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ION BOMBARDMENT SPUTTERING OF
GALLIUM ARSENIDE, GOLD AND TANTALUM

BY

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Doctor of Philosophy
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ABSTRACT

Sputtering yields have been measured for neon, argon and krypton sputtering of gold and for argon and tellurium sputtering of gallium arsenide in the energy range from 50 to 400 keV. Values of yield, estimated by activation analysis of sputtered deposits, are compared with other experimental results and with theory and are shown to be too high as a result of errors in ion dose measurement. Yields for gold and gallium arsenide are shown to increase by about 10% over the dose range from $10^{17}$ to $10^{18}$ argon ions/cm$^2$ as a result of changes in surface topography during sputtering.

Polythene hemispheres were used to collect sputtered atoms and are shown to be very efficient ($>90\%$) for gallium and gold atoms. Measurements of surface stoichiometry, sputtering of cooled and heated targets and the use of nickel coated collectors were carried out for gallium arsenide and led to the conclusion that the sticking efficiency of sputtered arsenic atoms was very low giving rise to lower estimates of arsenic yield compared with those of gallium.

The Rutherford backscattering technique has been used to assess the quality of tantalum thin films deposited on glass and on vitreous carbon substrates by R.F. Sputtering and by electron beam evaporation. Sputter deposited films were shown to be superior with respect to purity and reproducibility.

Effects of implanting to very high doses ($>10^{18}$ions/cm$^2$) with argon, nitrogen or oxygen ions were examined by backscattering which has been shown to be a very useful tool for studying thin films. Estimates of ion ranges were compared with L.S.S. theory and sputtering yields were also calculated for the different ions used. Finally the limitations of the backscattering method are discussed with respect to very high impurity levels.
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INTRODUCTION

The work which will be described in the following sections is divided into two fairly distinct areas. The first area involves a study of the high energy sputtering yields of gold and gallium arsenide when bombarded with one of several species of ions. The second topic is concerned with an investigation using Rutherford backscattering analysis, of the quality of electron beam evaporated and sputter deposited tantalum films used for the production of resistors and capacitors and of the effect of ion implantation into these films.

(i) Sputtering, the emission of particles from a target surface under the impact of bombarding neutral or charged particles, has been the subject of investigation for more than a century.

The disintegration of cathodes in gas discharge tubes is an example of how the importance of the sputtering phenomenon was brought to the attention of experimentalists. A more up to date example of the sputtering problem is in the development of surfaces to contain controlled nuclear reactions for power generation. In particular, any future controlled fusion reactor may suffer from undesirable cooling effects in the plasma if there is appreciable sputtering of particles from the reactor wall. Other areas where sputtering plays an important part include the erosion of surfaces of satellites and ion-propulsion electrodes, ion getter pumps for vacuum systems, the controlled deposition of thin films and the cleaning and etching of surfaces.

The study of sputtering has provided a valuable contribution towards the understanding of atomic collision processes. Measurements of sputtering yields, velocities and trajectories of ejected particles and energy thresholds for sputtering have led to an improved knowledge of the collision cascade which takes place when an ion is incident on a target and of the interatomic potentials and the mechanisms governing momentum transfer and atomic displacement which are used to explain and predict such collision events.
Theories which have been put forward to describe the process of sputtering have developed in conjunction with the findings of the experimentalists. An example of this concerns the 'hot-spot' theory which was one of the first theories of sputtering and postulated an evaporation process as a result of thermal energy deposited into the target by the bombarding particle. Subsequent measurements of the ejection velocities of sputtered particles demonstrated that this model was not valid. It is now accepted that the sputtering process is predominantly due to momentum transfer during ion-atom and atom-atom collisions. Perhaps the most notable theory of sputtering is due to Sigmund, who considered sputtering as a process of energy transfer through a cascade of many two-body collisions. Sigmund's theory shows the dependence of sputtering on the energy of the incident particle and has proved to be very successful in predicting sputtering yields for many ion-target combinations.

Gold was chosen as a target material to be used in the present study because it is known to have a high sputtering ratio (the number of atoms sputtered for each incident particle), it has been studied by several workers and there are therefore results for comparison and it has a high neutron capture cross-section. The latter is an important consideration because the activation analysis technique was used for the measurement of sputtered deposits.

Polycrystalline targets of gold have been sputtered in the energy range from 50-450 keV and the sputtering yields measured for neon, argon and krypton ion bombardment. Results are compared with Sigmund's theory and with the results of other experimentalists.

Most studies of sputtering have been confined to elementary targets. There are very few results in the literature concerning sputtering of binary materials and most of the results that have been reported are for sputtering of metal alloys. Partly because of the lack of information on compound semiconductors but also because of its importance as a device material it was decided to measure sputtering yields for gallium arsenide. Gallium and arsenic also have convenient isotopes with reasonable neutron cross-sections such that activation analysis of gallium arsenide is fairly straightforward.
Single crystal gallium arsenide targets have been sputtered with 50-400 keV argon ions and 50-350 keV tellurium ions. In addition some experiments using argon ions have been carried out at elevated temperatures and at liquid nitrogen temperature.

(ii) Tantalum Films: Interest in the use of tantalum for the fabrication of thin film resistors and capacitors began about twenty years ago. Metals deposited as thin films generally have higher resistivity and lower temperature coefficient of resistance (TCR) than the bulk metal and metals such as tantalum can be anodically oxidised to form protective layers over thin film devices. Tantalum nitride, which has a small, positive TCR, is usually preferred for making resistors. Tantalum oxide has a high dielectric constant and is therefore ideal for the production of metal/oxide/metal film capacitors. The small, negative temperature coefficient of capacitance (TCC) of tantalum oxide can be offset by the positive TCR of tantalum nitride to produce temperature compensated R-C networks. The development of a cross-over technology allowed for increased complexity and complete tantalum film passive networks are now widely used in many analogue, digital and microwave applications.

The electrical parameters, particularly resistivity and TCR, of a tantalum film device, depend on the impurities present in the film and can therefore be adjusted by controlling the impurity level. Impurities are usually incorporated into a film during growth using a reactive sputtering technique. Ion implantation, which is a process whereby ions of almost any desired impurity species are accelerated such that they penetrate into a target surface, offers a superior method of controlling impurity concentration. Films have been ion-implanted, with this objective in mind, at the University of Surrey.

The present study of tantalum films has been an attempt to characterise the films used for the ion-implantation work. The quality and purity of the starting material is obviously very important to the ion-implantation process so the Rutherford backscattering technique has been used to examine tantalum films and to measure uniformity and purity. Implanted films have also been analysed to measure
the depth of the implanted ions and to estimate the sputtering rate of tantalum for argon, nitrogen and oxygen bombardment.
1. REVIEW

1.1 Sputtering

1.1.1 Definition of Sputtering:

When an energetic particle 'strikes' a solid surface it may be reflected by collision with a surface atom or it may penetrate into the solid. If the particle penetrates the surface it loses energy and slows down within the target material. The energy loss process comprises loss by interactions with electrons associated with the target atoms and loss by violent, elastic collisions with the target atom nuclei. The particle may undergo many such elastic collisions before coming to rest and each collision will impart energy to the struck target atom which will recoil and strike other target atoms. The result is a collision cascade and many target atoms will be set in motion. If the trajectory of any of these atoms intercepts the target surface and the atom has sufficient energy to overcome surface binding forces such that it escapes from the surface then that atom is said to have been sputtered.

We define a sputtering yield, $S$, as 'the average number of target atoms sputtered from the surface per incoming ion.'

For very thin targets it is possible for forward or transmission sputtering to take place but in the present study where thick targets were used we are only concerned with backward sputtering.

1.1.2 Historical

The first observation of sputtering is attributed to Grove (1) who in 1852 noted the pitting and disintegration of cathodes during a series of glow discharge experiments. The field of study became known as 'cathode sputtering' and a lot of qualitative work has been carried out using this technique.

Unfortunately the pressure in a glow discharge tube is so high ($\geq 0.1$ Torr) that the mean free paths for the ions and for the sputtered atoms are much smaller than the dimensions of the tube. Charge exchange processes give rise to multiply charged ions, molecular ions and ionisation of sputtered atoms which are also ionised by secondary electrons ejected from the target surface. In addition a large fraction
of the sputtered material, which is put as high as 90\% by Von Hippel (2),
diffuses back to the cathode. It was quite a long time before it was
appreciated that the above processes were taking place and that they
ruled out the possibility of making any quantitative measurements of
sputtering yields using the glow discharge method as it existed. The
efforts of those such as Blechschmidt (3) who measured sputtering yields
for H\textsuperscript{+} on ten metals, N\textsubscript{2}\textsuperscript{+} on thirteen metals and Ar\textsuperscript{+} on fifteen metals
prove therefore to be fruitless, as Carter and Colligon point out (4)
in their very comprehensive review of sputtering.

If the gas pressure in the discharge tube is reduced this results
in increased path lengths for the ionising electrons as well as for the
sputtered atoms and the discharge is consequently reduced. Penning and
Moubis (5) overcame this problem by applying a magnetic field parallel
to the direction of discharge which increases the electron path lengths
and hence ionisation while having the added effect of reducing secondary
electron emission. In this way current densities of 10-20 mA/cm\textsuperscript{2} were
produced at a pressure of 10\textsuperscript{-5} Torr.

Similar arrangements have been used by many experimentalists
such as Gillam (6) who measured yields for Ar\textsuperscript{+} sputtering of Cu\textsubscript{3}Au
alloys and Ogilvie et al. (7) for He\textsuperscript{+}, Ar\textsuperscript{+}, Xe\textsuperscript{+} and O\textsuperscript{+} sputtering of Ag.
Useful and reproducible results were obtained but the method has serious
drawbacks. The ions have a large energy spread, they can be multiply
charged and they do not have a clearly defined angle of incidence.

Fetz (8) replaced the cathode by a mercury pool and added a grid.
The discharge voltage could now be lowered which resulted in a smaller
number of multiply charged ions and the angle of incidence was better
defined. Wehner (9) also used this method.

The greatest remaining problem of the glow discharge method of
sputtering is that of the unsuppressed secondary electrons which
contribute to readings of ion current so that the total charge (or
number of incident ions) into a sample cannot be measured very accurately.
This in turn leads to inaccurate estimates of sputtering yields. A
further problem with the mercury pool is that the target must be maintained
at a temperature in excess of 300\textdegree C to prevent the formation of a
mercury film on the surface.
1.1.3 The Use of Ion Beams for Sputtering Yield Measurements

With the advent of high intensity ion sources and very highly sensitive detectors interest has moved towards the use of ion beams produced by particle accelerators for the study of sputtering. The ion beam method provides several advantages over the glow discharge system:

(i) Ion beams are usually analysed by steering in a magnetic field which removes unwanted species and charge states.

(ii) The analysis is also momentum selective so that the beam is monoenergetic. In practice most accelerators have very highly stabilised high voltage supplies so that ions entering the analyser have a very small spread in energies.

(iii) The range of possible energies is very wide. It is possible to do sputtering experiments from threshold values of a few eV up to the MeV region. Perhaps five accelerators would be required to cover the whole of this region.

(iv) The measurement of current at the target is usually much more precise than in a glow discharge system. It is normal practice to fit some sort of secondary electron suppression and Faraday cups are widely used.

(v) High vacuum conditions are achieved in the target chamber and beam line by the use of differential pumping systems which isolate the ion source region. Charge exchange processes are consequently very greatly reduced.

(vi) Ion beams can be collimated so that the angle of incidence is very well defined. In addition the target can be moved around so that the angle of incidence is varied.

(vii) Target temperature can be varied using hot or cold target stages.

(viii) There is a much wider choice of ion and target and we also have the capability of selecting molecular beams. Some accelerators can even separate heavy isotopes.
Ion current is easily controlled. This is particularly important when working with semiconductors and other materials where beam heating effects could be damaging.

Whichever method is employed, that is cathode sputtering or ion beam sputtering, the important consideration is that the ion current density is sufficiently high to sputter the target surface clean of absorbed gases and maintain this clean surface during the experiment. If this situation is achieved then reproducible, quantitative results should be obtained.

1.1.4 Measurement of Sputtering Yield

This involves measurement of the total charge at the sample and measurement either of the amount of material removed from the sample or the amount of material deposited on a collector. Measurement of the sputtered material has been carried out using several different methods:

(i) Weighing of target (10): The target is weighed before and after sputtering and the difference in weight, with an estimated allowance being made for implanted ions, is used to estimate the number of sputtered atoms. This method is better suited to the cathode sputtering method where ion currents are considerably higher, giving rapid removal rates.

(ii) Weighing of collector: The weight gain of the collector is calculated by weighing before and after sputtering. The collector is arranged so that all atoms sputtered from the target must strike its surface (and hopefully remain on the surface).

(iii) Quartz Oscillator (11): The target is attached to a crystal oscillator and as the mass of the target changes during sputtering the change is very sensitively detected by a corresponding change in the frequency of the oscillator.

(iv) Activation Analysis: This is the method which has been employed in the present work. It involves the activation of the collected sputtered deposit and the subsequent counting of its activity. The count rate is compared with that from a standard of known weight which is activated at the same time as the deposit. A variation of the method is to sputter an active target and then count the activity of the sputtered deposit.
(v) Measuring Electrical Resistance of a Thin Target (8, 12).

(vi) Masking part of target and measuring the depth of the crater produced by sputtering.

(vii) Optical measurement of the thickness of sputtered layers (13).

1.1.5 Characteristics of Sputtering Yield

(i) Dependence on Target Material: Low energy bombardments of many different metals were carried out by Wehner et al. using low energy mercury ions (13) and later noble gas ions (14, 15) to study the variation of sputtering yield with target material. The experiments employed the discharge tube method with high currents and hence high target temperatures (up to 500°C). Results indicated that, with one or two deviations, the sputtering yield follows the 'd' shell electron concentrations and also the reciprocals of the heats of sublimation of the target materials. In materials with filled 'd' shells ion ranges are smaller and their energy is deposited closer to the target surface which leads to higher probability of sputtering taking place.

Almén and Bruce (10, 16) found a similar trend for higher energy ion-beam sputtering of different target materials. Fig. 1(a) shows their results for 45 keV Kr bombardment and Fig. 1(b) shows the 'd' shell concentrations for the different target materials (15).

(ii) Variation with Ion Species: Fig. 2 shows the results of Almén and Bruce (10) for 45 keV sputtering of silver, copper and tantalum using a range of different ions. The yields increase through each group of elements to reach a maximum for the inert gas. There is then a big drop in yield to the beginning of the next group. The reason for this trend could be the change in interatomic potential with the systematic variations of electron screening density or it may be the result of precipitation effects due to exceeding the solubility limit of the ions in the target as shown by Andersen and Bay (90).

(iii) Variation with Ion Energy: There is a threshold energy below which no sputtering takes place. This energy, which is typically a few eV, is dependent on the ion-target combination and is a function of the surface binding energy associated with the target. Above this
Fig. 1(a): Variation of Sputtering Yield with Target Material

Fig. 1(b): Concentration of Electrons in Outer 'd' Shell as a Function of Atomic Number. Ref. (14).
threshold the yield increases quadratically at first as shown in Fig. 3 which shows yields obtained by McKeown (11) for argon sputtering of gold and then almost linearly up to a maximum at an energy in the keV region. This energy is again dependent on the ion-target combination. Beyond the maximum the yield decreases due to the ion energy being deposited deeper and deeper into the target such that target atoms are displaced too far from the surface for sputtering to take place. This can be seen from the work of Almén and Bruce (10) in Fig. 4.

(iv) Angular dependence of Sputtering Yield: The sputtering yield is sharply dependent on the angle of incidence of the bombarding ions although it is difficult to estimate the precise dependence because of effects of surface roughness and ion reflection which can be large at glancing angles of incidence. Molchanov et al. (17) bombarded Cu with 27 keV Ar ions and found that there was no reflection for an incident angle, \( \alpha \), of 70° but for \( \alpha = 78° \) the fraction of ions reflected was 6% and this increased to 17% for \( \alpha = 82° \) and 22% at 84° (where \( \alpha = 0° \) corresponds to normal incidence of the ion beam on the target surface). The results of Molchanov et al. together with those of Rol et al. (18) and Wehner (19) are shown in Fig. 5.

The generally accepted relationship is, \( S_\alpha = S_0 \sec \alpha \)

where \( S_\alpha \) = Sputtering Ratio for ions incident at angle \( \alpha \)

to target normal.

\( S_0 \) = Sputtering Yield for ions normal to target surface.

This gives a curve which increases in a sweep from \( \alpha = 0 \) but the curve has a maximum at \( \alpha \leq 70° \) and then falls sharply to zero at \( \alpha = 90° \) which corresponds to the ion beam travelling in a direction parallel to the target surface.

(v) Dependence on Target Temperature: Fetz (8) found that for mercury ion bombardment of a molybdenum target the sputtering ratio doubled when the target temperature was increased from 400°C to 1,000°C. Wehner (20) noted a small increase in the sputtering ratio when the temperature of a platinum target was increased from 300°C to 650°C. Wehner concluded that the increase in yield was due to the desorption of mercury ions from the target surface where they inhibit sputtering at lower temperatures.
Fig. 2: Variation of Sputtering Yield with ion species

Fig. 3: Low energy 'quadratic' sputtering yield curve
Fig. 4: Sputtering Yield Variation with Ion Energy in the keV Region. Almén and Bruce. Ref. (10)

Fig. 5: Angular Dependence of Sputtering Yield. Molchanov et al. (17), Rol et al. (18) and Wehner (19)
Almén and Bruce (10) bombarded Ag, Pt and Ni targets with 45 keV Kr ions and found that the yield for silver remained constant up to 600°C and then apparently increased due to a contribution from evaporation. For platinum and nickel the sputtering ratio decreased slowly between 200°C and 600°C. This is explained as an increase in annealing as the temperature increases. This process leads to the damage produced by an ion incident in the target lattice being repaired before another ion is incident in the same region.

1.1.6 Sputtering Theories

1.1.6.1 Thermal Evaporation Models: An early, basic model of sputtering was due to Von Hippel et al. (2,21). Known as the 'Hot-Spot Theory' and later developed by Townes (22) it postulated a mechanism whereby the incident particle raises the temperature of a small region to such a high temperature that sputtering results from a process of evaporation. Later experimental work displaced this model because of several discrepancies, not least of which, as Kaminsky (23) points out in his review of sputtering, is the fact that the mean energies of sputtered particles are orders of magnitude greater than thermal energies.

Thompson and Nelson (24) used a time of flight method to measure the energy spectrum of particles sputtered from gold under Xe\(^+\) and Ar\(^+\) ion bombardment. They observed a low energy peak of 0.15 ± 0.03 eV for 43 keV Xe\(^+\) bombardment which accounted for 12% of the total sputtered yield and a peak of energy 0.20 ± 0.05 eV for 42.5 keV Ar\(^+\) which accounted for 4% of the total yield. Thompson and Nelson proposed a contribution from evaporation caused by a localised, heated spike.

1.1.6.2 Collision Models: The dominant sputtering process is undoubtedly the transfer of momentum from the incident particle to the target atoms. Such a process was suggested originally by Lamar and Compton (25) who postulated that ions penetrated the target surface, were reflected from lower atomic layers and struck surface atoms as they travelled in an outward direction. Several theories have since been based on this mechanism, with the assumption that there are many more collisions involved, and among these are the treatments by Keywell (26,27), Goldman and Simon (28) and Rol et al. (18).
There are three recent theories concerned with the sputtering yield of polycrystalline and amorphous targets. They are summarised in a review paper by Tsong and Barber (29) and are the theories of Thompson (30), Sigmund (31) and Brandt and Laubert (32).

Polycrystalline materials are generally assumed to behave as amorphous materials in so far as any anisotropic effects will be small and can be averaged out. The problem then becomes one of random slowing down in what is assumed to be an infinite medium and the steps taken are as follows:

(i) Determine the energy loss in collisions.

(ii) Determine the number of primary and secondary recoil atoms.

(iii) Calculate how many of these recoil atoms arrive at the surface.

(iv) Calculate how many of the atoms arriving at the surface have sufficient energy to overcome surface binding and appear as sputtered atoms outside the solid.

The expressions for the sputtering yield which result from the three major theories are as follows:

(i) Thompson's Theory:

\[
S = \frac{\pi^2 a_0^2 n^2 E_R M_1 (Z_1 Z_2) e}{8e E_b M_1 + M_2} \sec \psi
\]

where;

\(a_0 = \text{Bohr Radius}\)

\(n = \text{density of atoms}\)

\(E_R = \text{Rydberg energy (13.6 eV)}\)

\(E_b = \text{binding energy}\)

\(M_1, M_2, Z_1, \text{ and } Z_2 \text{ are the masses and atomic numbers of the bombarding and target atoms}\)

and \(\psi = \text{angle of incidence}\).

It is seen that \(S\) is independent of \(E_1\), the ion energy. This applies for \(E_b \leq E_1 \leq E_a\), where \(E_a\) is the energy required to give a distance of closest approach of 'a', the atomic radius, in a head on collision.
(ii) Sigmund's Theory:

\[ S(E) = 0.0420 \alpha \frac{S_n(E)}{U_0^{0.2}} \]

where: \( \alpha \) is a factor which depends on \( m \) and \( M_2/M_1 \) (\( m \) is a number between 0 and 1 chosen to fit a power approximation of the Thomas-Fermi cross-section).

\( U_0 \) is the height of the surface potential.

\[ S_n(E) = 47\pi Z_1^2 e^2 a_{12}^3 \left[ \frac{M_1}{M_1 + M_2} \right] s_n(\epsilon) \]

from Lindhard et al. (33)

where: \( \epsilon = \frac{M_2 E/(M_1 + M_2)}{Z_1^2 e^2 / a_{12}} \)

\[ a_{12} = 0.8853 a_0 \left( Z_1^2 + Z_2^2 \right)^{-\frac{1}{2}} \]

\( s_n(\epsilon) \) is the reduced nuclear stopping cross-section for Thomas-Fermi interaction (Lindhard et al. (33).)

\( a_0 \) is the Bohr Radius.

The validity of the above expression extends from about 1 keV to 1000 keV and the sputtering yield follows approximately the Lindhard stopping power (34).

(iii) Theory of Brandt and Laubert:

\[ S = (\gamma \epsilon_{12} / U_2) s_{12} \lambda_0 \sigma(\epsilon) \]

where: \( \gamma \) is a geometrical factor depending on the angle of incidence

\[ \epsilon_{12} = Z_1 Z_2 e^2 (M_1 + M_2)/a_{12} M_2 \]

\( U_2 = \) displacement energy

\[ s_{12} = \left[ 8M_1 M_2 / (M_1 + M_2)^2 \right] z_2^2 / (z_1^2 + z_2^2) \]

\( \lambda_0 \) is a constant and is \( 3.25 \times 10^{-3} \) for most metals

\( \sigma(\epsilon) \) is the scaled nuclear stopping power.
The yield follows the Lindhard stopping power in a way similar to that of Sigmund's yield.

1.1.7 Sputtering of Single Crystals

The bombardment of single crystal targets has provided a great amount of information on the sputtering mechanism. An example of this is given by the work of Cooper and Comas (35) on the sputtering of (100) and (110) monocrystalline silver targets with low energy (~200 eV) argon ions. The sputtered deposits were distributed in the form of characteristic spot patterns which could not be reproduced by sublimation of the same targets at temperatures up to 815°C. The deposits which collected during the sublimation process were found to have distributions which were almost exactly cosine. This experiment reinforces the evidence for a mechanism of momentum transfer rather than a thermal evaporation process.

In 1957 Silsbee (36) suggested that energy could be transported along a line of atoms in a single crystal and that the energy could be focused into the line. This followed the experimental observation of Wehner (20) in 1956 that the sputtering of single crystals gave significantly different results than those obtained for polycrystalline targets. This observation was followed by similar results from several different experimental groups. These included the demonstration by Thompson (37) of preferential ejection in the close-packed directions from gold foils bombarded by high energy (> 300 keV) protons and the spot patterns of Anderson and Wehner (38) for the bombardment of Cu, Ni and Au crystals by mercury ions. Southern et al. (39) looked at the spot patterns produced by sputtering of Cu with argon ions.

The principal results of these experiments are summarized in a review of ion bombardment of surfaces by McCracken (40):

(i) The spot structures have been observed over a wide range of target materials and for incident ions with energies from 10 eV to nearly 1 MeV.

(ii) The halfwidth of the spots normally increases with target temperature.

(iii) The intensity and sharpness of the spots increase with the degree of close-packing of the lattice structure.
The spot pattern is affected by the orientation of the ion beam with respect to the target surface and the crystal orientation.

It was shown by Liebfried (41), using a hard-sphere approximation, that a collision sequence is focused if $D < 2R_T$ and $\cos \theta_0 > D/2R_T$ where,

- $R_T$ is the combined radii of the two colliding spheres
- $D$ is the interatomic spacing in the row of atoms under consideration
- $\theta_0$ is the angle made by the primary recoil with the atomic row.

The above expression implies that the degree of focusing will be greatest when $D$ is least, which is true for the close-packed directions; the $<111>$ directions for b.c.c. crystals and the $<110>$ directions for f.c.c. crystals.

Most of the recent evidence suggests, however, that focused collision sequences do not make a predominantly large contribution to the sputtering yield. Computer simulations by Torrens and Robinson (42) and Harrison et al. (43) show that such sequences are only a few collisions in length. Van Veen and Fluit (43) showed that focused collision sequences are mostly directed into the crystal. Hofer (44) compared the yields from hexagonal-close-packed crystals (Zn and Mg) for the $<1120>$ close-packed direction and the $<2023>$ direction where only a pair of atoms can be involved. The yields for sputtering by 10-40 keV rare gas ions led Hofer to conclude that focused collisions contribute only 25% of the total emission along the $<1120>$ direction, which implies that the contribution to the total yield is far less than this.

Focusing is found to be a low energy-phenomenon which will take place only below a critical energy and which contributes to ejection spot patterns but does not give a complete explanation of their presence. An alternative explanation was proposed by Lehman and Sigmund (45) in terms of a surface ejection model. The random collision cascade reaches the collision which is just below the surface. An atom is then sputtered if sufficient energy is transferred to it from the cascade to overcome surface binding. Sputtering will therefore occur most readily in directions of maximum energy transfer. These directions are where a sub-surface atom can
pass through a hole formed by a ring of surface atoms or where it can have a direct collision with a nearest-neighbour surface atom. In both cases the result is a higher ejection rate in directions corresponding to crystal lattice axes and spot patterns are produced accordingly. The results of Hofer (44), which have already been described, are strong evidence for this model.
1.2 Tantalum Thin Films

A deposited film of metal generally shows a higher value of resistivity and a less positive temperature coefficient of resistance (TCR) than the bulk metal. This difference in properties is explained by the incorporation of impurities into the film during deposition, the formation of defect centres and the scattering of electrons at the film boundary. Since these properties of high resistivity coupled with a low TCR are ideal device characteristics the idea was conceived of using metal films to produce integrated passive circuits.

Tantalum is a natural choice for such circuits because, in addition to the above properties, it can be anodically oxidised to form a protective layer which will resist corrosion. The first tantalum resistive films were deposited at the Bell Laboratories in 1957 by Basseches (46) who also developed the method of adjusting the resistance and protecting the film by anodic oxidation. The high dielectric constant of tantalum oxide was exploited by Berry and Sloan (47) who developed the first metal/oxide/metal film capacitor from tantalum in 1959. Further work was reported on the stability of oxidised tantalum film resistors (48), the electrical properties of sputtered films (49, 50) and evaporated films (49) and the manufacture of tantalum integrated circuits (51).

Much of the earlier work suffered from poor vacuum systems and the films were therefore poorly defined in composition and structure. Later work by Gerstenberg and Calbick (52) indicated the influence of impurities such as carbon, nitrogen and oxygen which led to the development, by Gerstenberg (53), of tantalum nitride, which is the basis for the majority of resistive films today. Another development, by Parisi (54), is tantalum oxynitride which can be made to have a temperature coefficient of resistance that can balance the negative temperature coefficient of capacitance (TCC) of tantalum capacitors. Tantalum oxynitride can therefore be used to fabricate temperature compensated R-C networks. Sato et al. (55) have obtained zero TCR's by vacuum heat treatment of tantalum nitride films.

The simplest use of a tantalum nitride film has been a discrete resistor on an embossed ceramic substrate (56) which has been in high-level
production for several years. The stability of the tantalum nitride resistor has led to its use in repeaters for submarine cables (57). The first commercial manufacture of a thin film resistor network for an electronic switching system was in 1963 and today such components are used in digital, analogue and microwave circuits. The increase in circuit complexity has required the development of a crossover technology (58) to cater for the large number of interconnecting elements on a film. A study of termination materials for tantalum nitride resistors (59) has shown that Ti-Pd-Au provides better corrosion and interfacial stability than other terminations considered.

Work has been going on in the Department of Electronic and Electrical Engineering at Surrey for some time concerned with the electrical properties of tantalum based films. It has been suggested above that the desired electrical properties of a film can be produced by controlling the level of impurities such as carbon, nitrogen and oxygen. Tantalum films are usually grown by electron-beam evaporation or by sputtering. Sputtering with reactive gases (nitrogen or oxygen) has been adopted for most thin film work because the film can be doped as it is deposited. The disadvantage of the sputtering method is the poor control over the amount of impurity incorporated into the film.

Efforts at Surrey have been directed towards the use of ion implantation for doping films. Ion implantation is a technique which gives very good control over the dose and depth profile of impurity atoms introduced into a target. The method therefore offers a possible means of tailoring the electrical characteristics of a thin film device to the desired values. Most of the ion implantation at Surrey has been concerned with resistors (60, 61) but more recently a study of tantalum capacitors has been carried out (62).

Electrical conduction in thin films is usually explained in terms of a dual metallic/activation conduction process, models for which have been proposed independently by Hardy et al. (63) and by Waterhouse and Westwood (64). The activation process takes place in the situation where the film consists of metal islands with an insulating phase between them, and the resistance can be expressed as,

\[ R = R_0 e^{E/kT} \]
where \( R_0 \) is a constant and \( E \) is the activation energy.

The activation energy is the energy required to transfer a conduction electron from one metal island to another and is dependent on island size and spacing both of which are dependent on film thickness.

If we differentiate the above expression for resistance we have,

\[
\frac{dR}{dT} = -R_0 \cdot \frac{E}{kT^2} \cdot e^{E/kT}
\]

The temperature coefficient of resistance (TCR) is defined as,

\[
\frac{\Delta R}{R} = \frac{1}{R} \frac{dR}{dT}
\]

and therefore,

\[
TCR = -\frac{E}{kT^2}
\]

The dual conduction process results from the fact that thin films are neither completely discontinuous (islands) nor completely continuous. They have both metallic and activation conduction processes operating in parallel. The metallic process has a positive TCR and in theory it should be possible to balance the positive and negative components to produce a film which is completely stable, that is a film with zero TCR. This was one of the aims of the ion implantation project for which the present characterisation study was carried out.
2. EXPERIMENTAL PROCEDURES

2.1 Target Assemblies

(i) Assembly for 600 keV Accelerator: All of the sputtering experiments using gold and gallium arsenide targets at room temperature and gallium arsenide targets at elevated temperatures were carried out using a stainless steel target assembly which was designed by I.H. Wilson and made in the workshops of the Department of Electronic and Electrical Engineering. A diagram of the assembly is shown in Fig. 6. It consists of a copper block on which the sample is mounted, with a copper/constantan thermocouple (a) for monitoring the sample temperature and a heater (b) which can be used to raise the target temperature. The ion-beam is defined by apertures (c) and (d) and sputtered atoms are collected on the polythene collector (e). The collector is supported by the hemispherical dish section (f) which is filled with liquid nitrogen. The polythene collectors are therefore maintained at temperatures in the region of liquid nitrogen temperature (77°K) in order to increase the sticking probability for sputtered atoms striking the collector surfaces. This section also acts as a cold vapour trap, so reducing the pressure in the target/collector region. A third function of the hemisphere is as a Faraday cup for charge collection and it is therefore electrically connected to the target.

Around the cup is a wire mesh cage (g) which is negatively biased to suppress secondary electrons. A second wire mesh cage (h) outside the first is connected to earth and screens the whole charge collection system. The wire mesh construction of the cages was chosen so that their presence would not severely affect pumping speed in the target region.

Fig. 7 shows the electrical connections and also the position of a secondary collector. This was used to collect atoms which were reflected from the main collector in order that an estimate of sticking efficiency could be made. The secondary collector was placed in the target plane so that sputtered atoms could not strike it directly.

(ii) Assembly for Lintott accelerator: For the low temperature experiments on gallium arsenide a very much smaller target assembly was
Fig. 6: Target Assembly for Sputtering Experiments using the 600 keV Heavy-Ion Accelerator

Fig. 7: Beam Path and Electrical Connections for Target Assembly used on 600 keV Accelerator
required to fit the target chamber. The Lintott target chamber was used because it had a facility for cooling targets, using liquid nitrogen, which was not present on the 600 keV system.

The purpose of sputtering at low temperature was to investigate the change in ratio (if any) of the gallium and arsenic yields. For this reason it was not necessary to try to produce absolute values of yields and therefore the fact that the reduced space necessitated a much simplified assembly was not felt to be a serious disadvantage. The construction used is shown in Fig. 8. The earthed aperture plate (a) defines the beam which then passes through the larger aperture in a negatively biased suppressor plate (b) to strike the sample (c). Sputtered atoms are collected by the collector (d) which is supported by the suppressor. The collector is a flat square of polythene and is not cooled in this assembly. Therefore the collection of sputtered atoms will not be as efficient as it is by the cooled, hemispherical collectors used in the larger assembly.

The sample is cooled by liquid nitrogen which is poured into the reservoir behind the sample. The temperature is not monitored but the sample and the liquid nitrogen are separated only by two thin, copper walls and a mica sheet and therefore the sample temperature will approximate to that of the liquid nitrogen.

2.2 Sample Preparation

(i) Gold Samples: The gold targets were all cut from 0.5 mm thick sheet of high purity (99.995%) metal and were therefore polycrystalline in structure. The 7 mm square targets were thoroughly degreased and washed and were then etched in aqua-regia (three parts HCl: one part HNO₃) and washed again prior to being used.

(ii) Gallium Arsenide Samples: The gallium arsenide targets were all from bulk grown, single crystal material. They were mainly semi-insulating although no great importance was attached to their electrical properties. Wafers of 0.5 mm thick material, sawn from ingots of (100) and (110) orientation, were polished on a Hyprocel-Pan-W pad using a solution of 1% Br in methanol to remove about 0.25 mm from the surface. The wafers were then diced into 5 mm squares using a wire saw after which they were thoroughly degreased in trichloroethylene and acetone. The squares were then etched for ten minutes in a rotating beaker containing
Fig. 8: Target Assembly used for Sputtering with Lintott Accelerator
a solution of 0.75% bromine in methanol and degreased again as above. Finally they were further cleaned in a reflux bath of iso-propyl-alcohol.

(iii) Tantalum Films: Some of the films used were supplied by Ultra Electronics Ltd. They were made by sputter deposition of tantalum on Corning 7059 glass substrates. The one inch square slides were each divided into nine pieces, using a wire saw, to provide samples of a convenient size. These samples were degreased and washed before use.

The majority of the tantalum films were prepared in the department by I. Sheikh using a Vacuum Generators U.H.V. evaporator. The base pressure in the evaporator was $2 \times 10^{-9}$Torr and this rose to around $5 \times 10^{-7}$Torr during an evaporation. One inch square Corning 7059 glass slides were again used as substrates and these were very scrupulously cleaned before the films were deposited. The slides were placed in a rack and were ultrasonically cleaned in a teepol solution for half an hour and then washed in distilled water. They were then placed in methanol in the ultrasonic bath for five minutes and were finally washed for two hours in flowing, deionised water.

The quality of the evaporated films was found to depend, very critically, on this cleaning process. If the slides were not cleaned in this way the resulting films had many pinholes.

A wire saw was used to produce samples of about 8 mm square which were degreased and washed in the normal way.

In addition to the films on glass substrates some films were deposited on vitreous carbon substrates. These came from the same sources as the glass substrate films, that is Ultra Electronics Ltd. and I. Sheikh.

I. Sheikh also produced some tantalum films on glass substrates which had previously been covered with a layer of evaporated aluminium ($\approx 100 \, \text{Å}$). By dissolving the aluminium using a solution of NaOH or a saturated solution of HgCl$_2$ the tantalum films were floated off the substrate and were then placed on copper microscope grids. Each copper grid had a single hole of 1 mm diameter and it was arranged that the tantalum spanned this hole to give an area of unsupported film.
The idea of the vitreous carbon substrates and of the unsupported films was to facilitate analysis of the films by Rutherford backscattering which will be described later.

2.3 Preparation of Collectors

The standard collectors which were used for the majority of the experiments with gold and gallium arsenide targets were in the form of polythene hemispheres of radius two inches. These hemispheres were made using a vacuum forming rig belonging to the Department of Metallurgy and Materials Technology.

The vacuum forming process involves heating a square sheet of polythene, of around 1 mm thickness, which was clamped across a female mould. The heater is a square array of standard electric fire elements. When the polythene has softened sufficiently the mould is pressurised by an electric pump which blows air through a number of small holes in the surface of the mould, causing the polythene sheet to be stretched. The mould is then evacuated by reversing the air flow and the polythene is drawn into the mould to produce a hemisphere which is then cooled. The collectors were trimmed to the required size and a hole was made in each collector at the centre to allow the beam to pass through. Finally the collectors were washed in methanol and then in distilled water before use.

The flat collectors used as secondary collectors and for the low temperature sputtering experiments were simply cut from polythene sheet and then washed.

2.4 Accelerator Facilities

(i) 600 keV Heavy-ion Accelerator: This machine was used for most of the sputtering experiments. It has been described elsewhere by Cracknell et al. (65) but briefly it consists of a Sames electrostatic generator which supplies the accelerating potential on to the bun of the accelerator. The bun encloses a Nielsen ion-source and the associated hardware and power supplies for extraction and focusing of the ion beam. The accelerator drift tube is horizontal and consists of 26 sections connected by a resistor chain to give a constant field along the tube. An analysing magnet at the earthed end of the tube steers the beam into one of two beam lines, one at 45° and one at 90° to the accelerator tube.
The 90° line was used for all of the sputtering experiments carried out on the 600 keV accelerator.

Two sets of electrostatic deflection plates which were positioned in the beam-line just in front of the target chamber provided X and Y scanning facilities and also, by applying D.C. bias to the plates, a means of steering the beam through the very small hole (3 or 4 mm) in the target assembly aperture. Scanned beams were used for all experiments. The beam was scanned in both X and Y directions at frequencies of ~500 Hz for horizontal scanning and ~50 Hz for vertical scanning using saw-tooth generators. This provided a raster scan which was monitored on an oscilloscope to avoid standing patterns. The beam spot size varied with energy and different ion-source conditions but was typically 2 mm in diameter and was over-scanned with respect to the target aperture to give a uniform current density over the target.

Pressures in the accelerator tube and in the beam-line were of the order of \(10^{-6}\) Torr and the target chamber pressure was typically \(3 \times 10^{-6}\) Torr during the experiments.

(ii) Lintott Isotope Separator: The Lintott is a commercial version (Lintott Model 8-12) of a machine which was developed at Harwell by Freeman (66). It has a nominal maximum energy of 80 keV although it is intended to increase this to 180 keV. The machine is designed to produce very high currents (up to 1 mA) with excellent mass resolution from an arc source.

For the purposes of the low temperature sputtering experiments the machine was used to provide a very modest current around 0.3 \(\mu A\) of 50 keV Ar⁺.

The pressure in the beam-line was about \(1 \times 10^{-7}\) Torr and in the target chamber it was \(5 \times 10^{-7}\) Torr during sputtering.

(iii) 2 MeV Van de Graaff Accelerator: This machine was used for the Rutherford Backscattering measurements which were made on the tantalum films and on some of the gallium arsenide targets. The machine produces a very stable, mono-energetic beam of light-ions. Analysis is by magnet and the beam is then collimated to give a parallel beam (± 0.03°) of usually 1 mm diameter at the target. The target stage comprises a three-axis,
motorised goniometer, although this was not required for the measurements. The target holder has electrostatic suppression of secondary electrons and the target chamber and beam line pressures were of the order of \(1 \times 10^{-5}\) Torr and \(1 \times 10^{-6}\) respectively.

2.5 Sputtering of Gold

2.5.1 Energy Dependence: Gold targets were bombarded in the energy range 50 to 450 keV to investigate the sputtering yields for neon, argon and krypton ions.

The normal procedure adopted was to begin at the low energy end of the range and work upwards. Thus a typical experiment would involve bombarding a target with a dose of \(2 \times 10^{17}\) ions/cm\(^2\) of 50 keV argon ions and collecting the sputtered atoms on a polythene collector. The liquid nitrogen reservoir behind the collector was then emptied by blowing air through it, to prevent condensing of water vapour, before the target chamber was let up to air so that the collector could be removed and another one put in its place. The target was then bombarded to a dose of \(2 \times 10^{17}\) Ar\(^+\) ions/cm\(^2\) at 100 keV. The process was repeated in steps of 50 keV up to the maximum energy of the range. In this way successive bombardments result in ions coming to rest deeper into the target and therefore in undamaged regions. It was felt that this approach would minimise any possible dose effects.

Beam currents used varied from 0.5 \(\mu\)A to 3 \(\mu\)A depending on the energy of the bombardment. The machine was designed for high energy operation and the maximum current falls off steadily below about 150 keV because of difficulty in focussing the beam. This tendency can be offset to some extent by the shorting out of some of the drift tube sections which improves the low energy performance. Ion doses varied from \(1 \times 10^{17}\) ions/cm\(^2\) to \(5 \times 10^{17}\) ions/cm\(^2\), with the higher doses being used for the neon bombardments where the sputtering yield was lowest.

The thermocouple mounted in the copper block to which the sample was fixed showed that the maximum rise in temperature during ion-bombardment was of the order of \(30^\circ\)C above room temperature.
2.5.2 Dose Dependence: Two experiments were carried out to find out if there was any detectable change in sputtering yield as a function of bombardment ion dose.

(i) In the first experiment a target was sputtered with a 100 keV argon ion beam, up to an initial dose of $5 \times 10^{16}$ ions/cm$^2$. The collector was then changed and the target was bombarded with a further $5 \times 10^{16}$ ions/cm$^2$ of argon at the same energy. The experiment was completed after six different 100 keV bombardments by which time the sample had received a total dose of $1.1 \times 10^{18}$ ions/cm$^2$.

(ii) In this experiment the procedure was similar to that of section 2.5.1 except that the experiment was begun at the high energy end. Argon ions were used and the first bombardment was at an energy of 450 keV. The collector was then changed and a second bombardment was carried out at 400 keV. The energy was reduced, again in 50 keV steps down to the last energy of 50 keV.

The reverse argument now applies where the ion ranges are concerned. Successive bombardments are now into material which is damaged and already has implanted argon ions. If there are dose effects, therefore, they should be evident if a comparison is made of the two plots of energy dependence, one for increasing energy and the other for decreasing energy.

2.5.3 Sticking Coefficient: The polythene collectors used for the gold experiments were cooled by liquid nitrogen as already pointed out and, therefore, the sticking coefficient for sputtered gold atoms striking a collector should be very high. Nevertheless it was decided to try to get an estimate of this coefficient by the use of a second collector. This collector was made in the form of a flat disc of polythene with a hole at the centre and it was placed in the same plane as the target as shown in Fig. 7. In this position it is not possible for sputtered atoms to strike the collector directly but atoms which are reflected from the main collector should strike the second collector and stick to it.

The secondary collectors were each left in position for several bombardments so that they would have collected sufficient gold atoms to
be within the detection sensitivity limit of the activation analysis technique.

2.6 Sputtering of Gallium Arsenide

2.6.1 Energy Dependence: The procedure was largely the same as that for the gold experiments. The energy dependence was measured for sputtering by argon ions in the energy range of 50 keV to 450 keV. In addition yields were measured for tellurium ions in the range 50 keV to 350 keV. In the case of tellurium bombardment the upper energy limit of 350 keV is set by the magnet which cannot 'bend' Te\(^+\) ions of greater energy through 90° into the beam-line.

Experiments were again started at 50 keV and the energy increased in stages. Ion doses were from around 1 \(\times\) 10\(^{17}\) ions/cm\(^2\) to 5 \(\times\) 10\(^{17}\) ions/cm\(^2\) and beam currents were usually about 0.5 \(\mu\)A. Great care was taken with the gallium arsenide targets to make sure that target temperature did not increase significantly through beam heating which could lead to degradation of the target surface.

2.6.2 Dose Dependence: The sputtering yield was measured over the range of 4 \(\times\) 10\(^{17}\) ions/cm\(^2\) to 2.5 \(\times\) 10\(^{18}\) ions/cm\(^2\) using a beam of 200 keV argon ions. The first bombardment was to a dose of 4 \(\times\) 10\(^{17}\) ions/cm\(^2\) after which the collector was changed and a further bombardment of 3 \(\times\) 10\(^{17}\) ions/cm\(^2\) was carried out. Increments of 3 \(\times\) 10\(^{17}\) ions/cm\(^2\) were added until the total dose reached 2.5 \(\times\) 10\(^{18}\) ions/cm\(^2\).

2.6.3 Low Temperature Sputtering: Gallium arsenide targets were maintained at low temperature, using liquid nitrogen, during sputtering by 50 keV argon ions up to doses of around 2 \(\times\) 10\(^{17}\) ions/cm\(^2\).

A very full programme of work involving the Lintott accelerator meant that the experiment was restricted to a total of five bombardments and in addition an insulation leakage on the target assembly ruled out current integration on two of these runs. Fortunately the purpose of the experiment was to compare the ratios of gallium yield to arsenic yield for low temperature sputtering with those found for sputtering from targets at room temperature and not to measure absolute values of yield. For this reason it is hoped that the problems of current integration should not prove to be too serious.
2.6.4 Elevated Temperature Sputtering: The sputtering of single crystals was referred to in Section 1.7. The examples referred to in Section 1.7 were all concerned with the spot patterns produced by the sputtering of metal targets. It is fundamental to ion-implantation studies of semiconductors, however, that heavy-ion bombardment produces a disordered surface layer in which the regular lattice arrangement of atoms is completely destroyed and that this is achieved after doses of around \(1 \times 10^1\) ions/cm\(^2\). This has been shown by many workers such as Mayer et al. (67) for silicon and germanium and Carter et al. (68) for gallium arsenide and gallium phosphide.

In order to produce spot patterns from single crystals it is necessary to maintain the temperature of the crystal target at a level high enough for re-ordering of bombardment-induced-damage to compete with the rate of displacement production so that the crystal lattice structure is not disordered. In the metal targets described this damage annealing during bombardment takes place at room temperature but for gallium arsenide it is necessary to heat the target.

MacDonald (69) obtained spot patterns for argon bombardment of germanium above a temperature of \(330 \pm 5^\circ\) C which corresponded to an abrupt transition of the target surface from a disordered to an ordered structure. Anderson (70) has suggested that the transition temperature at low energies should increase with increasing rate of defect introduction, or bombarding ion current and Zwangobani and MacDonald (71) have indeed confirmed this dependence of the transition temperature on ion current and on incident ion mass and the crystallography of the target.

The purpose of the elevated temperature experiment was, therefore, to attempt to produce some ejection patterns. Furthermore it was hoped to compare the gallium and arsenic yields for ejection along different directions. In a binary crystal it is to be expected that ejection by focused-collision-sequences or by the surface-ejection model of Lehman and Sigmund (45) could give rise to enhanced sputtering of one species or the other depending on the crystal direction under consideration. Agranovich et al. (72) and Kapusta and Lebedev (73) have observed such preferential ejection for sputtering of the different faces of indium antimonide crystals by 70 keV argon ions.
In the present experiment crystals of (110) and (100) (parallel to surface) gallium arsenide were bombarded with argon ions to high doses (up to $10^{18}$ ions/cm$^2$) at temperatures of 100, 200 and 300°C.

2.6.5 Sticking Efficiency: Secondary collectors were used in the same way as they were for sputtering of gold so that an estimate could be made of the sticking efficiency for sputtered atoms of gallium and arsenic striking the polythene collectors. In addition measurements were made of sputtering yields using polythene collectors with a thin, evaporated layer of nickel on the surfaces where atoms were to be collected. The reason for this experiment was to make a comparison of the ratios of gallium yield to arsenic yield for collection on a nickel surface with those for collection on a polythene surface.

Measurements were made for argon sputtering at energies of 200 and 300 keV.

2.6.6 Measurement of Stoichiometry: Two methods were used to try to compare the stoichiometry of the gallium arsenide surface on unbombarded targets and on targets after sputtering.

(i) Rutherford Backscattering: The technique of Rutherford Backscattering will be explained in the following section. Briefly, however, the concentration of an atomic species in a target surface is proportional to the number of ions backscattered from the species. A comparison of these relative counts for gallium and arsenic will give a measure of the surface stoichiometry.

(ii) ESCA: Samples of bombarded and unbombarded gallium arsenide were analysed using ESCA (Electron Spectroscopy for Chemical Analysis) in the Structural Studies Unit of the Department of Metallurgy and Materials Technology. A descriptive treatment of the principles and capabilities of ESCA has been given by Baitinger and Amy (74).

A sample is placed in a vacuum ($\approx 10^{-7}$ Torr) and bombarded with X-rays. This results in the ejection of photoelectrons from a distribution of depths below the surface, typically 10 to 100 Å with a mean depth 20 Å. The energy of an absorbed X-ray quantum is partially used to overcome the electron binding energy and the remainder represents the kinetic
energy of the ejected electron. A high resolution energy analyser is then used to give a plot of kinetic energy versus the number of electrons which is the output spectrum. The energy of the incident X-ray is known so the binding energy of the ejected electron is obtained. Hence information on species and chemical binding is obtained.

2.7 Activation Analysis

2.7.1 Irradiation and Reaction Details: The polythene collectors were sent to A.W.R.E. Aldermaston for activation analysis of the sputtered deposits.

Irradiations were carried out using the Herald reactor facility. The collectors from the gold experiments were irradiated in a large sample rig where the thermal neutron flux was \(3.2 \times 10^{11} \text{n/cm}^2/\text{sec}\). Irradiation times were either two minutes or ten minutes depending on a visual estimate of the thickness of the gold deposit on a particular collector. The gallium arsenide samples were all irradiated for three hours in one of the vertical tubes in the reactor where the thermal flux was \(2.5 \times 10^{12} \text{n/cm}^2/\text{sec}\). The two different methods were adopted because of the large differences in the neutron capture cross-sections for the different reactions, the gold reaction having the greater cross-section. The appropriate reactions together with their cross-sections and product half-lives are given in Table 2.1.

<table>
<thead>
<tr>
<th>REACTION</th>
<th>CROSS-SECTION ((\sigma_c))</th>
<th>HALF-LIFE</th>
<th>(\gamma)-ENERGY</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{197}\text{Au}(n,\gamma)^{198}\text{Au})</td>
<td>98.8 barns</td>
<td>64.8 hr.</td>
<td>411.8 keV</td>
</tr>
<tr>
<td>(^{75}\text{As}(n,\gamma)^{76}\text{As})</td>
<td>4.3 barns</td>
<td>26.3 hr.</td>
<td>559.2 keV</td>
</tr>
<tr>
<td>(^{71}\text{Ga}(n,\gamma)^{72}\text{Ga})</td>
<td>2.8 barns</td>
<td>14.1 hr.</td>
<td>834.1 keV</td>
</tr>
</tbody>
</table>

Table 2.1: Details of the nuclear-reactions involved in the activation analysis of the sputtered deposits
2.7.2 Counting and Statistics: The polythene collectors were folded as tightly as possible all in the same way and secured with polythene sellotape so that the geometry was the same for all irradiations in a particular position in the reactor. This was done to minimise errors from any spatial variation in flux. Monitors in the form of gold discs for the gold samples and zinc wires for the gallium arsenide samples were attached to each collector so that any variation in neutron dose could be allowed for.

Standards were prepared for each of the species of interest by the evaporation on to polythene sheet of weighed aliquots of pure solution. The polythene sheets were then folded to simulate the sample shape and were irradiated in the same way complete with attached monitors.

All samples were 'counted' for γ-activity after a period of time long enough for any short-life products to have decayed but well within the half-life of the reaction of interest. A Li/Ge detector coupled to a 4000 channel pulse height multichannel analyser was used for counting from the gallium arsenide samples and a 3 × 3 in. sodium iodide scintillator and photomultiplier tube connected to a 400 channel analyser were used for the gold samples. Both counting systems were linked to a PDP8 computer system for data handling. All samples were counted for thirty minutes with the samples placed at a distance of 6 in. from the front face of the detector to minimise geometry effects.

Peak areas were evaluated by the PDP8 using the Sterlinski (modified Covell) method of computation (75). Corrections were applied for dose variation and for decay and samples were then compared with the standards so that an absolute measurement of the amount of material on a collector could be calculated.

As an indication of the reproducibility of the method three standards were prepared from each of separate solutions of Ga in HCl and As₂O₃ in NaOH. They were then irradiated and counted and gave specific activities (counts/µg/minute/unit flux) as follows:
From the gallium result the spread is seen to be of the order of 15% for the three samples.

Limits of detection were estimated to be 0.2 μg for gallium, 0.1 μg for arsenic and 0.02 μg for gold.

The statistics of the counting process depended on the amounts of material present in the sample since the counting time, as already pointed out, was fixed at 30 minutes for all samples. Typically 2.3 μg of gallium gave a peak containing 48000 counts with a R.S.D. (Relative Standard Deviation) of 4.6%. In the same sample 1.54 μg of arsenic gave a peak containing 12900 counts with a R.S.D. of 2.8%.

2.7.3 Calculation of Sputtering Yield: Having obtained a value for the mass of gold, gallium or arsenic on a collector by the activation analysis method the sputtering yield is then calculated as follows:

Let integrated ion current = DμC

\[ \therefore \text{Ion dose} = \frac{D \times 10^{-6}}{1.602 \times 10^{-19}} \text{ ions for singly charged ions} \]

\[ (1.602 \times 10^{-19} = \text{electronic charge } e) \]

Let deposit on collector, of atomic weight A, have mass W μg. Then the number of atoms in the deposit is given by:

\[ \frac{W \times 10^{-9}}{A} \times 6.025 \times 10^{26} \text{ atoms. [6.025} \times 10^{26} \text{ (Kg-mole)}^{-1} = \text{Avogadro's Number]} \]

\[ \therefore \text{Sputtering ratio, } S, \text{ is given by:} \]
The Rutherford Backscattering Technique

Rutherford Backscattering is used in surface analysis to provide quantitative mass and depth information. The method involves bombarding a target, in vacuum, with a collimated, monoenergetic beam of light ions, usually of helium or hydrogen. The present study employed 1.5 MeV helium ions. Most of the ions penetrate several μm into the target and come to rest but a few will collide with target atoms and will undergo elastic, wide-angle scattering by the Coulomb repulsion of the atomic nuclei.

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

\[
E = K_M E_0 = \left[ \frac{M_1 \cos \theta + \sqrt{M_2^2 - M_2^2 \sin^2 \theta}}{M_1 + M_2} \right]^2 E_0 \quad \ldots \ldots \ldots \ldots \quad (1)
\]

where \( K_M \) = Kinematic Factor

\( M_1 \) = mass of ion

\( M_2 \) = mass of target atom

\( \theta \) = scattering angle

\( E_0 \) = incident energy of ion

The above equation gives the energy of an ion scattering from a surface atom as a function of the mass of the target atom.
(ii) Depth Analysis: If the ion penetrates the target surface it will lose energy to the electrons of the target atoms by ionisation and excitation and after scattering it will lose further energy along its outward path. The ion will therefore leave the target surface with energy \( K_{M}^{E_{0}} - \Delta E \) where \( \Delta E \) is the energy lost by the ion on its path into and out of the target. To a first approximation the energy loss is proportional to the depth \( t \) of the scattering event so that,

\[
\Delta E = [S] \cdot t \\
\text{........................... (2)}
\]

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

(iii) Concentration Analysis: The backscattering yield from a depth \( t \) is proportional to the area density of scattering centres at that depth. Therefore the number of backscattered ions which can be related to scattering from a certain type of atom at depth \( t \) will give a measure of the atomic concentration at that depth.

The scattering process due to Coulomb interaction was treated classically by Rutherford (76) and can be expressed in terms of a differential scattering cross-section,

\[
\frac{d\sigma}{d\Omega} = \left( \frac{Z_{1}Z_{2}e^{2}}{2E\sin^{2}\theta} \right) \left\{ \cos\theta + \frac{1 - \left( \frac{M_{1}}{M_{2}} \sin\theta \right)^{2}}{\left[ 1 - \left( \frac{M_{1}}{M_{2}} \sin\theta \right) \right]^{2}} \right\}^{2} \\
\text{......................... (3)}
\]

where \( Z_{1} = \) atomic number of ion

\( Z_{2} = \) atomic number of target atom

\( e = \) electronic charge

\( \theta = \) laboratory scattering angle

\( E = \) energy of ion prior to scattering

\( \frac{d\sigma}{d\Omega} \) is usually abbreviated to \( \sigma \) or \( \sigma(E) \).
The important consequence of Equation (3) is that the cross-section for elastic backscattering is proportional to the square of the atomic number of the target atom. Thus the method is very sensitive when used to detect a heavy impurity near the surface of a light substrate. The sensitivity for detection of gold atoms is around \(10^{12}\) atoms/cm\(^2\) or \(10^{-3}\) monolayers. For light atoms the backscattering yield is greatly reduced and where the substrate is of a heavier material the contribution from the light impurity will be superimposed on the spectrum from the substrate.

A typical ion backscattering experiment is outlined in Fig. 9 which is taken from a review paper on ion bombardment by Dearnaley (77). The collimated beam of helium ions strikes the target which has an oxide film on the surface. A heavy impurity is buried in the oxide film. Ions are backscattered and some of these ions strike the silicon detector and produce pulses which are amplified and fed to a multichannel analyser. The analyser sorts the pulses according to height, which corresponds to energy, and hence a spectrum of yield against energy is produced. Such a spectrum is illustrated in the lower part of Fig. 9.

The heavy impurity peak is quite separate from the main spectrum as predicted by equation (1). The front (high-energy) edge of the main spectrum represents scattering from the metal atoms at the oxide surface and the continuum represents scattering from beneath the surface. The contribution due to scattering from oxygen atoms in the oxide layer is seen as a 'hump' in the continuum and the width of the hump is determined by the oxide thickness.

From scattering theory the number of ions detected due to single scattering from a heavy impurity at depth \(t\) is given by:

\[
C = \rho \frac{d\sigma}{d\Omega} (E) \delta t Q \Omega
\] ........................ (4)

where \(\rho\) = density of impurity atoms
\[
\frac{d\sigma}{d\Omega} = \text{scattering cross-section}
\]
\(\delta t\) = thickness of layer under consideration
\(Q\) = total number of ions striking
\(\Omega\) = solid angle of detector
An example of an actual spectrum obtained from a backscattering experiment is shown in Fig. 10. This spectrum is also taken from Dearnaley (77') and shows the result of scattering of 1.5 MeV He$^+$ ions from a bismuth implanted titanium specimen which has been subsequently oxidised. The heavy impurity, which in this case is bismuth, is again seen to give a peak which is well separated from the main continuum. The 3000 Å oxide film can be seen from the oxygen contribution and from the reduced Ti yield in the front edge of the continuum where Ti atoms have been replaced by oxygen atoms. The slopes of these parts of the spectrum indicate that the Ti:O ratio increases with depth in the film.

The smearing out of the impurity peak and of the front edge of the continuum is a result of detector resolution. In general silicon surface barrier detectors have energy resolutions in the range 12 to 20 keV (F.W.H.M.). This is equivalent to a depth resolution of the order of 200 to 300 Å.
Fig. 9: Arrangement of a Typical Ion Backscattering Experiment

Fig. 10: Spectrum of Helium Ion Backscattering from Bi-implanted Ti
2.9 Analysis of Tantalum Films

The Rutherford backscattering technique was used to assess the quality of tantalum thin films with regard to density and composition. The films used were produced by R.F. sputter deposition at Ultra Electronics Ltd. and by electron beam evaporation at the University of Surrey. Films implanted with argon, nitrogen or oxygen ions were also analysed to see the effect of high dose implantation ($> 10^{17}$ ions/cm$^2$) on thickness and density and to estimate sputtering yields.

2.9.1 Assessment of Film Quality:

(i) Uniformity: The uniformity of thickness of the films was examined by comparison of spectra obtained for samples from different parts of a substrate. Samples were prepared, as explained in Section 2.2, by dividing a tantalum film on a glass substrate into a number of pieces (usually nine pieces). A comparison of the spectra for nine such samples will give a measure of the uniformity across the substrate. For some of the samples several spectra were collected for different areas close together to see if there were any local variations in thickness.

(ii) Purity: For a thin tantalum film on a glass substrate or on vitreous carbon the situation is similar to that of a heavy impurity in a light substrate. The tantalum film gives rise to a peak in the backscattered spectrum which is well separated from the continuum. The width of the peak is given by,

$$\Delta E = [S] t$$ (see section 2.8)

where $t$ = thickness of film.

$[S]$ = energy loss parameter and can be expressed as,

$$[S] = \left[ \frac{K_M}{\cos \theta_1} \left| \frac{dE}{dx} \right|_{in} + \frac{1}{\cos \theta_2} \left| \frac{dE}{dx} \right|_{out} \right]$$
where \( K_M \) = kinematic factor defined in Section 2.8

\[ \theta_1 = \text{angle between sample normal and incident beam} \]

\[ \theta_2 = \text{angle between sample normal and scattered particle} \]

and stopping power \( \frac{dE}{dx} \) is assumed to be constant along the inward and outward paths.

The stopping power is a characteristic of the particular medium and in a medium \( A_B^m_n \), where \( A \) and \( B \) are two different elements in the atomic ratio \( m/n \), the effective stopping power can be expressed by Bragg's rule for the linear additivity of stopping cross sections as,

\[ \varepsilon_{A_B^m_n} = m\varepsilon_A + n\varepsilon_B \]

\( \varepsilon \) is the 'stopping cross-section factor' defined by Chu et al. (78) from,

\[ \Delta E = [\varepsilon]Nt \]

where \( N \) is the atomic density.

The film thicknesses were measured by talystep and values of \([S]\) calculated. These values were then compared with the experimental value of Linker et al. (79) and the theoretical value of Ziegler and Chu (80).

The heights of the tantalum peaks were also used to give an estimate of film composition.

Backscattering spectra for tantalum films on vitreous carbon substrates show a very large separation of the metal peak from the substrate continuum such that the contributions from medium mass impurities can be clearly seen in the intermediate region and can therefore be identified and quantified.
2.9.2 Analysis of Ion-implanted Films: Films were implanted with argon, nitrogen or oxygen ions. For his study of tantalum resistivity and TCR Goh (61) used ion energies such that the mean projected ion range ($R_p$), calculated from the Lindhard, Scharff and Schiött (LSS) theory (61), was about half of the initial thickness of the film to be implanted. The film was then bombarded in stages until it was all sputtered off the substrate. Typically a dose of $5 \times 10^{17}$ ions/cm$^2$ of 40 keV nitrogen was required to completely remove a film with an initial thickness of 500 Å.

For the Rutherford backscattering measurements the above practice was not adhered to. Several energies were used for films of a particular thickness and films of various thicknesses were implanted. Estimates of sputtering yield were made from the change in width of the tantalum peak. The change in the shape of the tantalum peak was related to ion range and this was compared with the LSS mean projected range.
3. RESULTS

3.1 Sputtering of Gold

3.1.1 Energy Dependence: The energy dependence of sputtering yield of gold in the range 50-450 keV for argon sputtering and 50-400 keV for neon and krypton sputtering is shown in Figures 11, 12 and 13. It is readily seen that the spread in the experimental points is too great to allow the drawing of an unambiguous curve through each set. The lines shown are consequently the best straight line fit in each case, using the least squares method.

Each line shows that the sputtering yield is slowly decreasing with increasing ion energy and that the yield is greatest for krypton, the heaviest ion.

Figures 14, 15 and 16 show the experimental results together with the theoretical sputtering curves of Brandt and Laubert (32) and Sigmund (31). The theoretical curves show very similar gradients to the experimental results in each case although the absolute values of yield are not the same. A comparison of the values of yield at an intermediate energy of 200 keV is made in Table 3.1.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Ion Mass Number</th>
<th>S (Experimental)</th>
<th>S (Brandt &amp; Laubert)</th>
<th>S (Sigmund)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neon</td>
<td>20</td>
<td>4.4</td>
<td>1.5</td>
<td>6.2</td>
</tr>
<tr>
<td>Argon</td>
<td>40</td>
<td>18.0</td>
<td>7.0</td>
<td>13.5</td>
</tr>
<tr>
<td>Krypton</td>
<td>84</td>
<td>54.0</td>
<td>30.0</td>
<td>27.0</td>
</tr>
</tbody>
</table>

Table 3.1: Comparison of Experimental and Theoretical Values of Sputtering Yield of Gold for 200 keV Ions.

For neon sputtering the experimental value lies between the two theoretical values while for both argon and krypton bombardment the experimental results are considerably higher than those predicted by the two theories.
Fig. 11: Energy Dependence of Gold Sputtering Yield for Neon Ions
Fig. 12: Energy Dependence of Gold Sputtering Yield for Argon Ions
Fig. 13: Energy Dependence of Gold Sputtering Yield for Krypton Ions
Fig. 14: Theoretical and Experimental Sputtering Yields of Gold for Neon Ions
Fig. 15: Theoretical and Experimental Sputtering Yield of Gold for Argon Ions
Fig. 16: Theoretical and Experimental Sputtering Yield of Gold for Krypton Ions
3.1.2 Dose Dependence: The sputtering yield of gold measured for 200 keV \( \text{Ar}^+ \) ions as a function of dose is shown in Fig. 17. The gold target was bombarded to a total dose of \( 1.1 \times 10^{18} \text{ions/cm}^2 \). The points in Fig. 17 represent yield values calculated from each collector for each increment of ion dose and are therefore a measure of the changing value of the yield. In Fig. 18 the points are plotted, using the same data, to represent the aggregate yield. In this case each point gives the yield calculated from the total sputtered deposits for the total number of ions incident on the target up to that point. Fig. 18 therefore has a smoother shape than Fig. 17 but both sets of points suggest that the sputtering yield is slowly increasing with ion dose, at least up to a dose of around \( 5 \times 10^{17} \text{ions/cm}^2 \). From Fig. 18 it seems that the sputtering yield increases from about 19 atoms per ion for a dose of \( 5 \times 10^{16} \text{ions/cm}^2 \) to about 23 atoms per ion for a dose of \( 5 \times 10^{17} \text{ions/cm}^2 \).

Fig. 19 shows the sputtering yield of gold for argon ions as a function of decreasing energy, where the first bombardment was at 400 keV and successive bombardments were at lower energies. The slope of Fig. 19 is rather more steep than that of Fig. 12 which shows the increasing energy dependence of argon sputtering of gold. This suggests that the fact that each bombardment after the first is into a damaged target region may have the effect of increasing the sputtering yield.

Plate 1 shows a micrograph taken using a Scanning Electron Microscope (SEM), of a typical gold target surface after removal from the target assembly. The surface shows various features from comparatively flat areas to quite high cones. The scale of Plate 1 is 10 mm: 5 \( \mu \text{m} \), so the projecting features are up to 5 \( \mu \text{m} \) in height. Plate 2 shows an area of cones on a gold surface. The large, flat-topped cone at the left of Plate 2 is about 7.5 \( \mu \text{m} \) in height.

3.1.3 Sticking Coefficient: A measure of the sticking coefficient for sputtered gold atoms striking the polythene collectors was made, as described in Section 2.5, by placing a flat collector in the target plane. These secondary collectors were left in the target assembly for several bombardments in order that they collected a measurable amount of gold and gave results typical of those shown overleaf:
Fig. 17: Incremental Sputtering Yield Variation with Argon Ion Dose for Gold
Fig. 18: Aggregate Sputtering Yield Variation with Argon Ion Dose for Gold
Fig. 19: Energy Dependence of Sputtering Yield of Gold (○ Decreasing Energy) for Argon Ion Bombardment compared with Fig. 12 (● Increasing Energy).
Plate 1: Typical Sputtered Gold Surface (2,000 × Magnification)

Plate 2: Cones on Sputtered Gold Surface (5,000 × Magnification)
<table>
<thead>
<tr>
<th>Total Ion Dose</th>
<th>Total Deposit on Main Collectors</th>
<th>Deposit on Secondary Collector</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1.6 \times 10^{18}$ ions/cm$^2$</td>
<td>1,534 µg</td>
<td>62 µg</td>
</tr>
</tbody>
</table>

If it is assumed that any atoms which do not stick on the main collector will be collected at the secondary collector then the above figures lead to an estimate for the sticking coefficient of 96%.
3.2 Sputtering of Gallium Arsenide

3.2.1 Energy Dependence:

(i) Argon Sputtering: The sputtering yield of gallium arsenide was measured for argon ions in the energy range from 50 to 400 keV. The results of these measurements are shown in Fig. 20. Once again the spread in the results is quite large so the lines drawn are best-straight-line fits to the measured values. It is seen that the measured yield for sputtering of gallium atoms is considerably higher than that for arsenic atoms throughout the energy range. Taking 200 keV, as an intermediate energy, the values of measured yield, taken from the fitted line, are about 1.5 atoms per ion for gallium and 0.5 atoms per ion for arsenic, giving a ratio of gallium to arsenic yield of 3:1. The sputtering yields of both gallium and arsenic show a decrease with increasing ion energy.

Most of the sputtering experiments were carried out using a beam defining aperture of diameter 3 mm. At one point it was decided to use a 4 mm aperture to increase beam current on target and hence reduce the time required for each experiment. The series of experiments using the larger aperture gave the results shown in Fig. 21. The values of yield are considerably higher than those of Fig. 20 with about 2.4 atoms per ion for gallium and 1.7 atoms per ion for arsenic at 50 keV, compared with values of 1.6 and 0.5 for gallium and arsenic, respectively, from Fig. 20 at 50 keV.

A subsequent series of runs was made using a 3 mm aperture and a 4 mm aperture in turn in an effort to reproduce the above difference in values. On this occasion, however, results were the same for both apertures and compared very favourably with the values of Fig. 20 for the 3 mm aperture. Attempts to correlate the different results with various parameters such as total ion dose, dose rate and average current density proved unsuccessful.

(ii) Tellurium Sputtering: The energy dependence of gallium arsenide sputtering was also measured for tellurium ions. The energy range was from 50 to 350 keV, the upper limit being set by the analysing magnet. The measured yield values are shown in Fig. 22. Again there is a marked difference between the measured gallium and arsenic yield values. Taking 200 keV as the reference energy for comparison the sputtering yield
Fig. 20: Energy Dependence of Sputtering Yield of Gallium Arsenide for Argon Ions.
Fig. 21: Energy Dependence of Sputtering Yield of Gallium Arsenide for Argon Ions (4 mm Aperture)
Fig. 22: Energy Dependence of Sputtering Yield of Gallium Arsenide for Tellurium Ions
for gallium at this energy is about 4.2 atoms per ion, from Fig. 22 and for arsenic it is about 2.2 atoms per ion. The yields again show a decrease with increasing ion energy, from about 4.4 (Ga) and 2.5 (As) at 50 keV to about 3.8 (Ga) and 1.9 (As) at 350 keV.
3.2.2 Dose Dependence: Measurements were made of the dose dependence of sputtering yield of gallium arsenide for 200 keV Ar\(^+\) ions. The measurements were made in stages, as described in Section 2.6, with the collectors being changed after each stage. The first bombardment was to a dose of \(3 \times 10^{17}\) ions/cm\(^2\) followed by a dose of \(4 \times 10^{17}\) ions/cm\(^2\). All subsequent bombardments were to a dose of \(3 \times 10^{17}\) ions/cm\(^2\) until a total dose into the target of \(2.8 \times 10^{18}\) ions/cm\(^2\) had been reached. The resulting values of sputtering coefficient, calculated from each collector, are shown in Fig. 23. Each point represents the value of the yield over the increment of ion dose for which the particular collector was in the target chamber, in the same way as the points of Fig. 17 for sputtering of gold. The aggregate values of sputtering coefficient were also calculated in the same way as for the gold results and are shown in Fig. 24. The points of Fig. 24 therefore represent the overall value of the sputtering yield calculated from the total sputtered deposits from all collectors up to that point.

The measurements of dose dependence were made as part of the series of measurements using a 4 mm aperture as described above and they show the higher values of yield which were referred to in the preceding section. The results again show measured values of gallium yield which are considerably greater than the arsenic values. Both Fig. 23 and Fig. 24 suggest that the sputtering yields for gallium and arsenic increase with ion dose up to a dose of about \(1.3 \times 10^{18}\) ions/cm\(^2\). From Fig. 24 it would seem that a target sputtered with \(3 \times 10^{17}\) ions/cm\(^2\) of 200 keV argon ions will give a gallium yield of 1.8 atoms per ion and an arsenic yield of 1.1 atoms per ion, while a target sputtered with \(1.3 \times 10^{18}\) ions/cm\(^2\) will give yields of 2.4 atoms per ion (Ga) and 1.5 atoms per ion (As).

A further point of interest from the dose dependence results is the fact that the ratio of gallium yield to arsenic yield does not change with ion dose. It might be expected that if the gallium yield is greater than that of arsenic, the target surface will become richer in arsenic such that the ratio changes to reach a stable level after a certain dose.

Plate 3 is a micrograph taken by SEM of the surface of a gallium arsenide target after bombardment to a dose of around \(10^{18}\) ions/cm\(^2\).
Fig. 23: Incremental Sputtering Yield Variation with Argon Ion Dose for Gallium Arsenide
Fig. 24: Aggregate Sputtering Yield Variation with Argon Ion Dose for Gallium Arsenide
Plate 3: Typical Sputtered Gallium Arsenide Surface (10,000 × Magnification)

Plate 4: Unbombarded Gallium Arsenide Surface (20,000 × Magnification)
surface is very rough with many pits which are typically 0.4 - 0.8 μm across. Plate h shows the surface of a gallium arsenide sample prior to bombardment. The surface is seen to be flat and almost featureless even though the magnification of Plate 4 is twice that of Plate 3. The boulder like feature in the top left hand corner is an impurity on the surface and was used to focus the micrograph.
3.2.3 Sticking Coefficient: Secondary collectors were used in the same way as for gold to try to estimate the sticking coefficient for gallium and arsenic atoms striking the polythene collectors. Again the secondary collectors were left in position for the duration of several experiments in order that they collected measurable amounts of material. Typical figures are given below:

<table>
<thead>
<tr>
<th>Total Ion Dose</th>
<th>Total Deposit on Main Collectors</th>
<th>Deposit on Secondary Collector</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Gallium</td>
<td>Arsenic</td>
</tr>
<tr>
<td>$9 \times 10^{17}$ ions/cm$^2$</td>
<td>8.6 µg</td>
<td>3.5 µg</td>
</tr>
</tbody>
</table>

These figures lead to values for sticking coefficients of 90% for gallium atoms and 92% for arsenic atoms, assuming that all of the sputtered atoms which are not collected by the main collector are collected by the secondary collector.

A set of argon bombardments was carried out using polythene collectors with a coating of nickel evaporated on to the collecting surface so that the ratios of gallium to arsenic on these collectors could be compared with those on standard collectors. The results of this experiment are given in Table 3.2.

<table>
<thead>
<tr>
<th>Ion Energy (keV)</th>
<th>Ga Yield (atoms/ion)</th>
<th>As Yield (atoms/ion)</th>
<th>Ratio of Ga:As</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>2.0</td>
<td>1.1</td>
<td>1.8</td>
</tr>
<tr>
<td>&quot;</td>
<td>2.0</td>
<td>1.0</td>
<td>2.0</td>
</tr>
<tr>
<td>&quot;</td>
<td>2.7</td>
<td>1.4</td>
<td>1.9</td>
</tr>
<tr>
<td>Av.</td>
<td></td>
<td></td>
<td>1.9</td>
</tr>
<tr>
<td>300</td>
<td>2.7</td>
<td>1.4</td>
<td>1.9</td>
</tr>
<tr>
<td>&quot;</td>
<td>2.4</td>
<td>1.4</td>
<td>1.7</td>
</tr>
<tr>
<td>&quot;</td>
<td>2.7</td>
<td>1.6</td>
<td>1.7</td>
</tr>
<tr>
<td>&quot;</td>
<td>2.7</td>
<td>1.5</td>
<td>1.8</td>
</tr>
<tr>
<td>Av.</td>
<td></td>
<td></td>
<td>1.8</td>
</tr>
</tbody>
</table>

Table 3.2: Sputtering Yield of GaAs measured using nickel coated collectors. Bombardment doses were $3 \times 10^{17}$ ions/cm$^2$ of argon in each case.
The average values of the Ga:As ratio from Table 3.2 are 1.9 for 200 keV bombardment and 1.8 for 300 keV bombardment. The corresponding values for standard collectors, calculated from the results of Fig. 20, are around 3 for both 200 and 300 keV bombardment. It is noticed, however, that the values of sputtering coefficient in Table 3.2 are considerably greater than those of Fig. 20. The coefficient for gallium is 2.0 – 2.5 compared with around 1.5 in Fig. 20 and for arsenic it is 1.0 – 1.6 compared with around 0.5 for Fig. 20. These higher values are similar to those of Fig. 21 obtained using a 4 mm diameter aperture although the above experiment with nickel coated collectors was carried out using a 3 mm diameter aperture.

3.2.4 Low Temperature Sputtering: This experiment was restricted to just five bombardments for the reasons outlined in Section 2.6.3. The measured results for the sputtering yields and for the ratios of gallium yield to arsenic yield are shown in Table 3.3.

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Ga Yield (Atoms/ion)</th>
<th>As Yield (Atoms/ion)</th>
<th>Ratio of Ga:As</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.5</td>
<td>0.6</td>
<td>2.5</td>
</tr>
<tr>
<td>2</td>
<td>0.9</td>
<td>0.4</td>
<td>2.3</td>
</tr>
<tr>
<td>3</td>
<td>1.0*</td>
<td>0.5*</td>
<td>2.0</td>
</tr>
<tr>
<td>4</td>
<td>2.0*</td>
<td>1.1*</td>
<td>1.8</td>
</tr>
<tr>
<td>5</td>
<td>3.1</td>
<td>1.6</td>
<td>1.9</td>
</tr>
</tbody>
</table>

Table 3.3: Sputtering Yields of GaAs at liquid nitrogen temperature for \(2 \times 10^{17}\) ions/cm\(^2\) of 50 keV Ar\(^+\).

*These values were calculated using estimates of total ion dose after insulation breakdown on target assembly.

It is seen that the ratio values are all around 2 with a mean value of 2.1. Since all five bombardments were into the same sample it was hoped that the ratio might change progressively following a readjustment of the surface stoichiometry due to the apparent preferential
sputtering of gallium. The fact that the target is cooled to liquid nitrogen temperature during sputtering should reduce the possibility of any thermally induced alteration of the relative atomic concentrations at the surface.

Table 3.3 suggests that there may be a slight reduction in the ratio of gallium yield to arsenic yield, from around 2.5 to around 1.9. On the strength of just five results, however, and on consideration of the typical spread of results, such as those of Fig. 20 for the energy dependence of sputtering coefficient, such a reduction cannot be confirmed or disproved.

The actual values of sputtering yield given in Table 3.3 show quite large variations, from 0.9 to 3.1 atoms per ion for gallium and from 0.4 to 1.6 for arsenic. The reason for such variations is probably the simple form of the target assembly used for this experiment.
3.2.5 Elevated Temperature Sputtering: This experiment was intended to produce ejection spot patterns as a result of the processes described in Section 1.7. Preliminary experiments indicated, however, that the gallium and arsenic deposits on the polythene collectors were not visibly detectable. This was true even though the bombardments were to a dose of $7 \times 10^{17}$ ions/cm$^2$ of 200 keV argon. This represents a total ion dose of about $5 \times 10^{16}$ ions incident on target for the 3 mm diameter aperture used.

One of the collectors was then divided into eight segments which were activated and counted separately in the hope that the presence of any spot pattern would be shown by the amounts of sputtered material on the different pieces. The result of this experiment was as shown in Table 3.4.

<table>
<thead>
<tr>
<th>Segment</th>
<th>Amount of Deposit Ga (µg)</th>
<th>As (µg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.5</td>
<td>0.1</td>
</tr>
<tr>
<td>B</td>
<td>1.5</td>
<td>0.2</td>
</tr>
<tr>
<td>C</td>
<td>0.9</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>D</td>
<td>0.5</td>
<td>0.3</td>
</tr>
<tr>
<td>E</td>
<td>1.0</td>
<td>0.1</td>
</tr>
<tr>
<td>F</td>
<td>0.5</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>G</td>
<td>0.9</td>
<td>0.1</td>
</tr>
<tr>
<td>H</td>
<td>0.8</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Table 3.4: Measurements of Sputtered deposits on Segments of a Collector

The collector segments were cut and numbered as shown below in Fig. 25.

Fig. 25: Collector divided into Eight Segments for Activation Analysis
The arsenic deposits given in Table 3.4 are all around the detection limit for the activation analysis technique and the amounts of gallium on the different segments do not suggest any orderly distribution of the sputtered deposit.

A sputtered deposit was seen on just one collector after a dose of $2 \times 10^{18}$ ions/cm$^2$ of 100 keV argon with the target heated to a temperature of 200$^\circ$C. The deposit was rather faint but the shape was seen to be in the form of a square with the corners pulled out as illustrated in Fig. 26. The deposit was displaced from the axis of the collector as suggested by the sketch.

Fig. 26: Illustration of Sputtered Deposit for Argon Bombardment of (110) gallium arsenide at 200$^\circ$C

The bombardment required to produce the 'pattern' of Fig. 26 was about four and a half hours in length and it was decided at this point that this method of looking at ejection patterns was not a satisfactory one. Results of analysis of collectors from elevated temperature sputtering are given in Table 3.5.
<table>
<thead>
<tr>
<th>Ion Energy (keV)</th>
<th>Target Temperature (°C)</th>
<th>Dose (ions/cm²)</th>
<th>Ga Yield (atoms/ion)</th>
<th>As Yield (atoms/ion)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>100</td>
<td>$7 \times 10^{17}$</td>
<td>1.1</td>
<td>0.2</td>
</tr>
<tr>
<td>100</td>
<td>200</td>
<td>$1 \times 10^{18}$</td>
<td>0.5</td>
<td>0.25</td>
</tr>
<tr>
<td>75</td>
<td>300</td>
<td>$2 \times 10^{18}$</td>
<td>0.6</td>
<td>0.3</td>
</tr>
</tbody>
</table>

Table 3.5: Measured Sputtering Yields for Argon Bombardment of Gallium Arsenide at Elevated Temperatures

The yield figures for the 100°C target are different from the results already given for room temperature sputtering in that the gallium yield is very high in comparison with the arsenic yield. The other results, for targets at 200°C and 300°C are very similar to earlier results with comparable values of measured yield and ratios of about 2:1 for gallium yield : arsenic yield.
3.2.6 Surface Stoichiometry:

(i) ESCA Analysis: ESCA was used to examine sputtered gallium arsenide surfaces. Analysis was carried out using aluminium $\text{K}\alpha$ X-rays and the ESCA target chamber was equipped with a 5 keV argon ion-gun which could be used for in situ etching of target surfaces.

Comparisons were made between the surfaces of bombarded and unbombarded samples using both the photoelectron peaks and the auger peaks. Both methods showed no change in stoichiometry due to sputtering. The ratios of counts in the gallium peak to counts in the arsenic peak were the same for bombarded and unbombarded surfaces.

The bombarded area of a sputtered sample is about 7 mm$^2$ which is quite small compared with the area of analysis which is the whole sample area of about 25 mm$^2$. This means that about 70% of the counts from a bombarded sample originate from an unbombarded part of that sample and this will obviously hide any changes caused by sputtering. Aluminium foil was therefore used to wrap a batch of sputtered samples in such a way that it masked all but the areas which had been bombarded. These samples were then analysed using ESCA but again the results showed no differences between surfaces of bombarded and unbombarded samples.

(ii) Rutherford Backscattering: Rutherford backscattering spectra were collected for bombarded and unbombarded gallium arsenide samples. Fig. 27 shows a spectrum for an unbombarded surface and it can be seen that there is very little separation in energy between the gallium and arsenic edges which represent scattering from surface atoms. This follows from a consideration of the scattering equation (Equation 1, Section 2.8) and the fact that the masses of gallium (mass number 70) and arsenic (mass number 75) are of almost the same magnitude.

The heights of the gallium and arsenic edges are indicated by horizontal arrows in Fig. 27 (gallium height is the total height less arsenic height) and give a ratio of 0.9:1 (gallium:arsenic) which compares very well with the theoretical value of 0.87:1 for a stoichiometric surface.

Spectra of bombarded surfaces were similar in shape to that of
Fig. 27: Rutherford Backscattering Spectrum of an Unbombarded Gallium Arsenide Target
Fig. 27 but the edges showed no clear separation between the gallium and arsenic energies. The measurement of heights on Fig. 27 is obviously a far from exact procedure but there are at least two distinct edges which can be assigned to scattering from gallium atoms and scattering from arsenic atoms. Spectra from bombarded samples did not show this distinction but had 'ragged' edges such that estimates of stoichiometry were not possible.
3.3 Tantalum Films

3.3.1 Assessment of Film Quality:

(i) Uniformity: A typical backscattering spectrum for a tantalum film on a glass substrate is shown in Fig. 28. The film has a thickness of ~2400Å and is a sputtered film deposited on glass by Ultra Electronics. The height of the tantalum peak for a given ion dose is a measure of the film density and the width (usually F.W.H.M.) is proportional to film thickness for films of equal density. The slope of the peak, increasing in height from right to left, reflects the \( 1/R^2 \) dependence of the scattering cross-section.

Several films, divided into pieces as described in Section 2.10, were examined and comparison of spectra heights and widths showed no detectable variations in thickness and density across any of the films and no local variations for spectra taken from adjacent spots. This applied to all the Ultra films and to the University of Surrey films over a range of thicknesses from 500Å to 2500Å. The width of the tantalum backscattering peak is given by:

\[
\Delta W = [S]_t.
\]

where \([S]\) is the energy loss parameter described in Section 2.10 and \( t \) is the film thickness. Values of \([S]\) for samples of the various films were calculated from the gradients of graphs such as those of Fig. 29 which shows peak width plotted against thickness measured by Talystep for several Ultra and Surrey films on glass substrates. Values of \([S]\) are shown in Table 3.6 together with the experimental value of Linker et al. (79) and the expected value from the stopping power data of Ziegler and Chu (80).

<table>
<thead>
<tr>
<th>Energy Loss Parameter [S] (eV/Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ziegler &amp; Chu</td>
</tr>
<tr>
<td>Linker et al.</td>
</tr>
<tr>
<td>Surrey on glass</td>
</tr>
<tr>
<td>Surrey on vitreous carbon</td>
</tr>
<tr>
<td>Ultra on glass</td>
</tr>
<tr>
<td>Ultra on vitreous carbon</td>
</tr>
</tbody>
</table>

Table 3.6: Comparison of [S] parameters for different tantalum films
Fig. 28: Typical Rutherford Backscattering Spectrum of a Tantalum Film on a Glass Substrate. Film Thickness is 2.400 Å
Fig. 29: Width of Tantalum Peak in Backscattering Spectrum as a Function of Measured Film Thickness
The values of $[S]$ for the Ultra films compare quite well with the value predicted by Ziegler and Chu and with the experimental value of Linker et al. while those of the Surrey films are considerably lower suggesting that the density of these films is lower due to a greater level of incorporated impurities. The value of $[S]$ was found to vary between different batches of the Surrey films which is evidently a result of different impurity levels from run to run.

(ii) Purity: Oxygen was found to be the dominant impurity in all of the films. This is illustrated very clearly by Fig. 30 which is a spectrum of a 1400Å Ultra film on a vitreous carbon substrate. The tantalum peak is scaled down so that its shape can be seen and it is noticed that the top of the peak is rounded at both edges compared with the peak of Fig. 28. This is assumed to be due to a reduction in the density of tantalum atoms at the two faces of the film where the oxygen content is high. The oxygen profile through the film is shown by the part of the spectrum marked by arrows. There is no nitrogen edge in the spectrum so there is little or no nitrogen in the film.

Spectra such as that of Fig. 30 were used to estimate film composition. Corrections were made for the $(Z_g/E)^2$ dependence of the scattering cross-section given by Equation 3 in Section 2.8 to produce depth profiles of the form of Fig. 31 which represents a 1000Å Ultra film on vitreous carbon. Again the oxygen is concentrated at the surface and at the metal-carbon interface; the oxygen composition reaching 40% (atomic per cent) at the surface and 20% at the interface with a value of about 15% at the centre of the film. These oxygen compositions were typical of most of the Ultra films. Surrey films generally contained more oxygen although films from different growth runs showed different amounts of oxygen. The composition, taken as the oxygen content within the film and not at the surface, varied from around 20% to 40%. Fig. 32 shows a depth profile, again corrected for $(Z_g/E)^2$ dependence of scattering cross-section, of a Surrey film of thickness 1600Å. It has a surface oxygen concentration of 50% and a level profile within the film with a concentration of 35%. Spectra for unsupported tantalum films, prepared at Surrey as described in Section 2.2 (iii), showed similar oxygen levels.
Fig. 30: Rutherford Backscattering Spectrum of a 1400 Å Ultra Ta Film on a Vitreous Carbon Substrate
Fig. 31: Composition Profile of a 1000 Å Ultra Sputter Deposited Ta Film on a Vitreous Carbon Substrate
Fig. 32: Composition Profile of a 1600 Å Surrey Evaporated Ta Film on a Vitreous Carbon Substrate
3.3.2 Ion Implanted Films: Tantalum films were bombarded with argon, nitrogen and oxygen ions at several energies and at several dose levels.

(i) Argon Bombardment: Fig. 33 shows some backscattering spectra for a 1200Å Ultra film on glass before bombardment and after three different doses of 40keV argon ions. The doses used were $7.5 \times 10^{16}$ ions/cm$^2$, $1.5 \times 10^{17}$ ions/cm$^2$ and $2.3 \times 10^{17}$ ions/cm$^2$.

The first bombardment produces a spectrum (2) which is narrower than that from the original film due to thinning of the film by sputtering. The shape of the tantalum peak is altered with the removal of the 'corner' at the high energy edge. This reduction in height is the result of tantalum atoms being displaced by the ion beam to be replaced by argon atoms with a consequent lowering of the film density at the surface. The altered depth can be estimated from Fig. 33 to be about 400Å. The projected range of 40 keV argon ions in tantalum is about 150Å according to the theory of Lindhard, Scharff and Schiøtt (LSS) (81). Values of LSS range for argon, nitrogen and oxygen ions in tantalum are shown in Fig. 34. If it is assumed that the argon implant depth profile is a Gaussian then the maximum range will be around 300Å. This shows reasonable agreement with the 400Å altered depth estimated from the backscattering spectrum. Spectrum (3) also indicates an altered depth of around 400Å. Spectrum (4) shows that the tantalum film is now altered throughout its remaining thickness and some argon ions are now passing right through the film and into the glass substrate.

The density of the tantalum film can be calculated by comparison of the height of the tantalum peak with the height of gallium arsenide spectra of the form of Fig. 27.

The scattering cross-sections can be related by Equation 3 of Section 2.7 to give:
Fig. 33: Backscattering Spectra for a 1200 Å Ultra film showing the effect of argon bombardment.
Fig. 34: Graphs of LSS Projected Range against Ion Energy for argon, nitrogen and oxygen in tantalum
where $Y = \text{backscattered yield}$

$N = \text{atomic density}$

$M = \text{atomic weight}$

$Z = \text{atomic number}$

The above equation relates gallium yield to tantalum yield and a similar expression is used to relate arsenic yield to tantalum yield.

The resulting relationships are,

$$\frac{Y_{Ga}}{Y_{Ta}} = \frac{N_{Ga}}{N_{Ta}} \times 0.193$$

$$\frac{Y_{As}}{Y_{Ta}} = \frac{N_{As}}{N_{Ta}} \times 0.217$$

The above expressions are summed to give,

$$\frac{Y_{(GaAs)}}{Y_{Ta}} = \frac{N_{(GaAs)}}{N_{Ta}} \times 0.410 \quad \text{(1)}$$

The relationship between spectrum heights must take into account the different stopping powers of gallium arsenide and tantalum for helium ions since the height represents the number of scattering events in a small increment of target thickness.

The stopping powers are taken from data produced by Northcliffe and Schilling (82). The stopping power for helium in germanium is used to represent gallium arsenide. The values used are 0.360 MeV/(mg/cm²)
for tantalum and 0.655 MeV/(mg/cm²) for gallium arsenide (germanium).

Equation (1) above now becomes:

\[
\frac{N_{\text{GaAs}}}{N_{\text{Ta}}} = \frac{H_{\text{GaAs}}}{H_{\text{Ta}}} \times 0.225
\]

where \(H_{\text{GaAs}}\) and \(H_{\text{Ta}}\) are the respective heights of the gallium arsenide spectrum and the tantalum spectrum for equivalent integrated beam current.

For the tantalum peak of Fig. 33 this ratio was found to be 1/8.9. The density of gallium arsenide is 5.37 g/cm³ which gives:

\[
N_{\text{GaAs}} = \frac{5.37 \times 6.02 \times 10^{23}}{147.2} = 2.2 \times 10^{22} \text{mols/cm}^3
\]

The atomic density of the tantalum film is now given by:

\[
N_{\text{Ta}} = 8.9 \times 2.2 \times 10^{22} \times 0.225
\]

\[
= 4.41 \times 10^{22} \text{atoms/cm}^3
\]

\[
\rho_{\text{Ta}} = \frac{4.41 \times 10^{22} \times 181}{6.02 \times 10^{23}}
\]

\[
= 13.3 \text{ g/cm}^3
\]

The density of bulk tantalum is 16.6 g/cm³ so the film density is quite a lot lower than the bulk value.

The thickness of the unbombarded film is 1200Å which is equivalent to,
The corresponding tantalum peak contains 269,000 counts and the counts under this and the other peaks of Fig. 33 are given in Table 3.7.

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>Counts in Peak</th>
<th>Ion Dose</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>269,000</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>205,000</td>
<td>$7.5 \times 10^{16}/\text{cm}^2$</td>
</tr>
<tr>
<td>3</td>
<td>117,000</td>
<td>$1.5 \times 10^{17}/\text{cm}^2$</td>
</tr>
<tr>
<td>4</td>
<td>47,000</td>
<td>$2.3 \times 10^{17}/\text{cm}^2$</td>
</tr>
</tbody>
</table>

Table 3.7: Tantalum peak areas for an argon bombarded film

An estimate of the sputtering yield can now be made since we can relate peak area to atomic density. The yields estimated from the three spectra (2, 3 and 4) are 1.7 atoms per ion, 2.0 atoms per ion and 1.9 atoms per ion respectively.

Surrey evaporated films were generally of lower density than Ultra films with values of around 11.5 g/cm$^3$. Values of sputtering yield obtained for Surrey films were in the region of 1.5 to 2.0 atoms per ion, very close to the values obtained for Ultra films. The highest ion energy used was 120 keV but no great difference in sputtering yield was seen between films bombarded at 120 keV and films bombarded at 40 keV.

The rate of thinning of the tantalum peaks, and hence the sputtering rate, was seen to decrease considerably when the films reached a stage where a large fraction of the ion beam was passing through the film and into the glass substrate with little contribution to the sputtering process.
Nitrogen Bombardment: Fig. 35 shows two superimposed backscattering spectra for a 1400Å Surrey evaporated film. The spectra were taken from the 'as evaporated' film and from the same film after a dose of $4.7 \times 10^{17}$ ions/cm$^2$ of 40 keV N$_2^+$. The film was evaporated on a vitreous carbon substrate and only the tantalum peaks are shown.

The peak for the as deposited film has a shape which suggests a high level of oxygen at the surface and the composition was found to be almost identical to that of the film in Fig. 32 (which was deposited at the same time) except that the film of Fig. 32 has a thickness of 1600Å.

After nitrogen bombardment the shape of the tantalum peak is altered considerably. The peak is again thinner due to sputtering but the reduction in the surface peak height is far greater than that observed after argon bombardment. One very obvious reason for this is the considerably higher ion dose used compared with the argon bombardment of the film of Fig. 33 but it was noticed that the height reductions were invariably more pronounced as a result of nitrogen bombardment.

The depth of the altered layer in Fig. 35 is around 450Å. The LSS projected range is 175Å for 20 keV N$^+$ ions. The bombardment conditions were $4.7 \times 10^{17}$ ions/cm$^2$ of 40 keV N$_2^+$ which is equivalent to $9.4 \times 10^{17}$ ions/cm$^2$ of 20 keV N$^+$ since the N$_2^+$ ion splits into two on striking the tantalum surface. The N$_2^+$ ion was used for all nitrogen bombardments because it ionises more easily than N$^+$. The LSS figure of 175Å suggests that the altered layer should be around 350Å so there is reasonable agreement with the 450Å indicated by the shape of the peak.

The average density of the tantalum film of Fig. 35 is 11.5 g/cm$^3$ and the peak counts are 850,000 and 670,000 for the unbombarded and bombarded cases respectively. Thus a value for the sputtering coefficient can be calculated as follows:
Fig. 35: Backscattering Spectra for a Surrey Evaporated Tantalum Film before and after Bombardment with Nitrogen Ions

Specimen VC4
40 keV N⁺
$4.7 \times 10^{17}$/cm²

Ta edge

as evaporated

After nitrogen bombardment

t = 1400 Å
The film has $N \times t$ atoms/cm$^2$

$$= 3.8 \times 10^{22} \times 1400$$

$$= 5.3 \times 10^{17} \text{atoms/cm}^2$$

.: no. of atoms sputtered is given by,

$$\frac{180,000}{850,000} \times 5.3 \times 10^{17} = 1.1 \times 10^{17} \text{atoms/cm}^2$$

Ion dose = $9.4 \times 10^{17} \text{ions/cm}^2$

.$$ S = \frac{1.1}{9.4} = 0.12 \text{ atoms/ion}$$

The sputtering yield is much lower than the value of 2 atoms per ion calculated for argon sputtering but the ion mass is less (14 compared with 40) and the energy is less (20 keV compared with 40 keV):

Another nitrogen bombarded film is shown in Fig. 36. In this case the film has a thickness of 2250Å and is a Surrey film evaporated on glass.

The spectrum for the unbombarded film shows a dip in the tantalum peak at a point around channel number 540. Similar dips were seen for other Surrey films particularly the thicker films where deposition was in two or more stages. The filaments of the evaporator had a very short life and had to be replaced during a run where thicker films were required. These films were therefore exposed to atmosphere between the separate depositions which apparently leads to incorporation of a higher level of oxygen in the region corresponding to the interface between the two parts of the film.

Another noticeable feature of Fig. 36 is that the spectrum for the bombarded film has the same width as that of the unbombarded
Fig. 36: Backscattering Spectra for Nitrogen Bombardment of a very thick (2250Å) Evaporated Tantalum Film
film and does not show the expected thinning of the tantalum peak due to sputtering. The explanation for this can be seen from a consideration of the stopping powers involved.

The altered layer in the tantalum peak can be approximated to a uniform strip with a density which is 85% of the density of the original film. If it is assumed that the altered layer of the film is tantalum nitride of composition TaN then it is obvious that there is an appreciable contribution to the stopping power from the nitrogen atoms in the film.

Using values of stopping power from the tables of Northcliffe and Schilling (82) and assuming that the stopping powers are additive we can write:

Stopping power for 1.5 MeV He\(^+\) in:

\[ \text{Ta} = 110 \text{ eV}/(10^{15}\text{atoms/cm}^2) \]

\[ \text{N} = 43 \text{ eV}/(10^{15}\text{atoms/cm}^2) \]

:. for unbombarded 1200Å strip:

\[
\text{Energy loss} = 110 \times \frac{N}{10^{15}} \times 1.2 \times 10^{-5}
\]

\[= \frac{1.32N}{10^{18}} \text{ eV} \]

and for the altered layer:

\[
\text{Energy loss} = 110 \times \frac{0.85N}{10^{15}} \times 1.2 \times 10^{-5} + 43 \times \frac{0.85N}{10^{15}} \times 1.2 \times 10^{-5}
\]

\[= \frac{1.56N}{10^{18}} \text{ eV} \]
The stopping power for the altered layer is greater by a factor of about 1.2 than that for the tantalum film. This means that the depth-scale of the tantalum nitride region is different from that for tantalum such that the bombarded film gives a spectrum with the same tantalum peak width as that of the unbombarded film even though the film is in fact thinner.

The LSS projected range for 75 keV nitrogen (the bombardment was with 150 keV $^1$N$^\circ$) is 600Å which predicts an altered layer of around 1200Å. The actual depth of the altered layer in Fig. 36 is about 1500Å so there is quite good agreement. The agreement is of course improved by the fact that the estimate of 1500Å is based on the stopping power for tantalum. In the light of the above calculation the 1500Å can be amended very approximately to 1250Å which represents very good agreement with LSS theory.

The inset in Fig. 36 is a plot of the bombarded spectrum subtracted from the unbombarded spectrum as a function of depth in the film and therefore gives an indication of the shape of the nitrogen profile.

The sputtering coefficient can be calculated in the same way as for the previous film to give a value of 0.1 atoms per ion. The value of sputtering coefficient for 75 keV nitrogen is therefore very close to the value of 0.12 estimated for 20 keV nitrogen.

(iii) Oxygen Bombardment: Backscattering spectra for a Surrey film on vitreous carbon are shown in Fig. 37 for an 'as deposited' film and after oxygen bombardment to a dose of $6.5 \times 10^{17}$ ions/cm$^2$ of 60 keV O$^\circ$. This represents $1.3 \times 10^{18}$ ions/cm$^2$ of 30 keV O$^+$ and is an extremely high dose bombardment.

The height of the tantalum peak has been reduced by more than a half but as in the nitrogen case the peak is not very much narrower than the unbombarded peak. The depth profiles for tantalum and oxygen concentrations, together with the background oxygen concentration in the unbombarded film, are plotted in Fig. 38. The profiles are corrected for $1/E^2$ dependence.
Fig. 37: Backscattering Spectra for Oxygen Bombardment of a 780 Å Surrey Film on Vitreous Carbon
Specimen VC5
60 keV $O_2^+$
$6.5 \times 10^{17}/cm^2$

![Graph showing depth profiles of Ta and O concentrations in 780Å Surrey Film](image)

Fig. 38: Depth Profiles of Ta and O Concentrations in 780Å Surrey Film
The counts under the different peaks are given in Table 3.8.

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>Counts in peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ta 'as deposited'</td>
<td>563,000</td>
</tr>
<tr>
<td>Background O</td>
<td>3,800</td>
</tr>
<tr>
<td>Ta bombarded</td>
<td>287,000</td>
</tr>
<tr>
<td>Total O</td>
<td>13,700</td>
</tr>
<tr>
<td>. . . 0 from implant</td>
<td>9,900</td>
</tr>
</tbody>
</table>

Table 3.8: Peak areas for an oxygen bombarded tantalum film

The peak areas of Table 3.8 can be used, as before, to calculate the film composition. From Equation 3 of Section 2.7 we can derive the relationship:

\[
\frac{Y_{Ta}}{Y_{O}} = \frac{N_{Ta}}{N_{O}} \times 124.5
\]

The density of the unimplanted film is 13.3 g/cm³ which gives an atomic density of 4.4 \times 10^{22} atoms/cm³ which is equivalent to 3.4 \times 10^{17} atoms/cm² for a film of 780 Å in thickness. The background level of oxygen in the film is therefore calculated from:

\[
N_{O} = 1.4 \times 10^{22} \times \frac{3.800}{563,000} \times 124.5
\]

\[
= 3.7 \times 10^{22} \text{ atoms/cm}^2
\]

\[
= 46 \text{ at%}
\]

After bombardment the tantalum peak is reduced to 287,000 counts, which is equivalent to 1.7 \times 10^{17} atoms/cm², from which the sputtering ratio is easily calculated to be 0.13 atoms per ion for 30keV O⁺ ions.
The total oxygen level after bombardment is $1 \times 10^{18} \text{ atoms/cm}^2$ of which about $7.2 \times 10^{17} \text{ atoms/cm}^2$ are due to the implant which suggests that about 55% of the implanted ions are retained in the film after a total ion dose of $1.3 \times 10^{18} \text{ ions/cm}^2$. 
4. ANALYSIS AND DISCUSSION OF RESULTS

4.1 Errors in Sputtering Yield Values

Error bars have not been drawn on any of the sputtering yield curves although it is evident from the spread in the results that quite large variations are involved. In fact the spread in results for gold varies from around ±12% for krypton sputtering to ±15% for argon and ±27% for neon. For gallium arsenide the spread in gallium results is ±17% for argon sputtering and ±14% for tellurium and the arsenic yields show spreads of around ±40% for sputtering by both argon and tellurium. These values are taken from the graphs and represent the variation from the central value of yield in each case.

Evaluation of sputtering yield involves making two sets of measurements. Firstly the number of ions striking the target must be known and secondly the number of atoms sputtered from the target must be measured.

(i) Measurement of Ion Dose: The ion dose is measured by integrating the beam current on target and the current integrator is accurate to better than 1% over the whole of the meter range. Possible sources of error are from any neutral component of the ion beam due to charge exchange after analysis and from inefficient suppression of the secondary electrons produced by ions striking the target surface. Measurements made by P. J. Cracknell (83), suggest that the neutral component represents less than 1% of the total ion beam for the vacuum conditions under which the present experiments were carried out. The design of the target assembly, which was described in Section 2.1, with its Faraday cup construction gives very good suppression of secondary electrons and any electrons which are not suppressed should be collected by the Faraday cup. The monitored beam current using this arrangement will be accurate to within 5%.

Another possible source of error concerns the design of the liquid nitrogen feed tubes to the hemispherical cooled section of the
collector. These tubes had to be split somewhere along their length so that the cooled section could be insulated from the feed-throughs which were grounded and the insulator arrangement had to be vacuum tight. The arrangement used consisted of anodised aluminium discs between flanges with an indium seal either side of each disc. Unfortunately the flange area, being very cold, proved to be a moisture trap and the collected water provided a leakage path across the insulators. The water was dried off as much as possible by heating the flanges with a blower and it was hoped that any remaining moisture, frozen by the addition of liquid nitrogen, would not introduce any appreciable error. The resistance between the cooled section and ground was checked before each run to make sure that it was high enough for the experiment to proceed but it is not known whether it ever changed during any of the experiments. Any error would have the effect of increasing the value of sputtering yield obtained but the size and frequency of any such errors are impossible to estimate.

(ii) Measurement of Sputtered Deposit: The sputtered deposits were measured by activation analysis at A.W.R.E. Aldermaston as described in Section 2.7. Gamma ray spectra were analysed using the Modified Covell method (75). This is a method which computes the total absorption peak areas of complex gamma ray spectra from a consideration of the peak half-widths and their baseline height to peak height ratios. A gamma ray peak is counted between limits such that it can be treated as a Gaussian curve except for the extreme left of the peak where a deviation occurs due, according to Heath (84), to Compton scattering. A correction function is applied to the extreme left hand side of the peak such that the tailing contribution from Compton scatter can be accurately described within the established limits. The modified Covell method gives very high precision for the evaluation of total absorption peak areas and is especially applicable to the situation where a small peak is sitting on a high background.

The number of counts from a collector is compared with the number of counts from a weighed standard in order to calculate the amount of sputtered material on the collector. The weight of the
standard is accurate to the precision of a microbalance which is several orders of magnitude better than the spread in results. If there are any systematic errors introduced by the method of peak area evaluation these errors will be greatly reduced, perhaps even eliminated, by the use of a standard since any error is common to the spectra from sample and standard.

The reproducibility of the method was checked, as described in Section 2.7, by irradiating three standards for GaAs and comparing the counts obtained. The spread in results was about 15% for gallium and about 8% for arsenic. These spreads represent the overall effects of statistical variations associated with counting, non-uniformity of neutron flux across a sample, differences in total dose which are not completely allowed for by the use of monitors and effects of small differences in counting geometries. Flux measurements which have been made in the various irradiation facilities of the Herald reactor (85) would suggest that the variation in flux across a one inch sample, which is about the size of a folded polythene collector, could be as much as 5%.

Another obvious source of error is the hole at the collector axis for the ion beam to pass through. It is evident that a fraction of the sputtered atoms passes through the hole and is not collected. This fraction is very small, however, and it is shown in Appendix 1 that it is in fact less than 1% of the total number of sputtered atoms.

The target chamber pressure during the sputtering experiments was around $3 \times 10^{-6}$ Torr. The pressure gauge was well removed from the cooled collector region, however, and so the pressure around the sample would be considerably lower than this.

A low pressure is important from two considerations. Firstly the mean free path of the sputtered atoms must be greater than the sample-collector separation in order that all sputtered particles reach the collector. Secondly the rate of adsorption of residual gas particles on the target surface must be low compared with the removal rate due to the ion beam so that the surface remains clean during sputtering. Obviously a contaminated surface will alter the sputtering yield of target atoms. The state of cleanliness of the
target surface is clearly a function of the system pressure, the ion beam current density and the sputtering yield. According to Pleshivtsev (86) a clean surface condition will be maintained providing that

$$6.25 \times 10^{18} j.S \gg 3.5 \times 10^{20} p.k$$

where, \( j \) = current density (A/cm²)
\( p \) = pressure (Torr)
\( S \) = sputtering coefficient (atoms/ion)
and \( k \) = sticking probability

$$3.5 \times 10^{20}$$ is the number of molecules of \( \text{N}_2 \) and \( \text{O}_2 \) incident on 1 cm² of a surface per second at a pressure of 1 Torr.

Taking a value of 10µA/cm² for \( j \) and assuming \( k \) to be unity, which is the worst case, the two sides of the expression are of very similar magnitude for the system pressure of \( 3.10^{-6} \)Torr. Since it is assumed that the pressure at the target is better than this then the expression is just satisfied. The experimental value of sputtering yield should be reduced if the target surface is covered with gas molecules and this has been verified by Almén and Bruce (10) and by Yonts et al. (87). Experimental results from the present study show generally greater values of yield than other experimental results which suggests that the effect of adsorbed molecules has not been a problem during this work. Some idea of the effect of the activation analysis results on the experimental spread of the sputtering yield curves can be obtained from a consideration of the gold results. It has been pointed out that the curve for neon sputtering showed a spread of ± 27% while the argon curve gave a corresponding value of ± 15% and krypton gave ± 12%. The collectors from which these results were produced had gold deposits of around 50 µg for neon sputtering, 150 µg for argon and 250 µg for krypton. All activated collectors were counted for 30 minutes irrespective of the amount of the deposit and the spread in results reflects the fact that the counting statistics are quite strongly dependent on the amount of deposit on a collector. The neon deposits are very low because the time for each sputtering experiment had to be kept to a reasonable length.
4.2 Sputtering of Gold

4.2.1 Energy Dependence: The three curves of energy dependence of the sputtering yield of gold for neon, argon and krypton bombardment (Figs. 11, 12 and 13) all show a decrease in yield with increasing energy. It is very noticeable however that the neon curve has the steepest gradient in terms of fractional change of yield with ion energy. The gradient of the krypton yield curve is the smallest of the three. The yields at 400 keV, when compared with those at 50 keV, show reductions of 25% for neon bombardment, 14% for argon and just 2% for krypton.

At low energies the predominant ion energy loss mechanism is by elastic collisions with target atoms. Each struck atom recoils and gives rise to a large number of high order recoils. Such recoil atoms have very low energy and can only be sputtered if they are originally located near the target surface. There are very many of these recoil atoms however and they account for a very large fraction of the sputtering yield. This low energy peak in the energy distribution of sputtered atoms is confirmed by the experimental results of Thompson (30) using a time of flight technique.

Lindhard et al. (33) used Thomas-Fermi theory to devise cross-sections governing ion-atom collisions in the keV region and showed that such cross-sections could be used to accurately predict ion ranges (81). The cross-section decreases with increase in ion energy such that the number of elastic collisions near to the target surface decreases with a consequent reduction in the number of atoms that are sputtered. The cross-section for inelastic collisions involving energy loss by the excitation of electrons associated with target atoms increases with ion energy in the keV region. It is usually assumed, as a rule of thumb, that the elastic and inelastic stopping power curves cross over at an energy of approximately \( M_1 \) keV, where \( M_1 \) is the atomic mass number of the ion.

Thus we can expect the region in which inelastic energy losses predominate to begin at around 20 keV for neon, 40 keV for argon and 80 keV for krypton which explains why the neon yield curve falls off more steeply than the other curves. Another contributing factor is the difference in the projected ranges for the three ions.
The ranges for 50 keV and 400 keV ions are shown in Table 4.1. The ranges are taken from LSS data compiled by Smith (88).

<table>
<thead>
<tr>
<th>Ion</th>
<th>$R_p$ (projected range) ($\text{Å}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>50 keV</td>
</tr>
<tr>
<td>Ne$^+$</td>
<td>250</td>
</tr>
<tr>
<td>Ar$^+$</td>
<td>160</td>
</tr>
<tr>
<td>Kr$^+$</td>
<td>100</td>
</tr>
</tbody>
</table>

Table 4.1: LSS Range Data for neon, argon and krypton ions in gold

The sputtering yield falls as the ion energy increases due to a greater fraction of the elastic collisions taking place deep inside the target where the displaced atoms cannot reach the surface. It is obvious from Table 4.1 that we would expect to see this effect to a greater extent in the neon case where 400 keV ions are penetrating to 1900 $\text{Å}$ than for argon ions and that the effect for krypton should be the smallest of the three.

The fact that the expected peaks in the curves are not seen is due to the large spread in yield values, as already pointed out. Reference to Figs. 14, 15 and 16 show that Sigmund's Theory predicts these peaks to occur at around 40 keV for neon ions, 75 keV for argon and 150 keV for krypton. This means that the neon peak is below the range of measurement and the argon peak is only just within this range. The fact that we might expect to see a peak in the krypton curve at 150 keV gives further explanation as to why the best straight line through the krypton results shows only a 2% reduction over the measured energy range.

For neon sputtering the experimental curve lies between the theoretical curves of Sigmund and Brandt and Laubert. Almén and Bruce (10) measured the yield for neon sputtering of gold at 45 keV and arrived at a value of 3.6 atoms per ion. EerNisse (89) found a value of 1.8 for 45 keV ions and Andersen and Bay (90) found values
of 3.5 for small doses and 2.4 for large doses, also using 45 keV ions. These values are shown below in Table 4.2 together with the yield measured during the present work and the values from theory.

<table>
<thead>
<tr>
<th></th>
<th>Present Work (50 keV)</th>
<th>Almén and Bruce</th>
<th>EerNisse</th>
<th>Andersen and Bay</th>
<th>Sigmund</th>
<th>Brandt and Laubert</th>
</tr>
</thead>
<tbody>
<tr>
<td>Small dose</td>
<td>4.9</td>
<td>3.6</td>
<td>1.8</td>
<td>3.5\textsubscript{1} and 2.4\textsubscript{2}</td>
<td>8.0</td>
<td>2.4</td>
</tr>
<tr>
<td>Large dose</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4.2: Values of Yield for Sputtering of gold by 45 keV neon ions

1: Small dose 2: Large dose

The same comparison for krypton ions is shown in Table 4.3.

<table>
<thead>
<tr>
<th></th>
<th>Present Work (50 keV)</th>
<th>Almén and Bruce</th>
<th>EerNisse</th>
<th>Andersen and Bay</th>
<th>Sigmund</th>
<th>Brandt and Laubert</th>
</tr>
</thead>
<tbody>
<tr>
<td>Small dose</td>
<td>5.4</td>
<td>24.5</td>
<td>17</td>
<td>37\textsubscript{1} and 25\textsubscript{2}</td>
<td>23</td>
<td>27</td>
</tr>
<tr>
<td>Large dose</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4.3: Values of Yield for Sputtering of gold by 45 keV krypton ions

1: Small dose 2: Large dose

For the argon case there is a greater quantity of experimental data and in addition to the results shown in Table 4.4 are the energy dependence curves due to Nenadovic et al. (91) and to Colombié (92) which are shown in Fig. 39.
Fig. 39: Comparison of Results of Argon Sputtering of Gold with Theory and other Experimental Results
<table>
<thead>
<tr>
<th>Present Work (50 keV)</th>
<th>19</th>
</tr>
</thead>
<tbody>
<tr>
<td>Almen and Bruce</td>
<td>10.2</td>
</tr>
<tr>
<td>EerNisse</td>
<td>5.8</td>
</tr>
<tr>
<td>Andersen and Bay</td>
<td>17.1 and 11.52</td>
</tr>
<tr>
<td>Sigmund</td>
<td>14.5</td>
</tr>
<tr>
<td>Brandt and Laubert</td>
<td>8.5</td>
</tr>
<tr>
<td>Colligon and Patel (38 keV)</td>
<td>12.3</td>
</tr>
</tbody>
</table>

Table 4.4: Values of Yield for Sputtering of gold by 45 keV argon ions

1: Small dose 2: Large dose

The 'small' and 'large' doses referred to in connection with the results of Andersen and Bay (90) are in the region of $10^{15}$ ions/cm$^2$ and $10^{17}$ ions/cm$^2$ respectively so the high dose results would be the appropriate ones to compare with the present experiments. The results of EerNisse (89) are based on ion doses of $1 - 5 \times 10^{15}$ ions/cm$^2$ which are low compared with the present work but the experiments of Almen and Bruce and of Nenadovic et al. are all for high dose ($>10^{17}$ ions/cm$^2$) sputtering.

The results show that the present work gives greater values of yield than any of the other experimental yields for neon, argon and krypton sputtering. In all the experimental results used for comparison the yield is calculated by measuring the weight loss of the target although Nenadovic et al. supported their results with a parallel measurement of collected deposits using spectrophotometry. The weight change due to implanted ions is allowed for but there is an error due to reflection of bombarding ions. This problem has been considered by Andersen and Bay (93) using reflection coefficients measured by Böttiger et al. (94) and they find that the error in $S$ is less than 1% in all cases where $S$ is greater than unity. Andersen and Bay use a term $m_1/m_2$ to correct for the mass of the incident ions where $m_1$ and $m_2$ are the atomic weights of the ion and the target material respectively. The term $m_1/m_2$ is added to their relationship for sputtering yield so it is quite unimportant if the ions are much lighter than the target atoms which is true of the situation under discussion.
It is quite likely that the yields measured in the present work are high due to the problem associated with insulation leakage which has already been discussed and there may also be a contribution due to neutral components. It was suggested in Section 4.1 that the neutral component is less than 1% (83) and this has been confirmed by more recent measurements carried out by Hemment (95) on the 600 keV ion implanter. Hemment measured a neutral component of around 0.4% for 50 keV argon ions at a base pressure of 8.10^-7 Torr. This figure rises to about 3% when nitrogen is leaked into the beam line to maintain a pressure of 1 x 10^-5 Torr. This figure is still very small but it represents the neutral component expressed as a fraction of the total beam current. All of the present experiments were carried out using a 3mm or 4mm aperture and the beam was scanned such that only a fraction of the total beam reached the target. In this situation any neutral component passing through the aperture may represent a very large fraction of the beam on target. In practice it was usually necessary to deflect the ion beam by the application of D.C. voltages to the X and Y scanning plates in order to see any target current which would suggest that the undeflected neutral beam was generally not aligned with the aperture. An examination for the presence of a secondary electron current while the ion beam was deflected away from the aperture would have shown if a neutral beam was reaching the target but this test was not carried out. Any neutral component will depend on the pressure in the beam line between the analysing magnet and the target chamber and on the position of the undeflected beam with respect to the aperture in front of the target. The effect is likely to be more important in the krypton case where the ion velocities are lower and the capture cross-sections for charge exchange correspondingly greater than for the other ions. Comparison with the results of Andersen and Bay (for large doses) shows that the krypton and argon yields obtained during the present work are greater by a factor of two whereas the neon yield is only 30% greater than that of Andersen and Bay.

It is noticed that Sigmund's Theory predicts a neon yield which is very much in excess of any of the experimental results and it is generally accepted that the reason for this overestimate is the absence of a surface correction term in the yield equation,
Sigmund's calculation of deposited energy distribution, $f(E, x)$, is based on the assumption of an infinite medium with an imaginary surface at $x = 0$. The yield therefore includes a contribution from reflected ions scattered more than once through the surfaces at $x = 0$. Experimentally, reflected ions do not contribute to the sputtering yield. Böttiger et al. (94) have estimated a theoretical correction term and shown that it is very important for large $M_2/M_1$ and low ion energies which is where Sigmund's neon curve is seen to deviate most from the experimental curve. Thus the $\alpha(M_2/M_1)$ term is too high under such circumstances.

For argon and krypton sputtering of gold Sigmund's Theory is in very good agreement with the experimental results of other workers shown in Tables 4.3 and 4.4. For argon sputtering Sigmund's value is slightly greater than most of the experimental ones while for krypton sputtering his value is slightly smaller than the experimental values. It can be shown from results of yields measured by Almén and Bruce (10) and by Andersen and Bay (90, 93) that the increase in yield with $Z_1$ is faster than is expected from Sigmund's theory. Fig. 40 is reproduced from Andersen and Bay (90) and shows their experimental measurements of sputtering yield as a function of $Z_1$. Measurements due to Almén and Bruce (10) and the theoretical function due to Sigmund (31) are also shown. The sputtering yields are normalised to the yield for argon ions. Thus Fig. 40 illustrates why Sigmund's theory gives high yields for argon sputtering and low yields for krypton sputtering. Sigmund (31) compared his theoretical yield curves with many experimental results and noticed that heavy ions gave more pronounced maxima in the energy dependence of sputtering yield than does the nuclear stopping power $S_n(E)$ on which Sigmund's theory and that of Brandt and Laubert are based. Sigmund suggests that the discrepancy is due to thermal spikes produced in the dense collision cascades resulting from heavy ion bombardment. The presence of thermal spikes was put forward by Thompson and Nelson (24) as an explanation of a peak at very low energy in the energy spectra of sputtered atoms from gold.

\[
S = \lambda \frac{S_n(E)\alpha(M_2/M_1)}{\mu_0}
\]
Fig. 40: Sputtering Yields of gold for different 45 keV ions, normalised to the yield for argon ions.
Thermal effects have been investigated by Andersen and Bay (90, 93, 96) using molecular beams to enhance the energy density of the cascade. The molecules dissociate on entering the target and each atom produces single collision cascades but overlapping is bound to occur. If sputtering is a linear function of energy density then this experiment should give the same sputtering yield per atom for atomic and molecular ions having the same energy per atom. The ratios of yield per atom for molecular ions to yield for atomic ions measured by Andersen and Bay are shown in Table 4.5 and they show quite clearly that the sputtering process becomes progressively more non-linear with increasing $Z_1$.

<table>
<thead>
<tr>
<th>Projectile</th>
<th>Target</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl - Cl$_2$</td>
<td>Si</td>
</tr>
<tr>
<td>Se - Se$_2$</td>
<td>Ag</td>
</tr>
<tr>
<td>Te - Te$_2$</td>
<td>Au</td>
</tr>
</tbody>
</table>

Table 4.5: Ratio of Sputtering Yield per atom for molecular ions to yield for atomic ions. Andersen and Bay (90, 93, 96).

Sigmund explains this non-linear feature of the sputtering yield in terms of a breakdown of the transport theory used to derive the yield. Within the cascade the energy distribution of moving atoms is approximately proportional to $E^{-2}$ (see Sigmund (31)). Moving atoms distribute their energy by collisions with stationary partners. When the cascade reaches a certain density this process must breakdown since there will be more moving atoms than stationary partners. At this point the moving atoms will be unable to distribute their energy to produce lower energy recoils and therefore a hump will be seen in the energy distribution curve. If this energy at the surface exceeds the binding energy then an enhancement in the sputtering yield is seen. Energy transport away from the dense cascade region is better described in terms of gas heat conduction than linear transport and hence the region is known as a thermal spike.
4.2.2 Dose Dependence: The values of sputtering yield plotted in Figs. 17 and 18 for 100 keV argon bombardment suggest that the yield increases with ion dose, at least up to a dose of around $5 \times 10^{17}$ ions/cm². The points of Fig. 17 which represent incremental values of yield, as explained in Section 3.1.2 have a very large spread and in particular the point at $3 \times 10^{17}$ ions/cm² is very high compared with the other points. The points of Fig. 18 are based on the aggregate ion dose at each point, however, and therefore give rise to a smoother form. If a curve were drawn through the points of Fig. 18 it would show the yield increasing from around 19 atoms/ion for a dose of $5 \times 10^{16}$ ions/cm² to around 23 atoms/ion for a dose of $5 \times 10^{17}$ ions/cm². The yield then appears to decrease to around 21 atoms per ion for a dose of $1.1 \times 10^{18}$ ions/cm². The shape of any curve through Fig. 18 is of course greatly influenced by the high value of yield measured at $3 \times 10^{17}$ ions/cm². If a lower value were substituted, say 20 atoms/ion, which is of similar magnitude to the first three points then the shape of the aggregate curve would show an increase from the initial value of 19 atoms/ion to a saturation value of around 21 atoms per ion after a dose of about $7 \times 10^{17}$ ions/cm². It is believed that the latter is closer to the actual situation. The change in yield therefore appears to be quite small (~10%) over the dose range $5 \times 10^{16}$ ions/cm² to $10^{18}$ ions/cm². This is reassuring from the point of view of the energy dependence measurements since these involved repeated bombardments at increasing energy into the same sample. Such measurements therefore unavoidably involve dose effects, particularly if dose effects are due to surface changes.

Several workers have measured dose dependence of sputtering yield. EerNisse (89) measured an increase in yield for sputtering of gold by 45 keV argon ions from a value of 5.8 atoms/ion for a dose of $1 \times 10^{15}$ ions/cm² up to 7.2 atoms/ion for a dose of $2 \times 10^{16}$ ions/cm². Andersen and Bay (90), however, found that the yield decreased from 17 atoms/ion for $10^{14}$ ions/cm² to 11.5 atoms/ion for $10^{17}$ ions/cm². The Andersen and Bay result was also for 45 keV argon sputtering of gold. EerNisse explains these different findings in terms of the initial target surface topography. He used shiny, etched gold foils (as did the present study) whereas Andersen and Bay used thin films of gold deposited on unpolished quartz discs.
Examination of Sigmund's equation for back-sputtering yield for perpendicular incidence,

\[ S = \frac{\lambda S_n (E_1, Z_1, Z_2)}{U_o} \]

suggests that the yield will change as a result of a change in \( S_n \) or \( U_o \). Andersen (97) points out that we can only expect a significant change in \( S_n \), the nuclear stopping power, in a situation where the sputtering yield is very low and the equilibrium concentration of projectile atoms consequently very high. In most cases dose effects will be as a result of a change in \( U_o \). A change in \( U_o \) may be caused by changes in the electronic structure or in surface topography.

If the projectile atoms do not diffuse or precipitate then a saturation must be reached after which the sputtering yield should remain constant. Experiments by Whitton et al. (98) and Carter et al. (99) resulted in a model which suggests that saturation occurs when the incident ion dose has been sufficient to sputter a depth equal to a maximum ion range. They assume this range to be where the stopping probability is 10 per cent of that at \( R_p \), the projected range. This occurs at a distance of around \( R_p + 2\Delta R_p \) where \( \Delta R_p \) is the standard deviation of the Gaussian range profile. This gives a value of ion dose,

\[ D = \frac{n(R_p + 2\Delta R_p)}{S_t} \]

where \( n = \) target atomic density

\( S_t = \) target sputtering coefficient

For 100 keV sputtering of gold this represents a dose of \( 2.7 \times 10^{16} \) ions/cm\(^2\) if the measured sputtering yield of 19 atoms per ion is used or \( 3.1 \times 10^{16} \) ions/cm\(^2\) if Sigmund's theoretical value of yield is used. It is evident therefore that any saturation in the value of sputtering yield due to an equilibrium concentration of implanted ions should occur after a value of dose below the range of measurement of the present experiment.
It is more likely that the change in yield observed is a result of surface topography changes with high dose bombardment. Plates 1 and 2 in Section 3.1.2 show the effect of ion bombardment on the gold surface. In particular the sputtering yield from the steep sides of the cones which develop on the surface would be enhanced by the lower angle of incidence of the ion beam. Fig. 5 of Section 1.5 shows the angular dependence of sputtering yield measured by Molchanov et al. (17), Roi et al. (18) and Wehner (19). One would expect to see an appreciable number of ions reflected due to low angle incidence on the cone faces (17) but these ions may in turn be incident on a flatter part of the target surface at an angle smaller than 90° so giving rise to a higher sputtering yield.

Any diffusion of defects during bombardment may give rise to dislocation networks as a result of defects migrating to preferential sinks such as grain boundaries. Nelson and Mazey (100) have pointed out that the production of such dislocation networks will affect surface topography and this is another possible explanation for the increase in yield, although perhaps the most probable cause of the surface roughening in this case is differential sputtering between grains as a result of varying orientation as pointed out by Hofer (44).

Colligon and Patel (101) suggest the possibility of a change in $U_0$ due to the interaction of gas-defect agglomerates, such as bubbles, with the receding target surface. These agglomerates would be produced by diffusion of defects and would be expected to saturate in size and density after a certain ion dose but this dose may be greater than that predicted by Carter et al. (99) for a saturation concentration of isolated, immobile argon atoms.

Colligon and Patel (101) observed an oscillatory dose dependence of sputtering yield of gold for argon bombardment. They used increments of dose of around $5 \times 10^{15}$ ions/cm$^2$ and $2 \times 10^{16}$ ions/cm$^2$ which are very much lower than the increments used in the present experiment but their average yield over the same range of dose also showed a slight increase. They also used polycrystalline foil targets similar to those used in the present study.
The dose dependence of yield was also examined by looking at the energy dependence as a function of decreasing energy as explained in Section 2.5.2. Fig. 19 shows the result of this experiment together with the points taken from Fig. 12 for increasing energy.

Successive bombardments for the increasing energy dependence experiment are into virgin material whereas for decreasing energy dependence they are into material which has already been bombarded. Thus any dose dependence effects should be evident if the two curves are compared.

From Fig. 19 it is seen that the points for decreasing energy show slightly lower values of yield and if a line were drawn through them it would be slightly steeper than a line drawn through the points for increasing energy. Within the limits of the spread in the experimental points, however, it is obviously not possible to show that there is a difference between the two sets of results.

We could expect to see a difference if the yield was affected by an increasing concentration of implanted ions within the target but it has been shown that the ion doses used during the present work are greater than those usually associated with such effects. The apparent small increase in yield shown by Figs. 17 and 18 has been explained in terms of a change in surface topography possibly associated with dislocation networks at the surface. These factors will apply equally to the increasing energy and decreasing energy curves and we can therefore predict that the two curves should be identical. The comparison shown in Fig. 19 is therefore in very reasonable agreement with theory.

4.2.3 Sticking Efficiency: The sticking efficiency was calculated from the gold deposit measured on secondary collectors as explained in Sections 2.5 and 3.1.3. Measurements were made over several bombardments for each secondary collector so that a reasonable deposit of gold was collected. The assumption was made that any gold atoms reflected from the main collector would be collected by the secondary collector. Fig. 7 of Section 2.1 illustrates that sputtered atoms are completely enclosed by the arrangement of main collector and secondary collector so the above assumption would seem to be a reasonable one.
The estimated value of sticking efficiency is 96% which suggests that the hemispherical form of collector is a very effective one. Nenadovic and co-workers (91, 102) measured sputtering yields for argon and xenon bombardment of gold from target weight loss measurements and by measurement of the deposit on hemispherical, glass collectors. They found that the yields calculated from sputtered deposits were up to 5% lower than those calculated from target weight loss and they explained the discrepancy in terms of a sticking efficiency less than unity. Their result is therefore in very good agreement with the present work which gives an estimate of 4% of sputtered atoms being reflected. The polythene collectors used in the present study were cooled by liquid nitrogen which should improve sticking efficiency, particularly for very low energy atoms, and this may explain the apparently slightly better efficiency.
Sputtering yields of gold have been measured for neon, argon and krypton ions in the energy range of 50 - 450 keV. Values of yield were found to be greater than those measured by several other workers. This is probably partly due to the fact that the ion doses used in the present work were high compared with those of other workers but it is believed that the yields may have been slightly overestimated during the present work due to current integration errors associated with insulation leakage and a neutral component in the ion beam.

The experimental points showed large spreads, probably as a result of the above errors, such that the energy dependence results were plotted as best straight line fits. The neon line showed the greatest fall off in yield with increasing energy and the krypton line the least fall off which is in agreement with what is expected from theory.

Comparison of the results with Sigmund's theoretical yield curves suggests that Sigmund's theory overestimates the yield for neon sputtering due, it is believed, to the absence of a surface correction term in the yield equation. The theory underestimates the yield for krypton sputtering due to a thermal spike contribution to the yield. The theory of Brandt and Laubert, which expresses sputtering yield in terms of the nuclear stopping power, has been shown to give a useful indication of the yield as a function of ion energy.

A small increase was seen in the sputtering yield of gold as a function of ion dose over the region of about $10^{17}$ ions/cm$^2$ to $10^{18}$ ions/cm$^2$. It was shown that the ion doses involved were far greater than those required to produce saturation concentrations of the implanted species and the yield increase was explained in terms of a change in surface topography probably associated with the formation of dislocation networks at the target surface and differential sputtering between grains of different orientation.

The sticking efficiency for gold atoms striking the polythene collectors was estimated by using secondary collectors in the target plane and was found to be around 96%.
4.3 Sputtering of Gallium Arsenide

4.3.1 Energy Dependence: The variation of sputtering yield with energy for gallium arsenide is shown in Figs. 20 and 21 for argon bombardment and in Fig. 22 for tellurium bombardment. The spread in results again necessitates the drawing of a best straight line through each set of points and these lines show the same trend as the gold results in that the yield is seen to decrease slowly with increasing energy.

Perhaps the most striking feature of the three sets of yield curves is the fact that the measured gallium yield shows a value greater than that of arsenic by a factor of 2 to 3 depending on which yield curves are looked at. Another surprising feature is the higher value of yields measured in Fig. 21 using a 4 mm aperture as explained in Section 3.2.1.

It it believed that the lower measured value of arsenic yield is due to inefficient collection of arsenic atoms and this will be discussed in the next section. For this reason the 'Experimental' yield curves referred to in Fig. 41 are plotted as twice the measured gallium yield in the belief that this gives a more accurate representation of experimental yield. Fig. 41 shows a comparison of experimental yields for energy dependence for argon and tellurium ions with the theoretical yields given by Sigmund for argon and tellurium sputtering of germanium. Germanium is used because its mass lies between those of gallium and arsenic and because it is very similar in density. Unfortunately the comparison is not a very convincing one since the theoretical germanium yields are considerably greater than the gallium arsenide yields. The large difference in yields is probably due to the ionic bonding contribution in gallium arsenide giving rise to a higher value of $U_o$.

The theoretical curves of Fig. 41 should be more reliable in their predictions of the energy for maximum yield. Thus one might expect a maximum in the sputtering yield for argon ions at an energy of around 40 keV and in the yield for tellurium ions at around 220 keV.

The measured values of total sputtering yield based on twice the gallium yield are seen to be around 3.2 atoms per ion at 50 keV.
Fig. 41: Comparison of Experimental Sputtering Yields for GaAs (plotted as twice the gallium yield) with Sigmund's theoretical yields for sputtering of Ge.
decreasing to around 2.6 atoms per ion at 400 keV for argon sputtering and for tellurium sputtering we have values of around 8.8 atoms per ion at 50 keV and 7.6 atoms per ion at 350 keV. Comas et al. (103) have estimated the sputtering yield for GaAs in the energy range 20 to 100 keV by masking their samples and measuring step heights after bombardment with argon ions. They found the yield to be around 6 atoms per ion for 50 keV argon and 1.5 atoms per ion for 100 keV ions. Pearmain and Unvala (104) obtained a value of around 4 atoms per ion for sputtering by 12 keV argon ions incident at 60° to the target normal. This angle of incidence would of course be expected to give a higher value of yield than for normally incident ions. The above results show yields which are similar in magnitude to those of the present study although the work of Comas et al. shows a much more rapid decrease in yield with energy beyond a peak value of around 6.4 atoms per ion at an energy of 40 keV.

The higher values of sputtering yield shown in Fig. 21 are believed to be the result of a neutral component in the ion beam striking the target. It was pointed out in the preceding section (4.2) that the neutral component may represent a large fraction of the beam on target as a result of the scanning method used. The fact that the higher measurements were not reproduced during a subsequent series of bombardments would suggest that the beam alignment was not so good on the latter occasion. The general practice was to adjust the D.C. bias on the X and Y plates for maximum current on target but it was not felt necessary at the time to record these bias settings. It is not therefore possible to correlate low bias voltages with high sputtering yields but it is believed that this theory offers the best explanation for the difference in yield values. The use of a 4 mm aperture would increase the probability of the undeflected beam reaching the target although it does not explain why the ratio of gallium yield to arsenic yield is apparently lower than that given by the results of Fig. 20.
4.3.2 Dose Dependence: The results of measurements of the dose dependence of the sputtering yield of gallium arsenide for argon ion bombardment are plotted in Figs. 23 and 24. They suggest a slight increase in yield up to a dose of between $10^{18}$ and $2 \times 10^{18}$ ions/cm$^2$ after which the yield appears to remain constant up to the limit of the measured range ($3 \times 10^{18}$ ions/cm$^2$). The behaviour is therefore very similar to that observed for argon bombardment of gold and can be explained in the same way by a gradual change in surface topography. Plate 3 in Section 3.2.2 shows the effect of high dose bombardment on the gallium arsenide surface which has the appearance of a network of craters. These craters are probably the result of the process discussed in relation to the gold results whereby gas bubbles or dislocation networks interact with the receding target surface.

It has already been pointed out in Section 3.2.2 that the dose dependence experiments belonged to the higher yield batch of experiments which resulted from using a 4 mm aperture to define the beam. The yields show the same discrepancy between the individual gallium and arsenic yields however and the gallium yield appears to be consistently greater than the arsenic yield over the whole of the dose range studied. Such differences in sputtering yield between the different species of binary targets have been reported, mainly in connection with the bombardment of alloys. Gillam (6) reported an altered surface layer of several atomic layers for noble gas bombardments of Cu$_3$Au. The surface initially became gold rich but subsequent bombardment sputtered three copper atoms to every gold atom. Wehner (105) sputtered nickel based alloys and steels and measured yields which reflected the stoichiometry of the starting material of the target.

It is generally agreed that stoichiometric sputtering takes place after a certain ion dose during which the relative surface concentrations of the component species are adjusted. The surface becomes richer in the low yield component. Experiments by Liau et al. (106) on several binary alloys showed that the surface was generally enriched in the heavier component to a depth corresponding approximately to the range of the sputtering ion. Since it is known that most of the sputtered atoms originate from the first few atomic layers it is apparent that radiation enhanced diffusion must contribute to the enrichment mechanism. The fact that the depth of the altered layer
corresponds closely to the ion range implies that the diffusion process is assisted by the defects produced within the collision cascade. Liau et al. observed that the steady state surface composition was independent of the ion mass which argues against better mass match and hence more efficient energy transfer as a mechanism giving rise to preferential sputtering of the lighter target species. Instead they point out that even with equal energy partition, the lighter component will suffer less energy loss and will have a better chance of escaping from the surface. The lighter component will therefore be sputtered from a greater depth than the heavier component.

Using the above argument it is clear that we would not expect to see any appreciable degree of preferential sputtering in the case of gallium arsenide in which the two components are almost equal in mass. Liau et al. sputtered samples of InP, GaP and GeSi and found no evidence of enrichment in any of the three materials even though they do not represent systems with equal mass components. They suggest that the amorphous layer produced during ion bombardment of semiconductors may greatly diminish diffusion and restrict the altered depth to a few atomic layers which would make it undetectable to the backscattering technique used for their measurements.

Comas et al. (103), however, looked at argon implanted gallium arsenide using Auger electron spectroscopy combined with sputter etching with a 2 keV argon beam and observed appreciable changes in stoichiometry at the sample surfaces. They measured changes of around 10% in the Ga and As signals and found an altered depth which was energy dependent and which was of the order of 30% greater than the projected range of the implanted ions. The changes observed by Comas et al., however, were in the form of a gallium enrichment at the surface which rather conflicts with the higher sputtering yield observed for gallium during the present work. Comas et al. noticed that the Ga/As signal ratio was dependent on their sputter-etch beam intensity and suggest that the implant-induced damage may be affecting the Auger lineshape rather than the sputtering yield ratio.
4.3.3 Surface Stoichiometry: Measurements of surface stoichiometry of bombarded and unbombarded gallium arsenide surfaces failed to show any change due to sputtering. The measurement techniques used were rather unsatisfactory however and do not prove that there was no change.

In the case of the ESCA measurements the analysis depth is of the order of $100\AA$ and no change was seen when photoelectron peaks and auger peaks were compared for bombarded and unbombarded samples. There could of course be a surface enrichment which is confined to a few atomic layers as suggested by Liau et al. and this would not be seen by the ESCA technique but there was certainly no evidence of the quite large changes seen by Comas et al. even after the same process of argon sputter-etching of the target samples.

The Rutherford backscattering technique does not satisfactorily resolve the gallium and arsenic contributions and although the two components can be identified in the spectrum shown in Fig. 27 for an unbombarded sample this was not the case for bombarded samples. It is probable that the surface roughness of the bombarded targets was the cause of a degradation in resolution.

If it is assumed that there is no surface enrichment of arsenic then in order for the gallium yield to remain higher than the arsenic yield there must be a process of in-diffusion of arsenic or out-diffusion of gallium and such a diffusion process will be sensitive to target temperature.

4.3.4 Low Temperature Sputtering: This particular experiment was restricted in length and was troubled by technical problems as was explained in Section 3.2.4. However a gallium arsenide target was bombarded to a total dose of around $10^{18}$ ions/cm$^2$ with 50 keV argon in five steps of $2 \times 10^{17}$ ions/cm$^2$. The target was maintained at or near to liquid nitrogen temperature (77°K) during the bombardments and the target current was low enough ($\sim 0.3 \mu A$) that there would be no beam heating of the target.

The results, which are shown in Table 3.2, give values of the gallium yield to arsenic yield ratio which compare very favourably with those for room temperature measurements and within the spread in
results there is no evidence of a trend towards a reduction in the ratio which has an average value of 2.1:1.

4.3.5 Elevated Temperature Sputtering: These experiments were carried out primarily in order to investigate the production of spot patterns. Spot patterns were discussed in Sections 1.7 and 2.6.4 when it was pointed out that a semiconductor target needed to be heated during bombardment in order that the surface region was maintained in a crystalline state. The experiment was discontinued when it was realised that it was not possible to produce visible deposits on the polythene collectors within a reasonable period of bombardment time.

Fig. 26 of Section 3.2.5 shows a sketch of the only visible ejection pattern produced and this was the result of a bombardment lasting for four and a half hours. The pattern is seen to be displaced with respect to the collector axis and this is obviously a result of the crystal orientation (which was (110)) being slightly out of alignment with the ion beam.

The pattern is approximately square and is similar to the square patterns observed by MacDonald (69) for argon sputtering of germanium single crystals. MacDonald observed separate spots at lower doses (\( \sim 2 \times 10^{16} \) ions/cm\(^2\)) and these spots overlapped to become square in form for high dose (\( \sim 10^{17} \) ions/cm\(^2\)) bombardment. The bombardment dose used to produce the pattern of Fig. 26 was \( 2 \times 10^{18} \) ions/cm\(^2\) which is probably why we do not see separate spots.

Table 3.4 of Section 3.2.5 lists the sputtering yields measured for three samples bombarded at different temperatures. The 100°C sample gives a gallium yield of 1.1 and an arsenic yield of 0.2 but the 200°C and 300°C samples give very similar results with values of 0.5 for gallium and 0.25 for arsenic at 200°C and 0.6 for gallium and 0.3 for arsenic at 300°C. The ratio of gallium yield to arsenic yield for the latter two results is 2:1 which is the same as the ratio for room temperature and low temperature bombardments. The values of yield are lower for the high temperature results but there was a certain amount of leakage from the heater power supply which contributed counts to the scaler measuring the integrated beam current. Allowance was made for these extra counts but if insufficient
allowance was made then lower estimates of yield would be produced.

It is also possible that the gallium arsenide sputtering yield is reduced as a result of the increased target temperature. Almén and Bruce (10) observed decreases in yield for Ni and Pt targets in the range 200°C - 600°C. They related this to annealing of target lattice damage during bombardment such that the incident ions never strike a highly damaged region. The same process may well apply to gallium arsenide targets. It is interesting that the 100°C result of Table 3.4 shows a value of gallium yield of 1.1 atoms/ion which is similar to the room temperature value of 1.5 atoms/ion for 200 keV argon. The lower values of yield in Table 3.4 are for target temperatures of 200°C and 300°C and the critical temperature for gallium arsenide, above which it remains crystalline during bombardment, is around 150°C (107). Thus the higher yield value for sputtering from an amorphous surface and the two lower values are for sputtering from crystalline surfaces. The very low value of arsenic yield for the 100°C sample throws some doubt on the validity of this particular result and there are only three results anyway but it appears probable that the sputtering yield is lower from a crystalline surface than it is from an amorphous surface. This can be explained in terms of a fraction of the ion beam becoming channelled in the crystalline target with no contribution to sputtering.

The measured gallium yield has been seen to exceed the measured arsenic yield by a factor of 2 to 3 using a 3 mm beam defining aperture and around 1.5 using a 4 mm aperture. This ratio is independent of ion dose over the measured range of $2 \times 10^{17}$ ions/cm$^2$ to $3 \times 10^{18}$ ions/cm$^2$ and is apparently independent of target temperature over the range of 77°C to 573°C. If a straightforward diffusion process is postulated with a temperature dependence of the form,

$$\exp \left( -\frac{1}{T} \right)$$

then the temperature range 77°C to 573°C would only affect the diffusion rate by 1%. Any diffusion process would, however, almost certainly be influenced by the large number of bombardment produced traps and defects and one would expect to see transitions in diffusion
behaviour, particularly above about 150°C, the critical temperature above which the gallium arsenide surface remains crystalline during ion bombardment.

In spite of the apparently higher gallium sputtering rate there does not seem to be any deviation from stoichiometry at the gallium arsenide surface, unless it is confined to the first few atomic layers such that it is not detectable by ESCA.

4.3.6 Sticking Efficiency: Results of the measurement of sticking efficiency for sputtered gallium and arsenic atoms were given in Section 3.2.3. The results are based on the assumption that any atom which does not stick to the main collector will strike the second collector and stick to it. Values of sticking efficiency were therefore expressed as the ratio of the amount of sputtered material collected at the main collector to the total amount of material on both main and secondary collectors.

The estimated values of sticking efficiency were 90% for gallium atoms and 92% for arsenic atoms.

The above assumption that any atom not sticking to the main collector will stick to the secondary collector seems reasonable since the geometry of the collector target region means that the sputtered atoms are completely surrounded by collector surfaces except for the target region and the hole in the main collector through which the ion beam passes. This hole has been discussed earlier in Section 4.1 and is shown in Appendix 1 to lead to an error in measured sputtering yield of less than 1% so it is unlikely to affect the measurement of sticking efficiency.

A closer consideration of the situation suggests, however, that the measurement of sticking efficiency is valid only if the efficiency is high. Thus if 90% of atoms stick to the main collector then hopefully 9% stick to the secondary collector. If the secondary collector only collects 50% of the atoms striking it then a value of sticking efficiency of 95% will be calculated. Thus the estimate is too high but the error is only 5½%.
If we now consider a situation where only 50% of the atoms stick to the main collector and the efficiency at the secondary collector is much worse, say 10% then we would estimate a value of 91% for the sticking efficiency and the error this time is 82%. Thus the estimated value of 92% for arsenic atoms may be a great overestimate of the real situation.

The sputtering of gallium arsenide has so far been assumed to be a process whereby single atoms, mostly neutrally charged, are ejected by a collision process. The work of Koval et al. (108, 109), however, suggests that this is not the case. They studied luminescence spectra and mass spectra of charged and neutral particles ejected from single crystal gallium arsenide by argon bombardment. Neutral particles were ionised by an electron beam prior to mass analysis. Koval et al. measured secondary ions in the mass range of 12 to 359 a.m.u. The secondary ions were made up of target particles and compounds and complexes comprising residual gases. Their main observations however were that gallium was detected as Ga⁺ (≈ 90%) and Ga₂⁺ (≈ 10%) and that the As⁺ line intensity is more than two orders of magnitude smaller than that of the Ga⁺. It was found that the neutral particles consisted of As, As₂, As₃, As₄ and GaAs. No gallium atoms or molecules were found in the mass spectrum of neutrals.

Koval et al. (108) found that about 50% of the arsenic was detected as As₂ and 25% as As₄, both of which will have generally lower velocities than those of As neutrals which made up about 25% of the total arsenic yield and of Ga⁺ ions. This would suggest that the sticking efficiency might be lower for arsenic than it is for gallium. It is fairly well documented as a result of molecular beam growth studies on gallium arsenide by several workers such as Arthur (110) and Foxon and Joyce (111, 112) that the sticking coefficients of As₂ and As₄ at gallium arsenide surfaces are very low and sometimes zero. The arsenic molecules only stick in appreciable numbers under certain conditions:

(i) In the presence of a flux of gallium atoms impinging on the gallium arsenide surface together with the arsenic.
(ii) After the surface has had a nominal monolayer (∼10^{15} atoms) of gallium deposited.

(iii) When the surface is held at a temperature above 775\textdegree K.

The same studies (110-112) also showed that the sticking coefficient of gallium on gallium arsenide was unity below a substrate temperature of 750\textdegree K.

It is of course not possible to conclude that the above applies equally to the sticking of sputtered gallium and arsenic to polythene surfaces at liquid nitrogen temperature but it would seem to be a probable explanation of the difference in the measured yields. Arsenic is very volatile and it would be reasonable to assume that reflected atoms and molecules of arsenic are removed along with gas molecules by the diffusion pump below the target chamber.

The experiment described in Sections 2.6.5 and 3.2.3 using polythene collectors coated with a layer of around 100Å of evaporated nickel was carried out in the hope that the sticking coefficient of arsenic would be better on a nickel surface and a different yield ratio would be seen. Nickel was chosen because it does not produce any competing reactions during activation analysis which would interfere with the counting process.

The values of yield measured are shown in Table 3.1 of Section 3.2.3. They are in the range of 2.0 to 2.7 for gallium and 1.0 to 1.6 for arsenic which are high values similar to the yields measured with the 4 mm aperture. The ratios of gallium yield to arsenic yield are in the range 1.7 to 2.0 with average values of 1.9 for 200 keV argon and 1.8 for 300 keV argon. These ratios are in the same range as the ratios for polythene collectors and do not therefore add any further information towards an explanation of the results.

Routine weighing of targets before and after bombardment was not carried out but such an attempt was made with about half a dozen samples. Unfortunately no useful results were obtained, presumably
because of handling problems. The samples were clipped in a vertical position on the target chamber by a spring clip which was made quite strong after one or two samples had fallen out during the lifting and lowering of the target assembly. It was noticed that the clip tended to chip the edges of the targets which is no doubt the reason why no information was obtained from the weighing experiments. The total deposit on a typical collector was of the order of 10 μg so it is required to measure to about 3 μg in order to show whether or not gallium and arsenic are ejected in equal amounts. This suggests that a method of weighing in situ, such as the quartz resonator technique used by Andersen and Bay (90) and EerNisse (89), is essential if reproducible results are to be obtained in order for comparisons to be made with deposits measured on the collectors.
SUMMARY

Sputtering yields of gallium arsenide have been measured for 50 - 400 keV argon ions and for 50 - 350 keV tellurium ions. The most striking feature of the results was the apparently higher value of yield of gallium compared with arsenic throughout all the experiments.

After an examination of surface stoichiometry, sputtering of targets at low and elevated temperatures and the use of nickel coated collectors it was decided that the reason for the apparent difference in yield was the low sticking efficiency for arsenic particles striking the collector surfaces and that gallium and arsenic are in fact sputtered in stoichiometric proportions.

The sputtering yield was seen to show a similar fall off with increasing ion energy to that seen for gold and the yield was also seen to increase slightly with ion dose in the $10^{17} - 10^{18}$ ions/cm$^2$ region in the same way as for gold.

From the results for sputtering at elevated temperatures there is some suggestion that the yield is lower for targets maintained above $T_c$ ($\approx 150^\circ$C) due, probably, to a fraction of the ion beam becoming channelled. A square ejection pattern was observed on the collector surface for a target bombarded at $200^\circ$C with $2 \times 10^{18}$ ions/cm$^2$ of 100 keV argon.

Measurement of sticking efficiency using secondary collectors has been shown to be valid only when the sticking efficiency is very high.
4.4 Tantalum Films

4.4.1 Unimplanted Films: Unimplanted films were examined by Rutherford backscattering analysis to investigate their uniformity of thickness and purity. The Ultra films and the University of Surrey films were found to have excellent uniformity in that no difference in width of the tantalum peak was observable in any of the backscattering spectra taken at different points across a film.

The energy resolution of the detector and multichannel analyser system was measured and found to be $18$ keV. The resolution was defined as the F.W.H.M. of the peak for a very thin gold film ($\sim 10\AA$) evaporated on to an aluminium substrate. Comparison of the relative positions of the gold peak and the aluminium edge in the spectrum gives the energy scale of the system. A resolution of $18$ keV corresponds to a depth resolution of about $150\AA$ for the tantalum films. The effect of this resolution is seen from the sloping edges of the tantalum peaks which would otherwise be vertical. In spite of this $150\AA$ resolution, however, the width of the tantalum peak (F.W.H.M.) was found to be constant within a single channel for the same film measured on several different occasions over a period of several weeks and is therefore a very precise and sensitive indication of any change in film thickness since one channel corresponds to about $30\AA$.

The uniformity of thickness across a film is obviously very important from the point of view of producing resistors with reproducible and consistent qualities.

Attempts to produce a film with small or zero TCR will involve a modification of the film properties, chemically or physically, as a result of the deposition process or of subsequent ion implantation but the thickness of the film will still be very important and will have a strong influence on the conduction processes. As the film thickness is increased the conduction process becomes more metallic and approaches that of the bulk material. Any fine balance of positive and negative TCR's therefore will always depend on film thickness and uniform thickness is important for homogeneous electrical behaviour.

The purity of the starting film is also very important with respect to the electrical performance. Tantalum is very reactive and
is very difficult to deposit as the pure metal. Any impurities in the deposition equipment such as adsorbed oxygen and residual hydrocarbons are inevitably incorporated into the film during growth.

It is seen from the results that the Ultra films which were deposited by argon sputtering show the higher purity levels but the oxygen level is very high with a value of about 15\% throughout the film which rises to about 20\% at the substrate interface and 40\% at the surface. The Ultra films were very consistent, however, which is a fundamental requirement of films to be used for device production. The level of oxygen throughout the Ultra films is somewhat higher at 15\%, than the 5\% reported by Wilcox and Westwood (113) for sputtered tantalum films having a b.c.c. structure which is the structure assigned to the Ultra films by Goh (61). Croset and Velasco (114), however, have reported oxygen concentrations as high as 17\% for b.c.c. and B-Ta films and they observed that the oxygen level decreased to 4\% with increased deposition rate.

The University of Surrey evaporated films were found to contain considerably more oxygen than the Ultra films with a typical concentration of around 20 to 40\% through the film rising to around 50\% at the surface. Oxygen depth profiles for typical Ultra and Surrey films are shown in Figs. 31 and 32. It is noticeable that the Surrey film does not show an enhanced oxygen level at the substrate interface as does the Ultra film. This can be attributed to the very low base pressure (2 \times 10^{-9} \text{Torr}) in the evaporation chamber prior to deposition with the result that the vitreous carbon substrate has a very clean surface before film growth commences. The Ultra film also has a small (~1\%) concentration of a medium mass impurity, of mass number about 40, which is not seen in the evaporated film. This is almost certainly argon which has been incorporated into the film during growth. It could possibly be potassium or calcium but this seems unlikely. Read and Altman (115) used emission spectroscopy to analyse sputtered tantalum films and determined that they contained less than 50 ppm of all metals except Mo and Nb (Mass numbers 93 and 96 respectively) which were present at levels of < 100 and < 200 ppm respectively. They measured argon concentrations of around 1.7 at\% for b.c.c. films, however, which compares very well with the level
seen in the Ultra film. The small levels of Mo and Nb are due to impurities in the tantalum target since they are not easily separated from tantalum.

The Surrey films showed different oxygen levels from film to film with levels of from 20% to 50% which is very unsatisfactory for resistor manufacture. These different levels are associated with the filaments which frequently burned out during growth runs. Replacement of a filament involved opening the system and although this was done by admitting high purity nitrogen rather than air it is certain that the partially grown film and the source were exposed to air and that oxygen was adsorbed. The dip in the tantalum peak of Fig. 36 and Section 3.3.2 is believed to be the result of oxygen contamination during a filament change. If the problem of filament life were to be solved the evaporated films produced in the Surrey UHV system would be of a superior and more consistent quality.

The high levels of oxygen in the Surrey and Ultra films are reflected in Table 3.6 which shows different values of $[\sigma]$, the energy loss parameter. The Ziegler and Chu (80) value of 133 is from their computation of stopping power data based on experimental results and the value of Linker et al. (79) is an experimental result for bulk tantalum. The result was actually for a 2.0 MeV helium beam and has been adjusted to compare with our 1.5 MeV results.

The value of $[\sigma]$ for the Ultra film on vitreous carbon is 14% lower than the value of Linker et al. for bulk tantalum and this figure compares very well with the measured oxygen concentration of 15% and with the measured density of 13.3 g/cm$^3$ which is about 20% lower than the density of bulk tantalum (16.6 g/cm$^3$). On this basis the Ultra films on glass substrates look better and their oxygen concentration is probably around 7%. For the evaporated films on vitreous carbon the value of $[\sigma]$ is 22% lower than Linker's value which compares with 20-40% of oxygen and the measured density is around 11.5 g/cm$^3$ which is 30% lower than the bulk density. The evaporated films on glass, however, give a slightly lower value of $[\sigma]$ which suggests a level of oxygen of around 24% compared with the 22% for the vitreous carbon substrates. Inferring the oxygen
concentration from the divergence in [8] from the value for the bulk metal is obviously an over-simplification of the situation but it serves as an approximate indication of the film purity.

4.4.2 Implanted Films: Tantalum films were implanted to high doses, from around $10^{17}$ ions/cm$^2$ to $10^{18}$ ions/cm$^2$, with one of three ion species: argon, nitrogen or oxygen. The films were then analysed using Rutherford backscattering and the spectra are shown in Figs. 33-38.

The general shapes of the different tantalum peaks show similarities, particularly the reduction in height at the high energy part of the peak corresponding to the surface of the film. This was explained in Section 3.3.2 as being due to a reduction in atomic density of tantalum at the surface as a result of the ion bombardment. Tantalum atoms are displaced, many being sputtered from the surface, to be replaced by atoms of argon, nitrogen or oxygen depending on the particular ion species. The analysing beam will see these atoms but they will contribute counts to a different part of the energy spectrum and hence the tantalum peak has the appearance of having a corner removed. The depth of the altered layer will depend on the range of the bombarding ions; the comparison between the two was made in Section 3.2.2 and they were shown to have a correspondance. Thus for an argon implanted film we saw an altered depth of 400Å compared with a total ion range of 300Å and for two nitrogen implanted films there were altered depths of 450Å compared with an ion range of 350Å and 1500Å compared with a range of 1200Å.

The altered depths were consistently greater than the corresponding ion ranges but they were estimated from a consideration of the tantalum stopping power only. The effect of including the contribution of the implanted ions to the total stopping power was demonstrated in Section 3.3.2 by a calculation to explain why the tantalum peak showed little or no thinning after $4.7 \times 10^{17}$ N$^+$ ions/cm$^2$ at 75 keV. The altered depth becomes around 1250Å if the nitrogen stopping power is included and the agreement with LSS total range (1200Å) is then very good indeed. Similarly the effect of argon atoms on the 1.5 MeV He$^+$ beam will improve the comparison between altered depth and LSS range.
The argon bombarded film shows the smallest change in peak height at the surface; the comparison being shown very clearly by Figs. 33 and 35. The reason for this is the different values of sputtering yield measured for argon and nitrogen bombardment. Argon was estimated to have a yield of 2 atoms per ion and nitrogen around 0.1 atoms per ion. The fact that the argon sputtering rate is the greater by a factor of 20 means that the saturation concentration of implanted argon atoms will be much lower than that of nitrogen with a correspondingly smaller effect on the tantalum concentration at the surface of the film.

Using the equation due to Carter et al. (99) which was discussed in Section 4.2.2 in relation to the sputtering of gold we can calculate the expected dose required to reach saturation concentration levels of argon and nitrogen, for the films shown in Figs. 33 and 35.

For argon implanted at 40 keV with a sputtering yield of 2 atoms per ion the required dose would be around $5 \times 10^{16}$ ions/cm$^2$ and for nitrogen at 20 keV with a sputtering yield of 0.1 atoms per ion the dose would be $1.5 \times 10^{18}$. The actual concentrations of argon and nitrogen at saturation are difficult to estimate but are most likely going to be in similar proportions to the calculated doses and this explains why the reduction in height seen in the tantalum peak after nitrogen bombardment is so much greater than that for the argon bombarded film. The nitrogen dose for the film of Fig. 35 is in fact $9.4 \times 10^{17}$ ions/cm$^2$ so, according to Carter et al., the saturation dose has not yet been reached and the surface height of the tantalum peak should decrease even further. This was the highest dose used, however, so it is not known whether or not the saturation dose had been reached.

For the oxygen implanted film of Fig. 37 it is noticeable that the tantalum peak is reduced in height throughout the film and there is no distinguishable altered layer as was observed for the argon and nitrogen implanted films. Thus it would appear that the oxygen is distributed through the whole film which has retained its
original thickness although the tantalum atomic density is considerably reduced. The concentration profiles of tantalum and oxygen through the film are shown in Fig. 38 and the depth scale assumes that the film thickness is unchanged.

It was calculated that the sputtering yield for 30 keV O\textsuperscript+ ions was 0.13 atoms per ion and the number of tantalum atoms removed from the film was of the order of $1.7 \times 10^{17}$ atoms/cm\textsuperscript{2} which represents half of the number of atoms in the original film. Thus it seems unlikely that the film thickness is unchanged after such a high dose bombardment and more reasonable to assume that the film thickness has been reduced by a considerable amount, and that the retained oxygen atoms are contributing to the energy loss of the analysing beam such that the total energy loss is almost identical to that of the original film.

We can calculate the energy losses for the film in a similar way to that used for the nitrogen implanted film of Fig. 36. Values of stopping power for 1.5 MeV He\textsuperscript+ ions in tantalum and oxygen targets are taken from Northcliffe and Schilling (82) and are:

- For Ta: $110$ eV/10\textsuperscript{15} atoms/cm\textsuperscript{2}
- For O: $45$ eV/10\textsuperscript{15} atoms/cm\textsuperscript{2}

For the unimplanted film with 46 at% of oxygen:

Energy loss = $110 \times 3.4 \times 10^{17} \frac{10^{15}}{10^{15}} + 45 \times 2.8 \times 10^{17} \frac{10^{15}}{10^{15}}$

= $37.4 + 12.6$

= $50.0$ keV
For the implanted film:

\[
\text{Energy loss} = 110 \times \frac{1.7 \times 10^{17}}{10^{15}} + 45 \times \frac{1 \times 10^{18}}{10^{15}}
\]

\[= 18.7 + 45.0\]

\[= 63.7 \text{ keV}\]

The width (FWHM) of the tantalum peak for the implanted film is 49 channels compared with 46 channels for the 'as deposited' film. Thus if the energy loss for the original film is assumed to be 50 keV and the calculated loss of 63.7 keV is too high by about 20%. This is not unreasonable since stopping power data are very rarely known to be better than 5% and Bragg's rule of linear additivity of stopping powers may not be valid in the present situation where the oxygen level is 85 at%.

If we assume an energy loss of 53.3 keV and calculate the oxygen concentration in the implanted film from the energy loss we arrive at a figure of \(7.7 \times 10^{17}\) atoms/cm\(^2\) compared with the \(1 \times 10^{18}\) atoms/cm\(^2\) calculated from the peak areas. The oxygen peak areas could also be a source of error since they contain far fewer counts than the tantalum peaks as can be seen from Table 3.8. The background oxygen peak in particular has only 3,800 counts compared with 563,000 counts for the tantalum peak and the oxygen edge is at a very much lower energy than the tantalum edge which increases the probability of a contribution to the peak due to scattering from other atom types. If there is any nitrogen in the film the counts may contribute to the oxygen peak since the oxygen peak extends in energy from 0.55 MeV to 0.45 MeV and the nitrogen edge occurs at 0.47 MeV. Any spurious counts due to noise or perhaps multiple scattering will also give rise to a far greater error in the case of the oxygen peaks than they would for the tantalum peaks.

In sputtered films doped with oxygen the oxide has been identified by several workers (e.g. 116, 117) as \(\text{Ta}_2\text{O}_5\) although Goh (61) did not see \(\text{Ta}_2\text{O}_5\) in films implanted with oxygen up to a
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dose of $6.5 \times 10^{17}$ ions/cm$^2$. Goh identified Ta$_2$O$_5$ up to a dose of $10^{17}$ ions/cm$^2$ and at higher doses reported amorphous films of unresolved composition. If we postulate Ta$_2$O$_5$ as the oxide form with free oxygen making up the balance then we can use measured values of the density of Ta$_2$O$_5$ to give an approximate value for the film thickness since this cannot be estimated from the backscattering spectra. Wilcox and Westwood (113) measured the density of Ta$_2$O$_5$ as $8.01 \pm 0.08$ g/cm$^3$ so if we use a value of 8 the molecular density becomes $1.1 \times 10^{22}$ mols/cm$^3$ of Ta$_2$O$_5$. The thickness of the film is now calculated from the area of the tantalum peak for the implanted film ($1.7 \times 10^{17}$ atoms/cm$^2$),

$$t = \frac{1.7 \times 10^{17}}{2.2 \times 10^{22}} = 770 \text{Å}$$

Thus, using Ta$_2$O$_5$ as the film composition, it seems that the thickness is almost unchanged due to implantation. Lattice expansion of tantalum due to dissolved oxygen is well known and has been reviewed by Schneider and Langer (118). The lattice constant for bulk Ta is 3.3058 Å and the accepted figure for expansion due to oxygen (120) is 0.006 Å/at%. It is quite probable that free oxygen in the Ta$_2$O$_5$ film will similarly affect the atomic spacing and give rise to an increase in film thickness.

Perhaps more information would have been acquired if further oxygen implanted films, particularly with lower dose implants, had been studied. Unfortunately oxygen is a very difficult ion as far as implantation is concerned since it reacts with the ion source filament which is very quickly destroyed. The film studied was the only film to be successfully implanted with oxygen and unfortunately showed a very high level of oxygen in the 'as deposited' state before implantation.

An RF ion-source is now in service on the 600 keV accelerator which makes oxygen implantation more straightforward but unfortunately it was not available at the time of the experiments.
SUMMARY

Rutherford backscattering has been shown to be a useful technique for the assessment of the quality of tantalum thin films. Of the two types of films analysed the sputter deposited films were shown to have the better consistency and purity with around 15 at.% of oxygen in the films. The evaporated films showed varying levels of oxygen from 20 to 50 at.% . Both types had very good thickness uniformity over the area of the individual substrates which were one inch squares.

Sputtering yields were measured for ion bombarded films and were found to be around 0.1 atoms per ion for 20 keV nitrogen and for 30 keV oxygen and around 2 atoms per ion for 40 keV argon. Considerably larger reductions in height of the surface edges of tantalum peaks were seen for oxygen and nitrogen implanted films compared with argon implanted films and this was explained in terms of higher saturation concentrations of implanted ions as a result of the lower sputtering yields.

Altered depths of the tantalum peaks were shown to compare well with LSS theoretical ion ranges. It has been shown however that after very high dose bombardment the film thickness can no longer be estimated from the backscattering spectrum since neither the stopping power nor the atomic density are known for the implanted film.
CONCLUSIONS

Sputtering yields of gold measured for neon, argon and krypton bombardment were generally found to be greater than yields measured by other workers. This may have been due to a combination of reasons.

(i) Samples used were of rolled gold foil whereas several workers used evaporated films with consequently different surface topographies.

(ii) Insulation leakage may have caused errors in measurements of ion dose.

(iii) In most cases the ion doses used during the present work were greater than those used by other workers.

Large spreads were seen in the measured points for energy and dose dependences of sputtering yield. This is probably due to the current integration problems already referred to but the spreads could have been reduced if more measurements had been possible at each point. Unfortunately the large amount of time taken to achieve an acceptable pressure before bombardment and to blow off the liquid nitrogen from the assembly after bombardment meant that only three or four bombardments could be carried out in one day. It is felt that a target assembly of the type used by Colligon and co-workers (101, 119), which could accommodate up to 48 collectors, is very desirable from the point of view of obtaining data efficiently and in sufficient quantities. Colligon et al. also used an active target in conjunction with their own detection and counting system in contrast with the present work where each collector was individually activated. The use of an active target has the obvious advantages of increased economy and convenience but the method could not very well be used for gallium arsenide where the half lives are too short to allow the bombardments to be carried out in time.

Although it was not possible to see any maxima in the sputtering yield curves it was shown that the relative rates of fall-off in yield with energy for the different ions were in agreement
with theory. It has also been shown that Sigmund's theory predicts yields very well for medium mass ions but does not do so well for light and heavy ions.

From the results of dose dependence of sputtering yield it appears that the yield increases by around 10% over the dose range $10^{17}\text{ions/cm}^2$ to $10^{18}\text{ions/cm}^2$ due to changes in the surface topography of the gold samples and the effect of implanted ions.

Energy dependence curves for sputtering of gallium arsenide show the same fall off in yield with increasing energy as seen for gold targets. A large difference was seen between the amounts of gallium and arsenic collected on the hemispherical polythene collectors. After several experiments designed to investigate this discrepancy it was concluded that gallium and arsenic are sputtered in stoichiometric proportions but arsenic particles do not stick very well to the collector surfaces. Total sputtering yields were then assumed to be twice the value of yield measured for sputtered gallium atoms. On this basis the experimental values of sputtering yields of gallium arsenide are quite low, with values of around 3 atoms per ion for 200 keV argon and 8 atoms per ion for 200 keV tellurium, compared with values for gold of around 18 atoms per ion for 200 keV argon and 53 atoms per ion for 200 keV krypton. Since tellurium is the heaviest ion likely to be of interest as far as ion implantation into gallium arsenide is concerned and since the greatest ion dose is unlikely to exceed $10^{14}\text{ions/cm}^2$ it is clear that the effect of sputtering during implantation is unimportant.

Comparison of sputtering yields of gallium arsenide with those predicted by Sigmund's theory for germanium show that germanium yields are considerably higher. It is believed that the reason for the large differences is due to the atoms of gallium arsenide being more tightly bound to the surface as a result of the ionic contribution which is not present in germanium.

The difference in measured yields for gallium and arsenic atoms has demonstrated the importance of being able to measure target weight loss so that it can be compared with the deposits on the collectors.
The quartz resonator technique is probably the most sensitive way of doing this although its use is restricted to evaporated film targets and it could not be used for crystalline gallium arsenide. The intention at the beginning of the present work was to use activation analysis because it was a direct measurement of sputtered material and to avoid weight loss because it was indirect and involved a correction factor due to implanted ions. In retrospect this was a mistake since it is felt that if the target holder had been designed differently it would have been possible to use a microbalance to obtain meaningful measurements of target weight loss. This would hopefully have resolved the question of the discrepancy in sputtering yields in a straightforward manner. Unfortunately, however, it is believed that the method of clipping the targets in position led to slight chipping of the edges such that weights measured before and after bombardment did not correspond sensibly with the amount of material sputtered.

The third section of this project concerned the Rutherford backscattering analysis of tantalum thin films. The technique has been shown to be very valuable as a tool for the assessment of film quality. Films deposited on vitreous carbon substrates can be used to identify low mass impurities and it was shown that oxygen is the predominant impurity. The heights of the tantalum peaks were seen to be smaller for the Surrey films than for the Ultra films and this peak height depends on the oxygen concentration. Thus once the impurity has been identified it is possible to use the peak height to give a figure of merit for the purity of films on glass substrates where the impurity peaks cannot be distinguished from the substrate spectrum. The method can also be used to monitor the reproducibility of film quality and it was discovered that the Surrey evaporated films showed quite large variations in oxygen content.

For implanted films the technique was used to calculate sputtering yields for the different ions used and also showed the effect of different saturation concentrations of implanted ions depending on sputtering yield.

Thicknesses of altered layers were calculated approximately on the assumption that the tantalum atomic concentrations in those layers were proportional to the reduced heights of the tantalum peaks.
For low doses this method will give a reasonable answer but the reduction in peak height is due to a contribution to the stopping power from the implanted ions as well as to a reduction in tantalum concentration. At high doses therefore it is necessary to have an independent measurement of film thickness in order to calculate the altered depth and the tantalum concentration in the atomic region.

In principle it is possible to calculate the altered depth by using Bragg's Rule of additive stopping powers and by assuming the fraction of implanted ions retained in the film but we have a 20% discrepancy between energy loss measured in an oxygen implanted film and that calculated using Bragg's Law. It is therefore reasonable to conclude that the Rutherford Backscattering technique provides a very valuable method of analysing thin films with the reservation that if they are implanted to very high doses it is necessary to provide a depth scale by some other method.
APPENDIX 1: Calculation of Fraction of Sputtered Material passing through Hole in Collector

It is assumed for the purpose of this calculation that the angular distribution of sputtered material is cosine. Several measurements have been made by different experimentalists (e.g. 1, 2, 3) and most of them seem to agree that the distribution is approximately cosine if not exactly so.

The above diagram shows the arrangement of collector and sample. The size of the hole is exaggerated. Sputtering is assumed to be from a point source at the sample for the sake of simplicity. The distance from sample to hole is $R$ and the flux per unit area of sputtered atoms along the axis is represented by $I_o$.

Flux density along a radius at angle $\theta$ to the axis is given by:

$$I(\theta) = I_o \cos \theta$$

If we now consider a small annulus of area $\delta S$ between the
cones of half-angle $\theta$ and $\theta + \delta \theta$ then the total flux through $\delta S$ is
given by,

$$I_0 \cos \theta \delta S$$

and

$$\delta S = 2\pi R \theta \times R \delta \theta = 2\pi R^2 \theta \delta \theta$$

\[ \therefore \text{total flux through } \delta S \text{ is given by}, \]

$$I_0 2\pi R^2 \theta \cos \theta \delta \theta$$

and total flux through hole is given by,

$$I_0 2\pi R^2 \int_0^\alpha \theta \cos \theta d\theta$$

$$= I_0 2\pi R^2 \left[ \theta \sin \theta - \int \sin \theta d\theta \right]_0^\alpha$$

$$= I_0 2\pi R^2 \left[ \theta \sin \theta + \cos \theta \right]_0^\alpha$$

Similarly the total flux striking the collector is given by,

$$I_0 2\pi R^2 \left[ \theta \sin \theta + \cos \theta \right]_{\alpha}^{\pi/2}$$

$$R = 57 \text{ mm } \alpha = 0.0658$$

\[ \therefore \text{flux through hole} = 0.0021 I_0 2\pi R^2 \]

and flux striking collector $= 0.5687 I_0 2\pi R^2$

Fraction of sputtered atoms lost through hole is given
by,

$$\frac{0.0021}{0.5687 + 0.0021} \times 100\%$$

$$= 0.37\%$$
REFERENCES

76. E. Rutherford. Phil. Mag. 21, 669 (1911).


