deionized water until stable, clean conditions were reached and maintained. The treated substrates were then allowed to dry in a clean flow bench. When dry, they were loaded into the ultra high vacuum work station, ready for deposition of tantalum metal.

The vacuum station is pumped by a rotary pump fitted with an absorption trap to prevent backstreaming of hydrocarbons, a diffusion pump with a cold trap and a sublimation pump. The entire work area is bakeable up to 250°C to permit outgassing of the system. The working pressure at deposition is in the region of 10⁻⁸ torr or better.
The target source is made up of a tantalum slug of 99.99% purity placed in a tantalum crucible supported on a stainless steel carrier. The electron gun is positioned above the source and beam focussing is achieved electrostatically. The substrate carrier consists of a stainless steel hemispherical dome capable of holding eighteen glass specimens. Electrical connections to the outside world are provided for by glass-to-metal seals, and besides the normal terminals for the power supplies for the electron gun and focussing coils, resistance and temperature monitoring facilities are also provided for.

Before the films were deposited, the work chamber was baked out at 250°C for at least twenty-four hours after which the vacuum pressure reached between $10^{-9} - 10^{-10}$ torr. Next, the tantalum target was outgassed with the shutter closed until the system pressure stabilized at about $10^{-8}$ torr or better. After this, the shutter was opened and the deposition initiated. The conditions of evaporation were:- H.T. at 4 kV, filament current kept constant at 30 amps., and the substrate at a distance of 15 cm. from the tantalum source. During evaporation, the resistance of a control specimen was monitored continuously using a constant current source and a digital voltmeter. The time of evaporation was also noted with a stop-watch to determine the growth rate in conjunction with later thickness measurements obtained with a Rank-Taylor-Hobson Talystep. After the films have been grown, the system was
allowed to cool to room temperature and then brought up to normal atmospheric pressure by bleeding in oxygen-free nitrogen to minimise contamination.

Besides the control specimen for resistance monitoring, an aluminium coated substrate was also included in every batch of film deposited to obtain the self-supporting films required for transmission electron microscope studies.
3.2 Preparation of Specimens

After the tantalum films were grown and their thicknesses measured, electrical contacts, consisting of a gold layer over titanium were deposited in an Edward's coating unit at a pressure of about $8 \times 10^{-6}$ torr.

The tantalum thin films were then diced to the required size, $0.5 \times 2.5$ cm., using a diamond impregnated wire saw. After further cleaning and a final degreasing stage in an iso-propyl alcohol vapour bath, the films were ready for electrical measurements and implantation in the heavy ion accelerator. A talystep trace of a tantalum film edge is shown in Fig. 4, and a schematic diagram of a typical resistor in Fig. 5.

![Talystep trace of tantalum edge for Surrey Film using a non-contact mask.](image-url)
Fig. 5. Schematic drawing of a tantalum resistor.
3.3 Preparation of Self-Supporting Films for TEM

As mentioned earlier, aluminium coated substrates were included in every deposition run so as to obtain self-supporting films. No electrical contacts were grown on these films, instead they were diced into 3mm. squares using the wire saw. After the usual cleaning process, they were soaked in a dilute sodium hydroxide (NaOH) solution for about one-and-a-half hours until the aluminium backing had dissolved leaving the tantalum films free in solution. These films were then removed with great care from the sodium hydroxide solution with a wet 'spoon' and transferred into a Petri dish containing distilled water and allowed to soak for a further twenty minutes to remove traces of the alkali. After this process, the films were removed from the distilled water using 3.5mm. diameter copper grids taking great care not to allow the films to roll and to ensure that they were the right side up. The grids holding the tantalum were then placed carefully on a slightly moist filter paper to remove any excess water and then allowed to dry in a flow of filtered air. When dry, each film was examined first under an optical microscope and then using the transmission electron microscope to assess their physical integrity. Any film showing an excessive number of pin holes, tears or in which warping had occurred was discarded. Typically, the success rate of obtaining good films was about 80%.
3.4 Ion Implantation

3.4.1 The 600 keV Heavy Ion Implanter

The ion accelerator is of the open high voltage terminal design, the positive terminal being supplied by a 600 kV d.c. S.A.M.E.S. generator. A diagrammatic layout is given in Fig. 6.

The high voltage terminal, 'the bun', contains the ion source and associated power supplies and the power to this terminal is provided by an alternator within it which is driven by an insulated shaft connected to a synchronous motor tied down to earth potential.

The ion source is a Nielson type and comprises an evaporation furnace, a cylindrical ionisation chamber carrying a helical filament, a concentric anode and heat shield and an axial magnetic field. The filament serves a dual purpose in ionising the atoms and also in heating the evaporation furnace. If the source material is gaseous, a needle valve is used to introduce the gas. Fig. 7 shows a view of the bun, the analysing magnet, the beam line and the target chamber.

After production, the ions are extracted and focussed by an Einzal lens and then accelerated down the
600 keV HEAVY ION ACCELERATOR.

Fig. 6.
Fig 7 A: analysing magnet, B: high voltage terminal, C: target chamber
tube. The ions then pass through an analysing magnet capable of bending ions up to a limiting mass-energy product of 45 amu.MeV. The magnet coils are supplied by a 40 volts, 300 amps. stabilised supply giving a field stability of better than \( \frac{1}{10^3} \).

The stainless steel target chamber with various access ports is located about a further 3m. down from the magnet. Ion and sublimation pumps are used and gave a typical operating pressure of about \( 10^{-6} \) torr. The rest of the system is pumped by well trapped oil diffusion pumps.

The cross-section of the ion beam in flight down the accelerator tube is monitored by two oscillating wire detectors. Uniform irradiation of the specimen in the target chamber is ensured by two sets of electrostatic deflection plates to which are fed signals at frequencies of 60Hz and 900Hz.

A photograph of the stainless steel target holder is shown in Fig. 8. Although it can accommodate only one specimen at a time, all the necessary facilities for resistance monitoring, temperature coefficient of resistance studies, hot and cold implants are provided for. A T1/Advance thermocouple specially calibrated at the N.P.L. was used to measure temperature changes of the specimen and also of the heater block on which the target is mounted.
Fig. 8. Target Holder. (a) thermocouple (b) heating element (c) baffled-tank (d) suppression plate (e) lead out terminals (f) target-holder.
A baffled tank under the heater block permits the holder to be used at liquid nitrogen temperature if required. A heating element is wound around the outside of the heater block for high temperature work. The operating range of the holder is from \(-196^\circ C\) to about \(600^\circ C\).
3.4.2 Implantation Procedure

Immediately after the tantalum film resistor had been loaded into the implanter, a resistance measurement was obtained at atmospheric pressure and the temperature noted. This was followed by normal pump down procedures until an acceptable working pressure was established, this being typically about $10^{-6}$ torr. After a further hour, the resistance value, now measured in vacuum was recorded. At the same time the temperature of the film which had been allowed to reach ambient temperature of water pumped into the baffled tank was noted using the $T_1$/Advance thermocouple with an ice reference as the cold junction. The tantalum film was now ready to be implanted.

The energy of the implants was calculated from the Lindhard, Scharff and Schiött (LSS)\(^{(57)}\) theory such that the initial mean projected range ($R_p$) of the implanted ions was equal to one half of the film thickness. Appendices 1, 2 and 3 show the ion penetration ranges for argon, oxygen and nitrogen in tantalum.

It was found during the project that the 600 keV ion accelerator was very unsuited for producing oxygen ions. The highly reactive nature of oxygen drastically reduced the ion source filament lifetime to a few hours as compared with several hundreds of hours for argon and nitrogen. This often meant prolonged interruptions for repairs.
resulting in failure to complete the experiment. To try and overcome the problem of this contamination, carbon dioxide\(^{58}\), carbon monoxide and mixtures of argon plus oxygen have been attempted but so far without any success. The ideal solution would have been to use a radio frequency ion source but this was not available for the 600 keV machine.

At each of several predetermined doses, a self-supporting film was extracted from the target holder for examination in the transmission electron microscope. This necessitated the letting up to air of the target chamber every time such a film was required. Normally, three or more of these films were placed together with the usual film resistor to be irradiated so that electron microscopy could be performed at increasing doses.
3.4.1 In Situ Electrical Measurements

The tantalum film was held down on the target holder with phosphor bronze spring contacts and, as an additional measure to ensure good electrical connection, a small dab of silver dag was applied. The resistance value of the film was measured by passing a constant current of 10 micro-ampere (precision of better than 1 in 10⁴) through the resistor and the resultant voltage drop across it recorded on a four-and-a-half digit voltmeter. A Marconi bridge, type TF2700 was also employed to measure resistance as a back-up to ensure that the system was operating normally.

After implanting to a predetermined dose, the shutter in the beam line was closed and the resistance and temperature measured immediately afterwards. The heater was then switched on and the temperature of the film allowed to reach 100°C and stabilised at this value for half-an-hour, after which the resistance value was again recorded. With the heater now turned off, water was pumped through the baffled tank to cool the specimen and maintain it at a constant temperature. This was followed by another resistance and temperature measurement. A good check to ensure that the film had actually reached a uniformly constant temperature was to reverse the terminals of the digital voltmeter and if the two readings were different this indicated that the film had not reached equilibrium.
This procedure of measuring the film resistance at high and low temperatures with increasing dose was repeated until measurements became unstable which usually occurred at above 20 Mega-ohms. For a typical experimental run, about twenty or more points were obtained, and typically this took approximately twenty-four hours.

From the above measurements, we can calculate the TCR of our resistor (with room temperature as the reference) which is given by:

$$\text{TCR} = \frac{(R_h - R_1)}{(R_1 \times (T_h - T_1))} \times 10^{-6} \text{ppm/}^{\circ}\text{C} \ldots \ldots \ (i)$$

where

- $R_h$ = resistance value at $100^{\circ}\text{C}$
- $R_1$ = resistance at room temperature
- $T_h$ = $100^{\circ}\text{C}$
- $T_1$ = room temperature, about $22^{\circ}\text{C}$

Since, at elevated temperatures there is the possibility that the film might undergo ageing or annealing effects, the upper temperature limit of measurement was fixed at $100^{\circ}\text{C}$.

In the above expression (i), we have tacitly assumed that the resistance value changes in a linear fashion.
between $R_1$ and $R_n$. This is not strictly correct as it is generally true that when films exhibit negative TCR, there is at least one component of the conduction process which is characterised by an exponential type function:

$$R = R_0 e^{E/kT}$$

where

- $R = \text{resistance}$
- $R_0 = \text{constant, depending on the film}$
- $E = \text{activation energy}$
- $k = \text{Boltzmann's constant}$
- $T = \text{temperature in degrees Kelvin}$

Activation energies for the undoped and doped films have been computed from plots of $1/R$ vs. $10^3/T$ and these were found to lie between $10^{-4}$ and $10^{-5}$ eV. These values coupled with the relatively low temperatures employed introduce negligible errors to our linear approximation.

In thin film work it is usual to express resistance in units of ohms.square$^{-1}$ instead of ohms. A film resistor of $R$ ohms, with length $l$ and width $d$ units will have its sheet resistance quoted as $R/(l/d)$ ohms.square$^{-1}$. Multiplying this sheet resistance by its thickness $t$, gives us its sheet resistivity.
3.5 Transmission Electron Microscopy (TEM)

3.5.1 Room Temperature TEM Studies

During mounting of the microscope grids on the target holder, great care was taken to shield part of each grid from the incoming ions so that comparisons can be made between the irradiated and unimplanted regions afterwards.

A JEOL 100B microscope with a goniometer stage was used to examine the self-supporting films. It was operated at a fixed voltage of 100 kV corresponding to an electron wavelength of 0.0037 Å, with a claimed manufacturer's resolution of ± 25 Å. The size of the aperture used was 2 microns.

The standard procedure adopted for examining the films was as follows. Initially, the film was scanned at a relatively low magnification of $9 \times 10^3$ times to determine the uniformity of implantation and especially to ensure that the film had not been damaged during mounting and removal of the delicate grid. A typical area of the implanted area was then photographed at increasing magnifications of 9, 25 and $50 \times 10^3$ times. Diffraction patterns were then obtained for this same region of the film. This schedule was then repeated for other different areas. To gather as much information as possible
from the diffraction patterns, the goniometer was used to tilt the film to bring out, when available, other reflecting modes.
3.5.2 High Temperature TEM Studies

The JEOL 100B as used in the University of Surrey is not equipped to undertake high temperature studies. For this purpose, a JEOL 100C fitted with a special hot stage capable of heating specimens up to 1000°C by resistive heating was kindly loaned to the Department by JEOL (Japan) Ltd., at Colindale. Another more powerful microscope, the JEOL 200C similarly equipped with a hot stage was also employed with the kind permission of Cranfield Technical College of Bedford.

Special molybdenum grids capable of withstanding very high temperatures (about 1000°C) without contaminating or degrading the tantalum films under study were used.

Micrographs and diffraction patterns were obtained for films at increasing temperatures of 200°C, 400°C and 600°C. At each designated temperature the film was allowed to stabilise for at least half-an-hour, usually much longer to avoid image jitter as a result of the film 'moving' when hot. Although higher temperatures can be reached, this was not attempted as it was felt that the very good gettering property of tantalum together with the relatively poor vacuum pressure in the microscope column (about $10^{-5}$ - $10^{-6}$ torr) might lead to misleading results.
Some very crude high temperature studies were also attempted with the microscope at the University using the electron beam itself to heat the specimens. However, only very thin films were amenable with this method, usually for films less than about 50 Å (calculated) thick. Using this method it was not possible to measure or estimate the temperature of the films.
3.5.3 Calibration of the Camera Constant of the Microscope

A gold standard was used to calibrate the camera constant of the instrument after every run. A semi-transparent layer of gold was evaporated over the tantalum film in a coating unit and a composite diffraction pattern obtained. Subtracting the diffraction pattern from a tantalum film without this gold overlay yielded that due to the gold only, and as its d-spacings are well documented, the camera constant can be calculated from the relationship:

\[ R \cdot d = L \lambda \]  \hspace{1cm} (iii)

where \( d \) = the d-spacing in Angstroms (Å)

\( R \) = measured ring radius from the diffraction pattern, expressed in cm.

\( L \) = Camera length, expressed in cm.

\( \lambda \) = wavelength of 100 kV electrons (0.0037 Å)

\( L\lambda \) = camera constant

The camera length, which is the distance of the specimen from the photographic plate, was found to vary only slightly from specimen to specimen and was approximately 44.0 cm. However, it was found necessary to calibrate it every time a new specimen was examined in order to detect any malfunction of the microscope which otherwise could have easily led to an incorrect identification of
the material we are trying to analyse later on.

Two methods were employed to measure the ring diameters on the photographic plates from which the d-spacings were computed.

(i) A technical Circle. This consists of a rotatable platform with a T-piece riding on a vernier scale. Using this method, six readings of each ring diameter were measured for each plate. Some difficulty was experienced in determining the extremity of the rings, especially those far away from the centre where the images tend to be blurred as a result of spherical aberration inherent in the microscope.

(ii) A densitometer. This is an optical method, where a light source and a detector scan the plate and producing a graph of the relative intensities present. Several runs were required to ensure that the diameters rather than the chords of the rings were being measured. Typically, at least ten scans were performed on each plate. A trace of one such run is shown in Appendix 4.

After the ring diameters had been measured, the relationship given in (iii) was used to calculate the d-spacings of the films and these were matched against the ASTM card index for compounds of tantalum for
identification. If diffraction spots were available, as in some of the films, both magnitude and vector computations were carried out. A typical example of such a calculation is shown in Appendix 5.
4. RESULTS

4.1 Introduction

Tantalum thin films deposited by three independent sources have been examined.

These are:

(i) The Edwards' films (supplied by Edwards High Vacuum of Crawley) which were electron beam evaporated.

(ii) The Ultra films (supplied by Ultra Electronics Ltd.) which were sputtered deposited in an inert atmosphere of argon.

(iii) The University of Surrey films which were prepared in the Ultra High Vacuum Laboratory using electron beam evaporation.

Table 3, at the end of Section 4.2, gives the initial properties of these films. Self-supporting films were available for the Surrey films only and as such all the TEM results are for these films.

The results presented in this chapter will be divided into four parts. The undoped films will be dealt
with first followed by films doped with (i) argon, (ii) oxygen and (iii) nitrogen.
4.2 The Undoped Tantalum Films

4.2.1 TEM at Room Temperature

The micrograph of Fig. 9 was from a film grown at the University and taken at room temperature without any further treatment. The film was observed to be non-continuous, probably consisting of a matrix of tantalum islands separated by an oxide\(^{59,60}\). In our case these islands were approximately 100 Å in size separated by 25 Å of the oxide.

A diffraction micrograph of the same area of the film (shown superimposed in Fig. 9) exhibits four rather diffuse rings indicating that the film was quite amorphous. Table 1 shows the spacings and reflecting modes of these rings. There is some possibility that the first, strong broad ring is due to two materials, b.c.c. tantalum and its oxide TaO\(_2\).

-Table 1: U.H.V. Evaporated Tantalum Films

<table>
<thead>
<tr>
<th>Measured</th>
<th>ASTM Index No. 4-788</th>
<th>b.c.c. Tantalum</th>
</tr>
</thead>
<tbody>
<tr>
<td>d(Å)</td>
<td>d(Å)</td>
<td>(h k l)</td>
</tr>
<tr>
<td>2.29</td>
<td>2.34</td>
<td>110</td>
</tr>
<tr>
<td>-</td>
<td>1.65</td>
<td>200</td>
</tr>
<tr>
<td>1.38</td>
<td>1.35</td>
<td>211</td>
</tr>
<tr>
<td>1.14</td>
<td>1.11</td>
<td>220</td>
</tr>
<tr>
<td>0.89</td>
<td>0.88</td>
<td>321</td>
</tr>
</tbody>
</table>
Fig. 9  Virgin Tantalum Film Deposited at the University (unimplanted). Film thickness = 500Å.
Except for the first d-spacing, $d = 2.29 \text{Å}$, all the others are larger than those published by ASTM. This is probably an indication that the film contained absorbed gaseous impurities. Literature published by Read(61) has shown that it is possible for the unit cell of tantalum film to expand to accommodate impurities, resulting in slight variations of the measured d-spacings. In his paper he quoted d-spacing expansions of around 2%. Those measured above are about 2.5%.
4.2.2 TEM at High Temperature

A self-supporting film was subjected to temperatures up to 600°C. No change was observed between 200°C and 400°C, in either the micrograph or the diffraction pattern as compared with that of Fig. 9.

At 600°C a very striking change was observed as shown in Fig. 10. The previously uniform, semi-continuous 'orange peel' relief was replaced by larger grains varying in size from 50 to 5000 Å. Also, the diffraction pattern now had at least 15 sharp rings showing that there was now higher crystalline order. The spacings of the first seven rings, together with those for b.c.c and β-tantalum oxide (Ta₂O₅) are given in Table 2. From this table we can see that the oxide of the two phases have very similar d-spacings and at present we are unable to state with any degree of certainty whether our film was a mixture of the two phases of just β-tantalum oxide. The first ring, \( d = 5.23 \text{ Å} \) in our film, however, indicates that there was some β-tantalum oxide present in our film. It is interesting to note that Frade et al. (62) have reported that thermal crystallisation of his oxide of tantalum (he did not say which oxide, but presumably he meant the lower oxide) resulted in the formation of crystalline β-tantalum pentoxide.

Temperatures greater than 600°C were not attempted as it was felt that the vacuum pressure (of about \( 10^{-5} - 10^{-6} \) torr) in the electron microscope did not warrant such studies in view of the highly reactive nature of tantalum. As it is, the results obtained for the 600°C run should be viewed
Fig. 10 Virgin Tantalum after heat treatment at 600°C for ½ hour.
with this in mind and that contamination of the film might already have occurred.

Table 2: U.H.V. Evaporated Tantalum Film after Heat Treatment at 600°C

<table>
<thead>
<tr>
<th>Measured d(Å)</th>
<th>ASTM Index No. 19-1289 Beta-Ta₂O₅ d(Å)</th>
<th>ASTM Index No. 19-1300 b.c.c.-Ta₂O₅ d(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.23</td>
<td>5.28</td>
<td>-</td>
</tr>
<tr>
<td>3.87</td>
<td>3.88</td>
<td>3.78</td>
</tr>
<tr>
<td>2.85</td>
<td>2.86</td>
<td>-</td>
</tr>
<tr>
<td>2.44</td>
<td>2.44</td>
<td>2.45</td>
</tr>
<tr>
<td>2.02</td>
<td>2.02</td>
<td>2.02</td>
</tr>
<tr>
<td>1.81</td>
<td>1.83</td>
<td>1.83</td>
</tr>
<tr>
<td>1.65</td>
<td>1.66</td>
<td>1.65</td>
</tr>
</tbody>
</table>

Camera constant as determined by a gold standard = 43.5 cm.
4.2.3 Electron Reflection Work

In collaboration with T. Tunkasiri from Chemical Physics Dept. and using Electron Reflection\(^{(63)}\) \(\beta\)-type tantalum has been identified in our film together with b.c.c. tantalum but no \(\beta\)-tantalum was observed using TEM. There are probably several reasons for this anomaly:

(i) The films used for TEM were grown on aluminium coated substrates whereas those that were examined with electron reflection were deposited directly onto glass. This difference might have caused the tantalum to assume preferred orientations,\(^{(64)}\) thus suppressing the growth of one of the phases in preference to the other.

(ii) The stripping technique adopted for preparing the self-supporting films may have resulted in physical and chemical changes of the film.

(iii) Finally, it is possible that the \(\beta\)-tantalum may have been present in our self-supporting films but we have been unsuccessful in detecting it. On the other hand we may have assigned the d-spacings to the wrong material. It is well-known\(^{(65)}\) that tantalum and its compounds have in some instances very similar d-spacings. This is possibly the situation occurring here as the 1st ring can easily...
be assigned to TaO₂ or β-tantalum or even both.
4.2.4 Electrical Measurements

From plots of reciprocal resistance (1/R ohm\(^{-1}\)) against reciprocal temperature (1/T degrees Kelvin\(^{-1}\)) as shown in Fig. 11, the activation energies for the University and Edward's films were calculated. Whilst the University film had one activation energy of 8.8 \times 10^{-5}\text{eV}, the latter film had two, corresponding to 6.6 \times 10^{-5}\text{eV} from room temperature to about 100°C and 1.6 \times 10^{-5}\text{eV} from 100°C-300°C.

The Ultra film which was sputter-deposited, unlike the University and Edward's films which were grown by electron beam evaporation, exhibited a positive slope from which it is not possible to compute an activation energy. This implies that over the temperature range (22°C-300°C) in which the measurements were performed, a metallic type conduction mechanism dominates the charge transfer process, even though an activated component may be present.

The values of our activation energies are at least one order of magnitude smaller than those calculated from theory\(^{(66)}\). Hardy et al.\(^{(67)}\) have reported similar values for their tantalum films which will be discussed later.

Desserre and Goulet\(^{(68)}\) in their investigation of the
variation of the resistance during temperature cycling for their electron beam evaporated films suggested that the mean free path of the conduction electrons to be 970 Å. They determined this by fitting the Sondheimer's theory to their conductivity versus thickness data. Sondheimer's theory states that:

\[ \frac{\sigma}{\sigma_0} = 1 - \frac{3}{8} \left( \frac{L}{D} \right) \]  

(iv)

where:

- \( \sigma \) = conductivity of the thin film
- \( \sigma_0 \) = conductivity of the bulk metal
- \( L \) = mean free path of electron
- \( D \) = film thickness

Substituting the appropriate values from the Ultra and University films into the above relationship we obtain the mean free paths for the two films to be approximately 1000 Å. Although this figure agrees well with that of Desserre and Goulet for their films, it is very high compared to a good conductor like silver which has a mean free path of 500 Å. This is possibly due to the incorrect use of the Sondheimer theory. Since the change in conductivity of our films and those of Desserre and Goulet is probably the result of film structure and not that due to the intrinsic metal itself, Sondheimer's theory may not be applicable to these films.
Fig. 11. Conductivity vs. reciprocal temperature for the undoped films.
4.2.5 Summary of Results for the Undoped Films

Table 3 summarises the initial properties of the undoped tantalum films as deposited at: (i) the University, (ii) Edward’s High Vacuum Lab. (Crawley) and (iii) Ultra Electronics Ltd.
| TABLE 3 |
|-------------------|------------------|--------------------------------------------------|
| **Deposition Technique** | **Electron beam evap.** | **D.C. Diode Sputtering** | **Electron beam evap.** |
| **Vacuum Pressure** | not better 1 x 10^{-5} torr | base pressure 1 x 10^{-6} sputtered at about 1 x 10^{-3} torr | better than 2 x 10^{-10} torr before evap. and 2 x 10^{-7} during evap. |
| **Contaminants in vacuum system** | - | - | Mainly CO + CO₂ |
| **Thickness (Å) using Talystep** | 550 | 400 | 500 |
| **Resistance ohms/square** | 1.7 k | 81.0 | 72.0 |
| **Resistivity micro.ohm.cm.** | 9100.0 | 320.0 | 360.0 |
| **TCR/ppm/°C measured between room temperature and 100°C** | -500.0 | +150.0 | -200.0 |
| **estimated % free Tantalum** | No free Ta using X-ray. Oxide present probably Ta₂O₅ | about 80% b.c.c. Ta, using Rutherford backscattering (RBS). The rest oxide, not identified. | 65% Ta by Rutherford backscattering (RBS) Probably b.c.c. type using TEM. Beta-type detected using electron reflection. ESCA attempted but not conclusive. |
| **Substrate** | 7059 glass | 7059 glass | 7059 glass |
4.3 Argon Implanted Tantalum Films

4.3.1 TEM

A series of TEM micrographs together with their diffraction patterns are shown in Figs. 12(a), (b), (c) and (d) for a Surrey film, taken at increasing ion doses. Analysis of the diffraction patterns showed b.c.c. tantalum in (a) and (d), with (b) and (c) consisting of Ta$_2$O. It is apparent, that as the dose increased the crystallinity of the film improved (as in (a) - (c)) but at very high doses the film began to lose its crystal order as in (d), with the film becoming amorphous after this. The presence of Ta$_2$O was probably due to a bombardment induced chemical reaction in the film with the oxygen incorporated in it during deposition. It is interesting to note that the film reverted to its original b.c.c. tantalum form at high doses (as in (d)) and would appear to indicate that preferential sputtering of oxygen was occurring.\(^{(69)}\)

At a dose of $7.5 \times 10^{16}$ ions/cm$^2$ bubble-like features 12(b), appeared on the film. This phenomena has never been observed for films implanted with oxygen or nitrogen. A similar observation has been reported by Spitznagel et al.\(^{(70)}\) using argon although he used Zircalloy-4 films. He further added that other ions he used did not cause the same effect. No reasons were put forward for this observation but it is
quite probably due to the inert and insoluble nature of argon.
Fig. 12 (a) $9 \times 10^{15}$ ions/cm$^2$. (b) $7.5 \times 10^{16}$ ions/cm$^2$. (c) $1 \times 10^{17}$ ions/cm$^2$. (d) $1.7 \times 10^{17}$ ions/cm$^2$. 

Argon Implant at 50keV.
4.3.2 Electrical Measurements

Fig. 13 shows the resistivity versus dose plots for the Edward's and University films when irradiated with argon. We observed that the resistivity of the Edward's film, unlike that of the University's, decreased with increasing dose up to about $2 \times 10^{17}$ ions/cm$^2$ after which further irradiation caused it to rise. Prior to implantation, both films were desorbed in vacuum at about $10^{-6}$ torr for one hour, which probably meant that adsorbed surface impurities were not responsible for this observation in the Edward's film.

A TCR versus dose plot is also shown in the same Fig. for the University film and this changed from $-200$ ppm/$^\circ$C to about $-75$ ppm/$^\circ$C before the film became unstable. This would appear to support our earlier TEM results indicating that some sort of preferential sputtering was occurring in the film which made it more metallic with increasing ion dose.

From Fig. 14 we observed that the Edward's film was characterised by two activation energies, the first of $5.5 \times 10^{-5}$ eV from room temperature to about $110^\circ$C and the second of $2 \times 10^{-5}$ eV from $110^\circ$C to $300^\circ$C. For the University film there was only one activation energy corresponding to $4 \times 10^{-5}$ eV. Compared to the unimplanted films, all these values were less than those for the undoped film, results which again tended to show that the films were getting more metallic.
Fig. 13. Resistivity, TCR vs. dose plots for the argon implanted films.
Fig. 14. Conductivity vs. reciprocal temperature plots for the argon implanted films.

- Surrey (500 Å): Ar⁺, 50 kV at $1 \times 10^{17}$ ions/cm²
- Edward (560 Å): Ar⁺, 50 kV at $3 \times 10^{17}$ ions/cm²
4.3.3 The Sputtering Ratio of Tantalum Films

By implanting the film to open circuit, (i.e. punch through) it was possible to arrive at a crude estimation of the sputtering ratio, $S$, of tantalum. For argon, the sputtering ratio is 1.1 at 50 kV. It was estimated by dividing the total number of tantalum atoms per square cm for the 500 Å film, by the total number of argon ions required to bring the film to open circuit (defined as being greater than 20 M-ohms). The tantalum film was assumed to be pure and having a bulk density of 16.6 gm/cm$^3$. A figure for $S$ of 0.8 was obtained if the tantalum film had a density which was equal to $\frac{1}{3}$ its bulk density. This was probably the more accurate estimation as it is generally true that the real film density is usually less than its bulk value as a result of impurities and compound formation during deposition.

In Fig. 15 we reproduce a graph which was calculated by Sigmund$^{(71)}$ for the sputtering yield of tantalum for argon, together with experimental points obtained by other workers$^{(72)}$ and ourselves.
Variation of sputtering yield for Ta

· Exp. values for Ar⁺ (not from Surrey)

- Calculated values from Sigmund's theory

Δ Surrey film
4.4 Oxygen Implanted Tantalum Films

4.4.1 TEM at Room Temperature

A series of TEM micrographs for the University film which was taken at increasing oxygen doses, together with their relevant diffraction patterns are shown in Figs. 16(a), (b), (c) and (d).

At a relatively light dose of $1 \times 10^{16}$ ions/cm$^2$, highly crystalline b.c.c. tantalum was precipitated out from the film as in Fig. 16(a). Fig. 17 shows this more clearly where the contrast between the highly crystalline precipitates and the near-amorphous background b.c.c. metal is sharply brought out.

As the dose was increased, the film quickly lost this highly crystalline phase as shown in (b) which corresponded to a dose of $7.5 \times 10^{16}$ ions/cm$^2$. Analysis of the diffraction pattern showed the presence of Ta$_2$O in the film. At $1 \times 10^{17}$ ions/cm$^2$, both Ta$_2$O and b.c.c. tantalum were identified and the crystallinity appeared to have improved as in (c), after which a further increase in dose caused the film to lose its crystallinity and at $6.5 \times 10^{17}$ ions/cm$^2$ the film became amorphous.
Oxygen Implant

Fig. 16 (a) $1 \times 10^{16}$ ions/cm$^2$. (b) $7.5 \times 10^{16}$ ions/cm$^2$. (c) $1 \times 10^{17}$ ions/cm$^2$. (d) $6.5 \times 10^{17}$ ions/cm$^2$. 
Fig. 17 Precipitation of b.c.c. Tantalum (arrowed) at low Oxygen dose.

Dose = $1 \times 10^{16}$ ions/cm$^2$. 
4.4.2 TEM at High Temperatures

A tantalum film with an implanted dose of \( 1 \times 10^{17} \) ions/cm\(^2\) and an estimated thickness of about 400 Å was subjected to resistive heating in a JEOL 100C microscope at 200°, 400° and 600°C. No change was observed in the film in either its physical features or its diffraction pattern, a surprising result as it was expected that the b.c.c. tantalum which was earlier identified (see Fig. 16c) would have been converted to Ta\(_2\)O\(_5\) (see Fig. 10).

Fig. 18 shows a micrograph of a tantalum film, a part of which had received a dose of \( 1.5 \times 10^{17} \) ions/cm\(^2\). The other region was shielded from the ion beam and in good proximity to a heat sink. From the accelerating voltage and the beam current, the film was calculated to be absorbing about 0.1 watt/cm\(^2\). Using Dearnaley's results\(^{(73)}\), the film was estimated to be at approximately 200°C. A gradual change in features from a matrix type structure, to a more dense, closely packed region in the unbombarded area is observed. The shielded part of the film also appeared to have a more continuous structure compared to the as-deposited film even though the diffraction from this area still indicated a somewhat amorphous film. Features which looked like stacking faults and micro-twins, which were not present before
implanting can be seen in the unbombarded region.

A film with a dose of \(6.5 \times 10^{17}\) ions/cm\(^2\) and estimated to be about 90 Å thick was subjected to electron beam heating in the microscope in the University. The result is shown in Fig. 19 where the hot region (middle left-hand side of the micrograph) can be clearly distinguished from the rest of the film. At the centre of the hot spot, blister-like features, which were very evident in the unheated region of the film have been reduced in numbers. Although this did not change the overall character of the film which appeared to be semi-continuous, a diffraction pattern of the heated area exhibited good crystallinity, compared to the untreated portion which was almost amorphous. The compound, \(\text{Ta}_2\text{O}_5\) has been identified from this heated area. A composite micrograph of the heated region is shown on its own in Fig. 20.
Fig. 19 Electron Beam Heating of Oxygen Implanted Film.
Dose = $6.5 \times 10^{17}$ ions/cm$^2$. Ta$_2$O$_5$ (diffraction spots) is formed in the hot region. The rest of the film is amorphous.
Fig. 20 Hot Region of Fig. 19 shown magnified.
In Fig. 21 we have a graph of sheet resistivity and TCR versus oxygen dose. Except for a small 'hump' in the middle dose region, the sheet resistivity showed a smooth transition up to punch-through.

Two peaks were observed for the TCR:

(i) The first occurring at a relatively light dose, between $1 \times 10^{16} - 6 \times 10^{16}$ ions/cm$^2$, corresponding to the precipitation of highly crystalline b.c.c. tantalum which was reported in our TEM results (section 4.4.1). A plot of sheet resistance versus TCR for the same film emphasised this clearly as in Fig. 22 where the TCR peaked sharply towards positive values.

(ii) The second peak, in which the TCR actually crossed the x-axis to assume positive values before going negative again, occurred between $1.5 \times 10^{17} - 3 \times 10^{17}$ ions/cm$^2$. TEM analysis of the film (Fig. 16c) showed that $\text{Ta}_2\text{O}$ and b.c.c. tantalum were present in these films.

Between the two peaks, from $6 \times 10^{16} - 3 \times 10^{17}$ ions/cm$^2$, there was a plateau region where the TCR remained at
approximately -100 ppm/°C.

Values for the activation energies of the film are not available due to the difficulty in obtaining oxygen ions with the present ion source.
Fig. 21. Resistivity, TCR vs. dose plots for an oxygen implanted film.
(a) corresponds to ppt. of highly crystalline bcc tantalum at low dose.

(b) TCR now +ve due to impact dissociation of Ta₂O into Ta.

argon implanted film for comparison.
4.5 Nitrogen Implanted Films

4.5.1 TEM

A TEM micrograph for a University film which had been implanted with nitrogen to a dose of $1.5 \times 10^{17}$ ions/cm$^2$ is shown in Fig. 23. Table 4 shows the d-spacings, and from these, the compound $\text{Ta}_4\text{N}_5$ has been identified.

Terao$^{74}$ reported that he formed the compound $\text{Ta}_4\text{N}_5$ by heating a thin film of $\text{Ta}_3\text{N}_5$ at between 1100°C and 1800°C in vacuum. He had earlier obtained this $\text{Ta}_3\text{N}_5$ by heating an evaporated tantalum film in an atmosphere of ammonia.

Micrographs at lighter and heavier doses are not shown for our films as these are exactly similar to that of Fig. 23. The nitrogen implanted films, unlike the argon and oxygen irradiated films, did not exhibit any change in crystallinity or deterioration in the middle and very high dose regions, with the micrograph and diffraction patterns remaining remarkably constant throughout.

A film heated to 200°C, 400°C and 600°C was not affected and electron beam heating of a film which was estimated to be about 60 Å thick also showed no change indicating
that the nitride of tantalum is very stable.

It was also noted that the film did not have an island plus matrix structure as do the argon and oxygen implanted films but appeared to be continuous and single phase.
Fig. 23. Nitrogen Implanted Film, dose = $1.5 \times 10^{17}$ ions/cm$^2$. 
Table 4

Nitrogen Implanted Tantalum. Analysis of the Diffraction Pattern as Shown in Fig. 23

<p>| As Measured | Ta$_4$N$_5$ (Tetragonal) $^{(1,2)}$ |  |<br />
|---|---|---|---|</p>
<table>
<thead>
<tr>
<th>d($\bar{A}$)</th>
<th>I/I$_o$</th>
<th>d($\bar{A}$)</th>
<th>Intensity</th>
<th>hkl</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>-</td>
<td>4.834</td>
<td>M</td>
<td>110</td>
</tr>
<tr>
<td>3.65</td>
<td>10</td>
<td>3.623</td>
<td>M</td>
<td>101</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>3.420</td>
<td>m</td>
<td>200</td>
</tr>
<tr>
<td>2.49</td>
<td>100</td>
<td>2.487</td>
<td>S</td>
<td>211</td>
</tr>
<tr>
<td>2.16</td>
<td>100</td>
<td>2.159</td>
<td>S</td>
<td>310</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>1.810</td>
<td>m</td>
<td>202</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>1.733</td>
<td>m</td>
<td>321</td>
</tr>
<tr>
<td>1.53</td>
<td>90</td>
<td>1.524</td>
<td>S</td>
<td>420,312</td>
</tr>
<tr>
<td>1.30</td>
<td>80</td>
<td>1.295</td>
<td>S</td>
<td>213</td>
</tr>
<tr>
<td>1.25</td>
<td>50</td>
<td>1.244</td>
<td>m</td>
<td>422</td>
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<tr>
<td>-</td>
<td>-</td>
<td>1.137</td>
<td>m</td>
<td>600,512</td>
</tr>
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<td>1.08</td>
<td>20</td>
<td>1.081</td>
<td>m</td>
<td>620,413</td>
</tr>
<tr>
<td>0.99</td>
<td>40</td>
<td>0.988</td>
<td>m</td>
<td>631,503</td>
</tr>
<tr>
<td>0.96</td>
<td>40</td>
<td>0.960</td>
<td>M</td>
<td>622,314</td>
</tr>
<tr>
<td>0.88</td>
<td>30</td>
<td>0.878</td>
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<td>424</td>
</tr>
<tr>
<td>0.83</td>
<td>10</td>
<td>0.828</td>
<td>m</td>
<td>633</td>
</tr>
</tbody>
</table>

$^{(1)}$ From N. Terao, Jap. Journal of App. Physics, 10 (1971) 249

$^{(2)}$ 5 weak lines omitted

Camera constant = 43.5 cm using gold standard
4.5.2 Electrical Measurements

Sheet resistivity versus dose plots for the Ultra, Edward's and University films are shown in Fig. 24, and two peaks were observed for all the three films, accompanied by large negative TCRs as depicted in Fig. 25. A TCR plot for the 560 Ω Edward's film was not available and in its place we have used one for an 1800 Ω film (see Fig. 26 for its resistivity versus dose plot). Although this film also exhibited a large negative TCR, it crossed into the positive region before assuming negative values again. Whether this was also true for the 560 Ω film we cannot say as it was not possible to repeat the experiment due to a shortage of the film.

A set of results for the Edward's film for increasing thicknesses of 560, 1400 and 1800 Ω is shown in Fig. 26. As the films became thicker, the two peaks merged to form a single, broad peak indicating that the physical thickness of the films was one of the parameters which controlled the electrical behaviour in the films.

Electrical activation energies at the two peaks for a Surrey film have been calculated from plots of reciprocal resistance versus reciprocal temperature as in Fig. 27. At the first peak, with a film dose of $1.3 \times 10^{17}$ ions/cm$^2$, the activation energy of the
film was $5 \times 10^{-5}$ eV, and $4 \times 10^{-5}$ eV for the second peak corresponding to a film dose of $1.8 \times 10^{17}$ ions/cm$^2$. 
Fig. 24. Resistivity vs. dose plots for nitrogen implanted films.

- O Surrey (500Å)
- V Edwards (560Å)
- • Ultra Electronics (700Å)

Ion: Nitrogen at 40 keV

V-axis
- O, • from $10^2 - 10^5 \mu\text{n.cm}$
- V from $10^3 - 10^6 \mu\text{n.cm}$.
Fig. 25. TCR vs. dose plots for the nitrogen implanted films.
Fig. 26. Nitrogen implants for films of increasing thicknesses.
Fig. 27 conductance vs. reciprocal temperature plots for the nitrogen implanted films.
5. DISCUSSION

5.1 The Unimplanted Films

5.1.1 Film Thickness

At present we have studied films of thicknesses 450 to 650 Å with the exception of one batch of 1800 Å films which was supplied by Edward's High Vacuum. At the time of writing, films of less than and greater than 500 Å have been deposited by co-workers in the University. Their measurements showed that the sheet resistivity and TCR were dependent on the thickness of the film, with the resistivity decreasing and the TCR becoming less negative with increasing thickness and that these values seemed to be approaching some plateau. Marcus and Gersternberg et al. have reported such a plateau for their resistivity and TCR which became positive for a film thickness above 1000 Å. In both cases the resistivity approached, but did not attain, the bulk value of 13.6 micro.ohm.cm. for b.c.c. tantalum. We believe that the observed plateau is associated with the film changing from a semi-continuous to a continuous structure. From a TEM micrograph of our film in Fig. 9 it would appear that it is not continuous in nature but probably consists of a matrix of tantalum islands surrounded by oxide.

Nevertheless, it is clear that we can divide tantalum thin films into two categories depending on
their thickness:

(i) **Films less than 1000 Å thick.** Here the properties are dependent on the thickness and on the physical structure of the film. We can represent a film of this kind by a simple model shown in Fig. 28 (a).

(ii) **Films greater than 1000 Å thick.** The electrical properties of the film are now independent of the film thickness and is exhibiting the bulk property of the metal from which it is prepared. However, due to impurities and defects in the film the actual bulk value is not attained. A model of such a film is shown in Fig. 28(b).

If, as suggested, the threshold between the two categories of film is about 1000 Å, we can infer that the mean free path of the conduction electrons in the continuous tantalum films is about 1000 Å, i.e. when the scattering effects at the film boundaries become negligible. Earlier, in section 4.2.4, using Sondheimer's equation for the conductivity in thin films, we estimated that the mean free path of electrons in one of our 650 Å thick specimens was approximately 1000 Å. From the good agreement of our
Fig. 28(a) : 2-dimensional schematic showing discontinuous nature of thin film of less than 1000 Å thick. represents metal islands separated by insulating oxide. From this we see that the more discontinuous the film, the higher the proportion of oxide and impurities that can be incorporated in the film.
Fig. 28(b) : 2-dimensional schematic showing more metal islands touching one another to form a continuous film, i.e. like the bulk metal as film thickness becomes greater than 1000 Å.
calculated and inferred results it would appear that the 650 Å film was continuous enough to have enabled us to use Sondheimer's equation which is applicable only for a homogeneous, i.e. continuous film. Further results agreeing with ours have been published by Dessere and Goulet\(^78\) who calculated their mean free path of electrons in tantalum to be 970 Å.

5.1.2 Electrical Conduction Mechanisms in the Unimplanted Films

Using a similar model to that in 5.1.1, Hardy et al.\(^79\) proposed a dual, metallic/activation conduction mechanism for their sputter deposited films. The activation component is represented by:

\[
\sigma = A e^{-E/kT}
\]  

\[\text{................. (i)}\]

where \(\sigma = \text{conductivity}\)
\(A = \text{constant depending on the film}\)
\(k = \text{Boltzmann constant}\)
\(T = \text{Degrees Kelvin}\)

\(E\), the activation energy, is the energy that has to be supplied to an electron to transfer it from one metallic island to another island across an insulator. Using this relationship they reported the existence of two activation
energies for their films, $7 \times 10^{-4}$ eV and $3.4 \times 10^{-5}$ eV which were at least one order of magnitude smaller than their theoretical calculations based on Neugebauer and Webb's theory. To explain the second, smaller activation energy they proposed that this was the result of a competition between the metallic and activation components in their film at some critical temperature. Compared to their films in this work, the University film had one activation energy of $8.8 \times 10^{-5}$ eV whilst the Edward's had two, corresponding to $6.6 \times 10^{-5}$ eV from room temperature to about $100^\circ C$ and $1.6 \times 10^{-5}$ eV from 100 to $300^\circ C$. Since the film structure is probably highly dependent on the thickness of the films it is perhaps not surprising that there is no general agreement between our results and those of others. A similar theory to that proposed by Hardy et al. has been put forward independently by Waterhouse et al. but so far, the dual, activation/metallc theory cannot satisfactorily account for the one order of magnitude discrepancy between the as measured values and those calculated from theory. However, as it explains so conveniently the negative TCR that is often measured in practice, the dual conduction mechanism is generally accepted as the conduction process for thin film work. This theory will also explain the positive TCR in our Ultra film, i.e. no activation energy if we assume that in a near-continuous film the activation component is small compared to the metallic conduction.
A recent paper by Devenyi et al.\textsuperscript{(83)} puts forward a new theory accounting for the low activation energy in their Nb/Al\textsubscript{2}O\textsubscript{3} thin films by postulating that they behave like an amorphous wide-band-gap semiconductor. The close agreement between this new theory and experimental results may be of interest if it can be shown to apply to tantalum films as well. However, it is still too early to say definitely if there exists a single model which will explain satisfactorily all the measured results. Much more work has still to be done especially in the analysis of the physical structure and material identification of the thin films which are notoriously difficult to perform.

To complete this section for the undoped films, Table 5 shows the method of preparation and properties of tantalum films grown by workers elsewhere. From this, one can see that the properties for seemingly similar films vary enormously.
<table>
<thead>
<tr>
<th>Reference</th>
<th>Deposition Method</th>
<th>System Ultimate (torr)</th>
<th>Deposition Pressure (torr)</th>
<th>Substrate</th>
<th>Film Structure</th>
<th>Resistivity (µΩcm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gerstenberg &amp; Mayer</td>
<td>5 kV 0.25 mA/cm²</td>
<td>2x10⁻⁶</td>
<td>1.5x10⁻²</td>
<td>Glass</td>
<td>b.c.c.</td>
<td>50</td>
</tr>
<tr>
<td>Krikorian &amp; Sneed</td>
<td>1.6 kV 0.098-0.65mA/cm²</td>
<td>1-5x10⁻⁷</td>
<td>5x10⁻³ - 1.7x10⁻¹</td>
<td>Glass</td>
<td>7059 b.c.c.</td>
<td>30-8x10³</td>
</tr>
<tr>
<td>Cook</td>
<td>4-6 kV 0.3-0.5mA/cm²</td>
<td>10⁻⁷</td>
<td>~ 10⁻²</td>
<td>7059</td>
<td>β</td>
<td>200-700</td>
</tr>
<tr>
<td>Surrey</td>
<td>Electron gun evaporation</td>
<td>2x10⁻¹⁰</td>
<td>2x10⁻⁷</td>
<td>7059</td>
<td>b.c.c. + oxide</td>
<td>360.0</td>
</tr>
<tr>
<td>Coyne &amp; Tauber</td>
<td>4.5 kV 0.079-0.63mA/cm²</td>
<td>5x10⁻⁷</td>
<td>1.5-1.5x10⁻³</td>
<td>Quartz</td>
<td>Pt</td>
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<tr>
<td>Preston</td>
<td>3kV 0.25mA/cm²</td>
<td>3.5x10⁻²</td>
<td></td>
<td>7059 st.steel</td>
<td>β?</td>
<td>300-1000</td>
</tr>
<tr>
<td>Vratny &amp; Harrington</td>
<td>4kV target 0.25 mA/cm² film current varied</td>
<td>2x10⁻⁶</td>
<td>2x10⁻²</td>
<td>7059</td>
<td>β</td>
<td>40-70</td>
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<tr>
<td>Bomer &amp; Beck</td>
<td>2kV ~10mA/cm² Mercury diff. pump</td>
<td>~ 10⁻⁶</td>
<td>6-7x10⁻³</td>
<td>7059</td>
<td>b.c.c. β</td>
<td></td>
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<tr>
<td>Soenjak</td>
<td>Diffusion pump and turbomolecular pump systems</td>
<td>2.4-5x10⁻⁶</td>
<td>1-2x10⁻²</td>
<td>7059</td>
<td>β+ traces b.c.c.</td>
<td>140-180</td>
</tr>
<tr>
<td>Calbick</td>
<td>1.5kV</td>
<td>7x10⁻² - 10⁻¹</td>
<td></td>
<td>Carbon Coated 7059</td>
<td>Possibly β</td>
<td></td>
</tr>
<tr>
<td>Wasa &amp; Hayakana</td>
<td>0.2 3kV 0.05-6mA/cm²</td>
<td>&lt;10⁻⁶</td>
<td>1-1x10⁻⁵</td>
<td>glass</td>
<td>b.c.c.</td>
<td></td>
</tr>
<tr>
<td>Urazaliyev</td>
<td>3kV 0.41mA/cm²</td>
<td>5x10⁻⁶</td>
<td>2x10⁻²</td>
<td>NaCl</td>
<td>b.c.c. + TaO₂</td>
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</tr>
<tr>
<td>Parisi</td>
<td>6.6kV 0.2mA/cm²</td>
<td>2x10⁻²</td>
<td></td>
<td>Ta₂O₅ on glass</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Westwood &amp; Waterhouse</td>
<td>3.5kV 0.3mA/cm²</td>
<td>10⁻⁶</td>
<td>2x10⁻²</td>
<td>7059</td>
<td>β+ b.c.c.</td>
<td>~250</td>
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<tr>
<td>Mattox &amp; Kominiak</td>
<td>3.5kV 0.3mA/cm²</td>
<td>3.5x10⁻²</td>
<td></td>
<td>Graphite Ta</td>
<td>β+b.c.c. b.c.c.</td>
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</table>

**TABLE 5**
5.2 Implanted Tantalum Films

5.2.1 Introduction

When a thin metal film is implanted with energetic ions, complex interactions occur within the film which usually result in changes in the properties of the film. These changes may be:— (i) chemical, (ii) physical and (iii) electrical. In general, the electrical changes are the direct result of (i) and (ii), but at present it is not possible to identify the separate contributions due to them.

Rather than discuss the above three headings separately, we shall attempt to show how the electrical properties of the films are related to the effects of physical and chemical changes. The present dual, metallic/activation conduction mechanism appears to fit adequately our measured results for argon and oxygen implanted films and they agree with those of workers elsewhere. For the nitrogen implanted films the present theory appears to be inadequate to account for our experimental results. We shall propose another conduction model for this particular case which is based on the intrinsic electrical properties of the material formed.
5.2.2 Chemical Effects

If the ions inserted into the films are chemically reactive with the host metal, a compound or compounds may be formed as in a normal chemical reaction. In synthesising compounds by conventional chemical reactions, both reagents have similar concentrations and temperatures. In ion-implantation, however, we are essentially dealing with reactions of single atoms having very high energies, with target atoms greatly in excess and at arbitrary temperatures. Therefore, there is the likelihood that ion-implantation can lead to synthesis of compounds yet unknown or very difficult to synthesise normally. For example, G.K. Wolf has produced totally new compounds using ion-implantation and which were not possible using normal chemical techniques. He implanted Cr into Re₂(CO) to form Re-Cr-Carbonyl. Another good example, relevant to the present work, is the formation of Ta₄N₅ in our nitrogen bombarded films and which is known to be difficult to synthesise using normal means. Generally when tantalum reacts with nitrogen, as for example in a sputtering rig, the compounds Ta₂N and TaN are formed depending on the concentration of the nitrogen present in the system.

In addition from measurements of the electrical properties of our nitrogen implanted films we believe that the electrical conduction mechanisms are not due to the popular dual, metallic/activation type mentioned
earlier in section 5.1 for the unimplanted films. We believe that in this instance the intrinsic electrical properties of the compound formed are responsible for our electrical measurements. We deduced this from the very small activation energies measured, $4 \times 10^{-5}$ to $5 \times 10^{-5}$ eV, coupled with relatively large negative TCRs of between $-2000$ and $-3000$ ppm/°C. Compared with these, the undoped film had an activation energy of about $8.8 \times 10^{-5}$ eV and a TCR of approximately $-200$ ppm/°C obtained with $4.5 \times 10^{-5}$ eV and a TCR of approximately $-100$ ppm/°C for an argon implanted specimen. From these values, we see that we are unable to explain the large negative TCRs for the nitrogen films in terms of the dual, metallic/activation model. K. Heiber\(^{87}\) has reported that his $\text{Ta}_4\text{N}_5$, which was formed with difficulty using a conventional technique, exhibited a negative TCR of approximately $-1000$ ppm/°C and that this was the intrinsic property of the material. The TCRs for our films lie between $-2000$ and $-3000$ ppm/°C but considering that our films were probably exhibiting some thin film effects as well, the comparison with that of K. Heiber is quite good. Further support for this alternative theory as opposed to the dual, metallic/activation model comes from the recent paper published by Devenyi referred to earlier in section 5.1.2. This theory, based on the assumption that their films behave like an amorphous wide-band-gap semiconductor seems to give good agreement with experimental values and it may be of interest if it can be shown to be applicable to tantalum films as well.
For our argon and oxygen implanted specimens, the dual, metallic/activation conduction model of Hardy et al. is probably applicable to these films. TEM micrographs of the argon and oxygen irradiated films do exhibit matrix-like features which are typical of films characterised by this form of conduction mechanism. In contrast, the structure of the nitrogen implanted films of Ta₄N₅ appear to be one continuous phase (see Fig. 12, 16 and 23).

Even though argon does not react with tantalum, we observed that as a result of sputtering of the surface of the film which continuously exposed a fresh layer of the film to the surroundings, a secondary reaction occurred which resulted in the formation of Ta₂O. This, however, did not appear to affect the overall electrical properties of the specimen, Fig. 13 shows that the TCR is unaffected by dose, which suggests that the Ta₂O is probably formed only as a very thin layer at the surface. The less negative values of TCR observed with increasing dose is probably due to compaction of the film as a result of bombardment. When a film was irradiated with oxygen only Ta₂O was identified, this being the direct result of implantation.

In one of our earlier papers¹³ we postulated the formation of Ta₂N and TaN in our nitrogen implanted films to explain the presence of the two peaks in the resistivity vs. dose plots. We now know from hindsight that this is incorrect. At that time we had not developed our TEM
technique sufficiently to identify positively the compounds
and the reported formation of Ta$_2$N and TaN by other workers
using sputter deposition appeared to explain our results
very well and led us to believe that the same compounds had
been formed in our implanted specimens.

We now know that using implantation totally different
compounds are formed compared with sputter deposition. For
example, for nitrogen, instead of forming Ta$_2$N and TaN we
have Ta$_4$N$_5$. Similarly for oxygen we do not form Ta$_2$O$_5$
but Ta$_2$O. Thus we must be careful in using sputter
deposition results to indicate what happens in ion-implanted
samples.
5.2.3 Physical Effects

Regardless of whether or not the implanted ions are reactive with the target, sputtering always occurs which in our case results in the thinning of the film. Where inert ions like argon are employed this is the main cause for electrical changes in the film.

If compounds are formed as in the oxygen and nitrogen implants, impact dissociation in addition to sputtering may occur. For the oxygen implant we have:

\[
2\text{Ta} + O^+ \rightarrow \text{Ta}_2O
\]

implant ion

The effect of impact dissociation in the oxygen implant is clearly shown by the TCR vs. dose curve of Fig. 21, together with the micrograph of Fig. 16(c). The TEM results in Fig. 16(c), corresponding to the middle dose region of Fig. 21 indicate the presence of b.c.c. tantalum in the film which was not observed in the earlier micrograph of Fig. 16(b). The TCR which was negative at low doses has assumed positive values as a result of impact dissociation into a more metallic phase as the dose was increased.

For the nitrogen implanted specimens, we did not observe a process similar to that of the oxygen case implying that dissociation of the compound $\text{Ta}_4\text{N}_5$ did not
take place even at very high doses. From this we suggest that \( \text{Ta}_4\text{N}_5 \) is sputtered off as a composite compound as shown below:

\[
4\text{Ta} + 5\text{N}^+ \rightarrow \text{Ta}_4\text{N}_5 \rightarrow \text{Ta}_4\text{N}_5
\]

implant \hspace{2cm} sputtering

The negative slopes of the resistivity plots in Fig.24, matched by positive slopes of TCRs in Fig.25, suggest that the films became more metallic but at present there is no evidence to indicate impact dissociation as the cause. In Fig.25 we noticed that the TCR of the Edward's film assumed positive values. This 1800 Å film has been analysed by X-ray diffraction and shown to contain no free tantalum before implantation\(^{(89)}\) and is therefore not typical of our films as a whole. Whether or not this is the cause for the TCR to take on positive values we are unable to say from this one specimen.

As mentioned earlier, where no compound or compounds are formed, as in the argon bombardment specimen, sputtering is the main cause for electrical changes in the film as it is gradually thinned. In Fig.29 we show a theoretical and an 'as measured' plot for an argon implanted film.
Fig. 29.

- as measured
- calculated

<table>
<thead>
<tr>
<th>film thickness (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>500Å</td>
</tr>
<tr>
<td>230Å</td>
</tr>
<tr>
<td>90Å</td>
</tr>
<tr>
<td>0Å</td>
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</table>

<table>
<thead>
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<th>dose (x10^17 ions/cm²)</th>
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<td>20</td>
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The theoretical plot was calculated assuming that the film resistance is inversely proportional to thickness and that the resistivity was constant up to the open circuit condition. From the 'as measured' plot we see that it agrees well with the perfect resistor film up to about 20% of the total dose. After this, thin film effects, i.e. resistivity not proportional to reciprocal thickness, become more pronounced and at very high dose levels the increase in resistance is very rapid (not shown), usually changing by several orders of magnitude for a small increase in dose. We note a similar effect in our oxygen and nitrogen irradiated films in the early and final stages of implantation. However, the middle dose region is characteristic of the ions used, as the chemical effects become important.

It is known that under irradiation thin films may either lose or gain crystallinity\(^{(80)}\). In our argon and oxygen implanted films, we observe that there is an improvement in crystallinity with increasing dose up to very high levels when the films became amorphous. For argon we have:

semi-amorphous ——— crystalline ——— amorphous

implant            implant
(middle dose)     (very high dose)
In the oxygen case we have a semi-amorphous phase followed by precipitation of highly crystalline b.c.c. tantalum. This precipitation is replaced by a less crystalline phase of Ta$_2$O and b.c.c. tantalum with the film becoming amorphous at very high doses.

Unlike the argon and oxygen implants, the nitrogen bombarded film did not lose its crystallinity even up to very high doses implying that the compound Ta$_4$N$_5$ is very resistant to radiation damage.

As a result of sputtering, the distribution of the implanted ions is not a symmetrical Gaussian with the mean distribution in the middle of the film. Referring to a hypothetical model of a thin film under bombardment as in Figs. 30 (a) and (b), we have $\overline{R_p}$, initially in the middle of the film as in (a). Now, after half of the film has been sputtered away, $\overline{R_p}$ will be at the film/substrate interface and further sputtering will result in $\overline{R_p}$ lying in the substrate.

From this we can show qualitatively that the ion distribution in a film may be like that of Fig. 31 with the peak ion concentration of the ions near the surface of the film.$^{(93)}$ In addition, a large proportion of the ions supplied to the film actually end up in the substrate. Using the above simple model we estimated that by the time a nitrogen or oxygen implanted film had received half its
Fig. 30a. At the start of implantation.

Fig. 30b. After half of film sputtered away.
ion distribution if no sputtering

ion distribution as a result of sputtering ($\frac{1}{4}d$ sputtered off)

$\frac{1}{2}d$

film

$\frac{1}{2}d$

distribution after $\frac{1}{2}$ of film sputtered off

substrate

$\frac{1}{2}$ of total number of ions implanted into substrate.

Fig. 31 Ion distribution in film as a result of sputtering.
total dose there was sufficient nitrogen or oxygen to convert all the film into \( \text{Ta}_2\text{O} \) or \( \text{Ta}_4\text{N}_5 \) respectively.

Assuming this to be true, for the oxygen implanted film, further irradiation after this may cause the following to occur: (i) formation of a higher oxide (ii) impact dissociation and (iii) sputtering of the compound. At present, as mentioned earlier, we believe (ii) occurs in the oxygen specimen but not (i) and (iii). In the nitrogen case only (iii) takes place. From this we see that the proposed model for the distribution of ions in a film does to some extent explain our experimental results.

At present there is no satisfactory explanation to account for the two peaks in the nitrogen implanted specimens (Fig. 24). We can possibly attribute the presence of the first peak to the complete conversion to \( \text{Ta}_4\text{N}_5 \) of all the film in the middle dose region. As for the second peak, no plausible explanation exists at the moment, except to say that our results are reproducible. For the Edward's 1800 Å film only one peak was observed, but as the film, as mentioned earlier, was not representative of our films in general we cannot be certain if the appearance of the second peak is dependent on the film thickness.

To show that the distribution of the ions in the film does affect the presence of the peaks a series of graphs
for films of the same thickness but irradiated with increasing energies of nitrogen from 40 to 120 keV is shown in Fig. 32. Except for the 40 keV implant where \( R_p \) was in the middle of the film initially, the other three films did not exhibit any distinct peaks. The higher the energies, the smoother the graphs. This is perhaps not surprising if we consider that for any energy above 80 keV \( R_p \) was in the substrate, i.e. we were implanting the substrate and the effects we measure are probably due to sputtering only.

To complete this discussion, graphs of conductivity versus dose (drawn on a linear scale) are presented in Fig. 33 for the University films. From a practical point of view, the nitrogen plot is very interesting as there are two regions where the conductivity is insensitive to the impurity level. In comparison with films which were sputter deposited in nitrogen, Joly\(^{(91)}\) reported a very pronounced plateau region in his triode sputtered system, even though it was quite certain that his films (he did not actually identify them), consisted of Ta\(_2\)N and TaN and not Ta\(_4\)N\(_5\). M. Nakamura et al.\(^{(92)}\) reported a similar plateau region in their films and went on to identify the compounds formed as Ta\(_2\)N and TaN. They added further that the plateau was dependent on the gas discharge conditions which existed during sputtering and that this region could be shifted, to some extent, to suit their practical manufacturing requirements. They reported changes in TCRs in this region...
Fig. 32. Effect of $\bar{R}_p$ in tantalum films.
Ion Bombardment of Tantalum films (500 Å)

- Argon (Dose scaled to allow for higher sputtering rate)
- Oxygen
- Nitrogen

Conductivity mho/cm

Ion Dose x 10^{17} Ions/cm^2
ranging from between -50 to -300 ppm/°C. Our films had two plateau regions with corresponding TCRs ranging from -2000 to -3000 ppm/°C.
Tantalum thin films have been implanted with argon, oxygen and nitrogen to change their electrical properties. The result of physical and chemical changes arising from implantation have been examined and where possible correlated with the measured electrical data.

The undoped films were deposited by electron beam evaporation and sputter deposition but as the system parameters were different, it is difficult to make comparisons.

However, in general we have found that for the undoped films, the growth history like the film thickness and impurity content which we believe is related to film thickness determine the electrical resistivity and TCR. The thicker, purer films like those of Ultra Ltd. have positive TCR and small resistivity compared to the less pure films grown at the University which exhibited a negative TCR and larger resistivity. The Edward's films were found to contain no free tantalum but consisted of oxides of the metal which were not identified positively but possibly Ta$_2$O$_5$. These films were grown in comparatively poor vacuum conditions compared to the Ultra and University films which were deposited in very clean environments. Under these conditions we have positively identified TaO$_2$ as the main impurity.
The majority of the films used in this study were about 450 - 650 Å thickness. We now believe that this is not representative of all tantalum films in general as there is now some evidence to show that for films less than 1000 Å thick, the thickness is one of the chief parameters that control the electrical behaviour. Films greater than 1000 Å appear to be independent of thickness. We have put forward the model where the films become continuous above 1000 Å.

From the negative TCR and TEM micrographs of our undoped, argon and oxygen irradiated films there appears to be some agreement to the conduction theory put forward by Hardy et al. and also Waterhouse. They proposed a theory based on the dual, metallic/activation conduction mechanism. Films possessing such a conduction mechanism are characterised by a matrix of island type features which are composed of metal islands surrounded by an insulating phase. In the case of our very pure film which had a positive TCR this is explained by the fact that the metallic islands are touching one another to form a continuous chain which effectively by-passes the insulating phase if any.

When the films are subjected to energetic bombardment, roughly three regions can be distinguished in the resistivity vs. dose plots. The first and third regions corresponding
to the lightly and heavily doped regions are common to all the films. The second (middle dose) region is characterised by the ion species employed. For the argon irradiated film, which was used as a control, the main effect appears to be due to sputtering, and some Ta$_2$O is formed as a secondary reaction. In the case of the oxygen doped film the most striking feature is the excursion from negative to positive values of its TCR in the second region. This is explained by some form of impact dissociation of the oxide Ta$_2$O into a more metallic phase. When the films were implanted with nitrogen two peaks in their resistivity were observed for the thinner films but only one for the thicker ones. We also report the formation of Ta$_4$N$_5$ for these films, a compound which is not easily formed by conventional chemical reaction. Normally, using sputter deposition Ta$_2$N and TaN are formed. This leads us to the interesting possibility of using ion implantation for synthesising new compounds that are difficult or impossible to achieve employing conventional means.

We believe that for the argon and oxygen implanted films the dual, metallic/activation type conduction process as proposed by Hardy et al. is applicable to our films. For the nitrogen doped films this is not true and a conduction process based on the intrinsic electrical property of the material formed is probably more correct.

Finally, the author believes from this pilot study
that there is an interesting possibility of utilising ion implantation for controlling the electrical properties of thin metal films. It is also hoped that, from this study, the areas requiring more analytical and precise investigation have been brought out. This will be discussed in the next section.
7. FUTURE WORK

As a result of our present study, several points have come to light which we believe will require further examination.

Since our work is essentially aimed at controlling the electrical properties of metal films, which we have shown is possible to some extent it is logical we should study the conduction mechanisms in greater detail. Whilst TEM results have been useful in this direction, more quantitative data is required. Some work using Rutherford backscattering and ESCA have been attempted by co-workers to complement TEM but it is too early to say if these will be useful.

From our experiments we have noted that an oxygen implanted film exhibited a positive TCR in the middle dose region. A nitrogen implanted film had, on the other hand, a negative TCR. Now, using a mixed implant of nitrogen and oxygen it should be possible to achieve zero TCR resistors by mutual cancellation of their respective TCRs. A further benefit accruing from this is that we can at the same time also control the sheet resistivity of the film implying that our zero TCR resistor need not be restricted to a small range of resistance values.
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**Appendix 3**

**ELECTRONIC CROSS SECTIONS OF**

**CROSS SECTION SUB. E=10.0E0**

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<tbody>
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<td>Z</td>
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**ION: NITROGEN**

**SNR: 0.11E0E05**

**GAMMA 0.26E0**

**MIN 1.2E9**

**CASE 0.34E0E02**

**BES/SE 0.12E0E04**

**RHO/0.42E0E01**

**N 1.6E0E0E25**

**Z 73**

**TANTALUM**

**SUBSTRATE PARAMETERS:**

**NITROGEN IN TANTALUM**

**EVS RANGE STATISTICS:**

**NOTES:**

Appendix
Appendix 4  Densitometer trace of Ta₄N₅ plate (x 2)
APPENDIX 5

A typical diffraction spot pattern for an argon implanted film taken at a dose of $7.5 \times 10^{16}$ ions/cm$^2$ is shown below.

![Diffraction Spot Pattern](image)

Camera constant = 47.40 cm, using gold as standard.

Using the relationship $R_d = L$

where $R = \text{distance of spot from centre (mm)}$

$d = \text{d-spacing in Angstroms (Å)}$

$L = \text{camera constant (mm)}$

$\lambda = \text{wavelength of 100 kV electrons (0.037 Å)}$

From this we have $d_1 = (474 \times 0.0037)/7.25 = 2.40 \text{ Å}$

and similarly $d_2 = (474 \times 0.0037)/10.5 = 1.67 \text{ Å}$. 
These spacings correspond to tetragonal Ta$_2$O as in the ASTM file, no. 19-1297. The crystal system is cited as tetragonal with $a=b=4.72$ Å; $c=3.08$ Å.

For completeness, a check is made of the angle between a number of spots in the diffraction pattern for the indices that have been assigned. The angle $\phi$ between the two lines joining two diffraction spots to the central spot is given by (for the tetragonal system):

$$
\cos \phi = \frac{\left[ \frac{h_1^2 + k_1^2}{a^2} + \frac{l_1^2}{c^2} \right] + \left[ \frac{h_2^2 + k_2^2}{a^2} + \frac{l_2^2}{c^2} \right]}{\sqrt{\left[ \frac{h_1^2 + k_1^2}{a^2} + \frac{l_1^2}{c^2} \right] \left[ \frac{k_2^2 + k_2^2}{a^2} + \frac{l_2^2}{c^2} \right]}}
$$

WHERE $h, k$ and $l$ are the indices assigned to the spots. The calculated and as measured angle both equals 45° confirming that the diffraction pattern does indeed belong to Ta$_2$O.

The diffraction spot pattern for an oxygen implanted film (at a dose of $7.5 \times 10^{16}$ ions/cm$^2$) is shown below:

![Diffraction Pattern Diagram](image-url)
Using the same analysis technique as before, we have $d_1 = 2.4 \, \text{Å}, d_2 = 1.67 \, \text{Å}$ and $d_3 = 1.34 \, \text{Å}$. The spot pattern corresponds to cubic (b.c.c.) tantalum (ASTM card index no. 4-788). The calculated angle $\phi = 35^\circ$ and agrees with the angle as measured on the photographic plate.

In the cubic crystal system the angle $\phi$ is given by:

$$\cos \phi = \frac{h_1 h_2 + k_1 k_2 + l_1 l_2}{\sqrt{(h_1^2 + k_1^2 + l_1^2)(h_2^2 + k_2^2 + l_2^2)}}$$

where, $h$, $k$ and $l$ are the indices assigned to the spots.
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