Thin Film Adhesion Modification by MeV ions

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Abstract

The adhesion of a thin films, and in particular the way in which such adhesion may be improved by irradiation, is a rather poorly understood field of thin film technology. The radiation enhanced adhesion effect has been investigated through the use of Ultra High Vacuum sample preparation, analysis and irradiation techniques, in order to gain control over surface and interface composition.

In the systems studied, films deposited on atomically clean surfaces show good adhesion, and no evidence of enhancement due to irradiation is observed in the case of such clean interfaces. The results are entirely consistent with the radiation enhanced adhesion phenomenon being due to radiolytic effects on contaminant containing layers at the film/substrate interface. In addition, on silicon substrates the observations highlight the superiority of thermal cleaning over low energy sputtering as a route for producing a clean surface.

A model of the radiation enhanced adhesion observations for dirty interface systems is developed, which takes into account the two dimensional nature of the ion energy deposition process. All the observations on such systems are broadly consistent with an activation energy for the process of approximately 5 eV. This value is sufficiently large to bring about chemical bonding rearrangement at the critical film/substrate interface.
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CHAPTER 1

Introduction

Thin films are part of countless technologically important processes from semiconductor device fabrication at the small scale to wear and corrosion resistant coatings on mechanical components at the other end of the spectrum. One of the critical parameters of any thin film process is the adhesion of the film to the substrate. Whilst modern techniques of deposition and process control have resulted in improved reliability of adhesion behaviour, for many systems there exists no clear understanding of what the determining factors are.

The ability of fast heavy ions to dramatically improve thin film adhesion was first observed by Joe Griffith and co-workers at Caltech in 1981. At that time he was studying the ability of MeV ions to produce etchable damage tracks in dielectric materials, and wondered if the resulting atomic displacements might improve the adhesion of a metal overlayer. The observation that MeV ion irradiation did indeed produce technologically useful levels of adhesion, even between materials with no natural chemical affinity, lead to such measurements being repeated by many groups around the globe.

The aim of this study is to further the understanding of radiation enhanced adhesion phenomenon. The work that has been performed has also provided valuable insights into the nature of adhesive behaviour in general.

This dissertation begins with an introduction to the subject by looking at the origins of thin film adhesion and the ways in which it may be modified by radiation processes. Chapter 2 provides a brief review of the most important published experimental material, followed by a chapter covering the accepted theoretical approaches to radiation enhanced adhesion. The thesis continues with a chapter describing our chosen experimental approach, with particular reference to the unique experimental facilities developed as part of this programme. The experiments performed in the present work are described in the four chapters which follow,
involving a variety of film/substrate combinations. In chapter 9 we discuss the most important results of the experimental programme, and the implications for thin film processing technologies. In the final chapter the principle conclusions are briefly stated, and possible fruitful directions for future studies are highlighted.

1.1 Thin Film Adhesion

The nature of thin film adhesion, particularly for non-reactive couples of film and substrate, is rather poorly understood (Mattox 1973). For many, even the terms used to describe interfacial adhesion such as interfacial energy and adhesion energy cause confusion. These thermodynamic terms originate as follows. If any couple of film A and substrate B are brought into intimate contact from infinity the important equation used to describe the thermodynamics of a thin film interface arise simply by equating the energy terms that exist before and after the operation (Murr 1975). This is illustrated in figure 1.1, which shows that initially we have the two surface free energies, \( \gamma_{SA} \) and \( \gamma_{SB} \). The surface free energy results from the surface being a high energy state, since surface atoms (on average) have only half the number of neighbours with which to bond. In energy terms, the surface free energy is half the energy required to split a unit area of a crystal in two, since such an operation will produce two fresh unit area surfaces and is typically of the order of 1 \( \text{Jm}^{-2} \) which equates to some 0.5 eV per atom. It is precisely this energy which provides the driving force for the commonly observed surface reconstruction phenomena. When the two surfaces A and B are brought into contact, the surface energies are replaced by a single interface energy \( \gamma_{intAB} \), and a term due to any bonding processes that may occur, which is the energy of adhesion \( E_{ad} \). The energy of adhesion is precisely the amount of energy required to separate the film from the substrate. By equating the energies before and after being brought into intimate contact we have:

\[
\gamma_{SA} + \gamma_{SB} = \gamma_{intAB} + E_{ad}
\]
Figure 1.1: The thermodynamics of thin film adhesion. The initial energy state of the system is represented by the sum of the surface free energies. When film is in contact with substrate, these terms are replaced by the energy of adhesion, $E_{ad}$, and the interfacial energy. For a perfect epitaxial film, the interfacial energy would approach zero, and the energy of adhesion would simply be the sum of the surface free energies.
The best adhesion will result in cases with the largest value for the adhesion energy, $E_{\text{ad}}$, which from the above equation results when the interfacial energy, $\gamma_{\text{fA}\text{B}}$, is a minimum.

In the following sections we will outline some of the important factors which contribute to thin film adhesion.

1.1.1 Van der Waals forces

The natural variability in electron distributions around the atoms in the interface region give rise to transient electromagnetic dipoles which result in a net attractive force between atoms and molecules in close proximity to one another, and hence occurs between atoms of film and substrate. Although weak (of the order of 0.3 eV per atom) they may be entirely responsible for film adhesion in some unreactive systems of film and substrate. It is precisely these forces which are at work in the process of physisorption where no direct chemical reaction takes place at the surface.

1.1.2 Electrostatic forces

The bringing together of materials with different electron affinities will result in a redistribution of charge at the interface, just as occurs in the case of a p-n semiconductor junction. The driving force for such processes is the equalisation of the Fermi level at the boundary between the materials. The resulting electrostatic attraction across the interface can produce an effect of the same order as the Van der Waals forces above, and hence may be quite significant in some cases.
1.1.3 Image charge interactions

It has been shown that, in the case of metal films on a dielectric substrate, the electrostatic attraction between charged substrate species and their classical induced images in a metal overlayer may produce a significant part of the adhesion force of the system. This interaction is enhanced in the case of non perfect substrates, since charged defects may produce additional contributions.

1.1.4 Chemical interactions

There is considerable evidence that if the film species is chemically reactive with the substrate a good bond is likely to result. This is attributed to chemical reaction at the interface, which will reduce the interfacial energy thus benefiting the adhesion. Some see this as a rather empty argument, since if film species A reacts with substrate B to form a compound AB at the surface, what do subsequent A atoms arriving at the new surface find to bond to? Thus chemical reaction can be interpreted as moving the interface rather than eliminating it. This would seem rather a simplistic view, since by definition a solid must involve a minimum of three bonds per atom and thus chemical reaction can be envisaged as producing a finite region where mixed bonding occurs, reducing the interfacial energy and making the interface for failure to occur hard to identify, which may well be the ultimate goal in attempts to produce a strong film to substrate bond (Baglin 1987).

1.1.5 Mechanical effects

The idealised picture of an atomically flat substrate is only valid in a very small number of cases. Most substrates have surface roughness at a level far exceeding the film thicknesses used in the majority of the work described in this dissertation. Hence the morphology of the substrate surface can be expected to have a considerable effect on film adhesion. At the very least the contact area per unit area of
surface may be considerably enhanced (by a factor of two or more), and in some cases mechanically interlocked structures may be formed which will generally be of benefit to the adhesion of the film.

1.2 MeV Ion Interactions

The range of observable effects when a fast charged particle interacts with solid matter are many and varied, and have been the subject of innumerable studies since the discovery of alpha rays in the last century. The primary interactions of a charged particle, or ion, as it passes through matter are with the small highly charged nucleus (nuclear energy loss) and the less localised electron cloud surrounding it (electronic energy loss). Collisions between the ion and the target material nuclei are rare events indeed at high energies due to the small physical dimensions of the atomic nucleus (of the order of $10^{-15}$ m) and the short range nature of the coulombic and nuclear forces. When they do occur however, a large amount of energy may be transferred to the target atom, since the similarity of the masses of projectile and target make significant kinematic energy transfer possible. Such large energy transfer events give rise to knock-on projectiles, resulting in the well known collision cascade phenomenon at lower particle velocities where such nuclear collisions are more probable. Collisions between the ion and the atomic electrons of the target occur continually, providing a steady transfer of energy to the atoms of the target. The large mismatch between the masses of the ion and an electron result in only a small energy loss for each interaction. Such collisions are sufficiently numerous however, for this energy loss process to be dominant for all ions above an energy of some 10 keV per nucleon. The collisions with both electrons and the atomic nuclei lead to a range of excitation phenomena, from local excitation of a single atom to the creation of extended regions of atomic displacements, or defect zones, depending on the severity of the interaction and the properties of the target material. Some aspects of these interactions, with particular regard to those which may have some effect on thin film
adhesion, are discussed in the following sections.

1.2.1 Direct nuclear processes

Even at large impact parameters it is quite possible for a target atom to gain sufficient energy from the passage of a highly ionised fast particle for the atom to be displaced from its position in the lattice (of the order of 25 eV) (Hayes 1984). At smaller impact parameters, the target atom will receive more energy and may move a significant distance from its initial lattice location before coming to rest, perhaps displacing other atoms in the process. If the projectile ion has sufficient energy, a chain of such events may lead to a so called collision cascade (Brown 1986) as illustrated in figure 1.2, whereby the passage of a single ion results in a large number of atomic displacements. Such energy loss processes are dominant for low energy ions (less than 10 keV per nucleon). If such processes occur in the interfacial region between a film and a substrate as indicated in figure 1.2, it is quite possible for significant transfer of film species into the substrate and vice-versa to occur. Such blurring of a film/substrate interface is commonly referred to as ion beam mixing (Tsaur 1981, Collins 1969, Laugier 1981), and is often found beneficial to adhesion. In practice this is applied by the use of large current low energy ion sources (typically several milliamperes of 1-2 keV argon) and to be effective the short range of such particles requires their presence during the film deposition step. The use of such low energy ion bombardment during deposition are commonly referred to as ion assisted coating techniques and have been found to have other beneficial effects on the film properties over and above those of good adhesion, such as low residual stress and higher density.

Whilst such processes do still occur for the high ion energies used in the work described in this dissertation, the dominant processes in the high energy regime are the electronic effects discussed in the next section.
Figure 1.2: A schematic diagram of the process of ion beam mixing resulting from nuclear collision cascade. Note how the initially sharp interface between film and substrate may rapidly become blurred, with significant transfer of film and substrate species across the interface.
1.2.2 Direct electronic processes

For a projectile such as a 20 MeV chlorine ion passing through gold, the interactions with atomic electrons results in an energy loss rate some 200 times greater than that which goes directly to the atomic nuclei as described above (Ziegler 1977). The relative roles of nuclear and electronic energy loss are highlighted in figure 1.3 which shows the nuclear and electronic energy loss terms as a function of energy for a helium ion (Ziegler 1977). At the higher energies (above some 10 keV per nucleon) the electronic processes clearly dominate. Analogous to the preceding section, the collisions with atomic electrons will produce a range of excitations from exciting a single atom to producing a multiply charged defect, and since the electrons will have energies extending to several keV the excitation can be spread over a considerable region by electron-electron collisions. The extent of the excitation zone will depend on the ion mass and velocity and the properties of the target material, but may be significant at many atom diameters from the ion trajectory. A considerable fraction of the atoms in such a zone will be ionised, and if they happen to be just those atoms at the interface between a thin film and a substrate, it is quite conceivable that such excitation might lead to rearrangements in local bonding configurations particularly where these might involve native oxide/adsorbates/hydrocarbon contaminants for example. In some cases (see chapter 2) observations of just such interfacial bonding changes due to high energy irradiation have been made, although whether such changes would directly lead to better film adhesion is not so clear. Such changes in atomic bonding in the wake of a highly charged fast ion are often referred to as "hot chemistry" as many believe that under such non-equilibrium highly excited conditions it may be possible to form compounds and quasi-stable bonding arrangements at an interface that would not occur in the normal bulk phase (Baglin 1987, Sood 1985). Such chemistry may well be responsible for the improved bonding which results from irradiation of normally unreactive systems of film and substrate.
Figure 1.3: The variation of electronic and nuclear energy loss for helium ions in gold as a function of ion energy (Ziegler 1977). Note that above some 10 keV per nucleon the electronic component is dominant, and in the MeV energy range, the energy loss in electronic processes is typically two orders of magnitude larger than the nuclear component.
1.2.3 Radiation effects on the material

The primary processes described above give a brief picture of the immediate consequences of the passage of a high energy charged particle, leaving in its wake a central core of ionised target atoms with many of their atomic electrons heading off isotropically into the bulk. The consequences of such excitation is largely dependent on the electronic properties of the material. For example, in a metal the fast electronic relaxation time will rapidly quench the positively charged core region before the charges present are able to cause any atomic motion. The strong metallic bonding also makes permanent damage of the initial lattice less likely. In the case of an ionic insulator such as sodium chloride the result will be somewhat different. The fixed charges of the ions in such a structure result in very long electronic relaxation times, such that the positive ionised core is likely to remain so for a considerable time. This combined with the upsetting of the regular alternately charged cubic array of Na\(^+\) and Cl\(^-\) will more than likely lead to coulombic mutual repulsion (so called ion explosion) (Brown 1986) between like charges resulting in some permanent distortions to the crystalline lattice. Such defects as may be produced in the lattice are likely to remain permanently at room temperature as a considerable energy barrier will exist between the structure formed and the perfect lattice, requiring a high temperature anneal to restore order.

Metals and ionic solids represent the two extremes of the response of materials to irradiation. In the majority of dielectrics the response will be somewhere between these extremes depending on the degree of ionicity or covalency in the bonding of anion and cation. The response of semiconductors is less dramatic since they have much shorter relaxation times than do true insulators. Only in the large band gap semiconductors is there a significant level of damage driven by electronic excitation processes (Palmer 1977). In polymers the behaviour is more complex, since breaking of bonds leads, in many cases, to the loss of reactive radical species such as H\(^*\), Cl\(^*\) of F\(^*\) which results initially in cross-linking between polymer chains at low doses, giving way to carburisation of the material at higher doses (Brown 1985).
1.2.4 Atomic displacement by electronic processes in dielectrics

It has long been known that the passage of energetic particles through dielectric materials may result in displacement damage which can be subsequently developed by etching the material in a suitable medium (Fleischer 1975). Such etchable damage tracks have been studied by several groups and have added greatly to our understanding of the interaction of ions with materials. The continuum of defects produced along the ion trajectory forms a region which dissolves preferentially on exposure to the dissolving medium resulting in a track visible under a microscope.

The process which produces the atomic displacements may also lead to ejection of atoms from the surface (Haff 1976, Tombrello 1984). This ability of fast heavy ions to sputter dielectric materials has also been studied in a limited number of cases (Griffith 1986, Qiu 1982, Qiu 1983). High sputter yields are observed in some materials, which far exceed those which would be expected from simple nuclear collisions between ion and target, emphasising the electronic nature of the effect. The sputter yield also varies dramatically from one material to another in ways not yet fully understood; Si$_3$N$_4$ sputtering at one tenth the rate of SiO$_2$ for example (Qiu 1983). One of the most interesting observations made on this phenomenon (independently by this group and the group at Caltech by different methods) is that the sputtering effect appears to switch off below a certain critical thickness in the case of SiO$_2$ films on silicon (Qiu 1983). This thickness is around 2 nm, which corresponds roughly to the thickness of the native oxide on the average silicon wafer. This effect is perhaps a consequence of electron injection from the underlying silicon, which is able to quench the excited zone if the surface of the oxide is sufficiently close to the silicon/oxide interface. Whatever the reason, the observation has relevance to radiation enhanced adhesion, since if secondary atomic displacement phenomena are an essential component in the irradiation enhancement of films on SiO$_2$, then one might expect a thin native oxide substrate to behave rather differently to a thicker thermal oxide since displacements at the interface may be quenched in the former.
CHAPTER 2

Experimental Review

During the past three decades, we have witnessed a dramatic increase in the use of particle beams in various aspects of thin film technology. Plasma etching, sputter deposition, ion assisted coating are now well known techniques, as are analysis tools such as Secondary Ion Mass Spectrometry and Ion Scattering Spectroscopy. The ability of ion beams, as well as other forms of ionising radiation, to enhance the adhesion of thin films has been observed as a direct consequence of the increased use of ion beam processing techniques, and a brief and somewhat selective review of the relevant literature is given in the sections which follow.

The use of high energy ion beams for the modification of thin film adhesion began with the work of Griffith and Qui at Caltech in 1981. It was suspected that the ability of high energy heavy ions to produce etchable damage tracks in dielectric materials might also give rise to disruption and mixing at the interface between a thin metal overlayer and a dielectric substrate. Investigations of the irradiation enhanced adhesion of gold films on fused quartz were successful (Griffith 1982), requiring modest doses of $10^{15}$ ions cm$^{-2}$ of 10 MeV fluorine or 20 MeV chlorine to produce well bonded films. Adhesion enhancement was also observed in the case of teflon and ferrite substrates. At this early stage the mechanism was thought to be directly related to that responsible for the formation of damage tracks, which is essentially due to processes in the highly ionised central column formed in the ion wake, which persists long enough for atomic displacements to occur due to the long electronic relaxation time of dielectrics.

The work at Caltech was extended to include metal on semiconductor (silicon) and metal on metal (tantalum) systems where such track formation mechanisms should be very weak or absent completely. To their surprise, not only did adhesion enhancement occur, but the doses required were the same or lower than was the case
for dielectric substrates. This was interpreted at the time as strong evidence for the adhesion enhancement mechanism being different to that for track formation. This was a rather presumptive conclusion, in that it overlooked the fact that the substrates used almost certainly had a surface oxide layer present, as both silicon and tantalum readily oxidise when exposed to the atmosphere. Unless Ultra High Vacuum preparation techniques are used, such native oxide layers may well be present, and hence the critical interface in their studies (i.e. the one at which film failure occurred) may well still have been that between the gold film and a dielectric layer, namely the native oxide.

In the years which followed, such measurements were repeated in many laboratories, and a large variety of film/substrate combinations have been studied. However, due to a lack of available MeV ion facilities, a considerable number of measurements have been made with relatively low velocity ions, where a significant proportion of the energy deposition is directly producing nuclear recoils, and hence the observations are likely to be a combination of electronic excitation phenomena and recoil mixing. Also the choice, made by many groups, of glass as a readily available flat substrate is unfortunate as the radiation damage of the glass itself produces rather complex behaviour, which directly influences the adhesion of any film on its surface. Irradiation with low doses (5x10^{12} ions cm^{-2} 15 MeV chlorine) produces microcracks in the glass, producing adhesion enhancement by electrostatic attraction between the crack edges and any surface film (Wie 1985). As the dose is increased, the microcracks begin to close up and the adhesion falls back to close to the unirradiated level. At still higher doses (2x10^{14} ions cm^{-2}) the microcracks close up completely, and the adhesion is observed to improve, in line with observations of metal films on other dielectric substrates. Hence observations of adhesion modification on glass substrates should be viewed with caution, since the film adhesion tends to be dominated by gross morphology changes in the substrate, rather than by the more subtle processes which are observed in the case of certain other dielectric substrates.
With the above proviso, there have still been many important results reported in the open literature. These are discussed in the sections which follow.

2.1 Low energy ion beam effects

Low energy ion beams are a well established tool in the production of thin film structures. They perform an essential role in such diverse techniques as glow discharge cleaning, ion assisted coating techniques, plasma enhanced deposition techniques and ion implantation. In some cases the ions are present principally to enhance the adhesion (usually by removal of surface contaminant layers) of a thin film being or about to be deposited, and hence it was a natural progression to investigate the ability of ions to modify film adhesion as a post deposition treatment. In this case a prerequisite is that the ions have sufficient energy to reach the film/substrate interface, which puts an upper limit on film thickness (or lower limit on ion energy).

The main difference between low energy and high energy ions is that low energy ions lose a significant fraction of their energy directly in atomic collisions, which directly give rise to atomic displacements. Hence there will always be a tendency for some mixing to be produced at any sharp film/substrate interface.

The earliest recorded use of ions in this way dates back to the late sixties (Collins 1969), where argon ions of 120 keV energy were used to enhance the adhesion of aluminium films on soda glass substrates by a factor of 50-100. The threshold dose recorded was between $10^{14}$ and $10^{15}$ ions cm$^{-2}$, depending on the surface preparation of the glass prior to deposition. Since then adhesion enhancement has been observed in a variety of film/substrate systems such as Cu/SiO$_2$ (Gukelberger 1972), TiB$_2$/stainless steel (Padmanabhan 1981), Ag/glass and Al/glass (Laugier 1981), Cu/Cr (Bottiger 1984), Au/Mo, Ag/Mo, Cu/Mo and Al/Mo (Pronko 1984), Fe/glass, Al/glass (Battaglin 1986). Most are typified by a one order of magnitude increase in film adhesion and threshold doses of $10^{15}$ to $10^{16}$ ions cm$^{-2}$.
One of the most thorough and interesting studies of this type was carried out at the IBM Research Centre at Yorktown Heights (Baglin 1984, 1985a) where the effect of helium (200 keV) and neon (280 keV) irradiation of copper films on substrates of alumina, fused quartz, glass and teflon was assessed. The choice of ions was interesting since they were selected to produce equal amounts of electronic energy loss, but in the case of neon the nuclear component is some 10 times greater than for helium ions. Hence, if only electronic excitation processes are important, one might expect the two ions to be equally efficient, whereas if the nuclear component is the critical then neon would be expected to be far more effective. The effectiveness of the two ion beams on the systems studied varied greatly, but in no systematic way. For the teflon substrates, neon produced greater benefits at low doses (5x10^14 ions cm^-2), but was surpassed by the helium irradiations at higher doses (>3x10^15 ions cm^-2). Above this dose, the adhesion decreased for both beams due to substrate damage effects. This pattern was repeated for fused quartz substrates, with the helium irradiation surpassing the neon at a dose of some 10^16 ions cm^-2. The adhesion was only a factor of two greater than the as deposited case, but could be improved by a further factor of two by a 450 degree Celsius heat treatment after irradiation. For copper/alumina and copper/glass the neon irradiation was more effective than the helium ions by a factor 2 to 8 for all doses up to 3x10^16 ions cm^-2. This pattern changed after heat treatment however, when the helium irradiated samples rapidly caught up and even surpassed the adhesion of neon irradiated samples. From this we can see that the electronic stopping power alone falls a long way short of giving a thorough guide to the expected effects on the film adhesion. The dramatic changes after heat treatment are interesting as this suggests that diffusion processes are resulting in a more optimum interfacial configuration. Analysis of the substrates after peeling the film indicate that very little transfer of copper to the substrate occurs (less than one monolayer), and hence negligible mixing was produced across the interface even in the neon irradiated case.
2.2 High energy ion beam effects

The initial work at Caltech was quickly extended to a wider variety of film/substrate combinations as shown in table 2.1 (Werner 1983). In all cases initially poor adhesion was improved sufficiently by irradiation to pass the scotch tape adhesion test.

From this table it is clearly seen that we have something of a universal effect, with beneficial changes observed for metal films on metal, semiconductor and polymer substrates, as well as dielectric substrate materials. From the observations, other more detailed trends can be extracted which have been reproduced by other groups. Firstly, for a given system, a heavier ion of roughly the same velocity produces an effect at lower dose, as might be expected since the heavier ion will deposit more energy per unit path.

Table 2.1 Material and beam combinations tested (Werner 1983)

<table>
<thead>
<tr>
<th>Material</th>
<th>Beam</th>
<th>Minimum dose (ions cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au on Teflon</td>
<td>1.5 MeV He</td>
<td>$10^{13}$</td>
</tr>
<tr>
<td></td>
<td>1 MeV H</td>
<td>$10^{14}$</td>
</tr>
<tr>
<td>Au on SiO$_2$</td>
<td>20 MeV Cl</td>
<td>$2 \times 10^{15}$</td>
</tr>
<tr>
<td>Ag on SiO$_2$</td>
<td>20 MeV Cl</td>
<td>$2 \times 10^{15}$</td>
</tr>
<tr>
<td>Au on CaF$_2$</td>
<td>20 MeV Cl</td>
<td>$2 \times 10^{14}$</td>
</tr>
<tr>
<td>Au on ferrite</td>
<td>20 MeV Cl</td>
<td>$3 \times 10^{13}$</td>
</tr>
<tr>
<td></td>
<td>5 MeV F</td>
<td>$2 \times 10^{15}$</td>
</tr>
<tr>
<td>Au on Al$_2$O$_3$</td>
<td>20 MeV Cl</td>
<td>$5 \times 10^{15}$</td>
</tr>
<tr>
<td>Pd on Al$_2$O$_3$</td>
<td>20 MeV Cl</td>
<td>$2 \times 10^{15}$</td>
</tr>
<tr>
<td>Au on Si</td>
<td>20 MeV Cl</td>
<td>$10^{15}$</td>
</tr>
<tr>
<td>Ag on Si</td>
<td>20 MeV Cl</td>
<td>$5 \times 10^{15}$</td>
</tr>
<tr>
<td></td>
<td>10 MeV F</td>
<td>$10^{16}$</td>
</tr>
<tr>
<td>Au on InP</td>
<td>20 MeV Cl</td>
<td>$5 \times 10^{14}$</td>
</tr>
<tr>
<td>Ag on InP</td>
<td>20 MeV Cl</td>
<td>$5 \times 10^{14}$</td>
</tr>
<tr>
<td>Au on GaAs</td>
<td>20 MeV Cl</td>
<td>$5 \times 10^{14}$</td>
</tr>
<tr>
<td>Au on W</td>
<td>20 MeV Cl</td>
<td>$2 \times 10^{14}$</td>
</tr>
</tbody>
</table>
Secondly, the polymer substrates appear to be dominated by rather different processes, since modifications occur at much lower doses, and for lighter ions than for other substrates. This has been attributed to the breakdown of the long polymer chains due to the primary ionisation in the ion wake, which leads to the release of radical species in the polymer/metal film interface. Such radical species (e.g. F* from teflon) may lead to the formation of ternary compound species across the interface. For the other systems there is a trend towards higher doses for systems with lower atomic number constituents (n.b. the 20 MeV Cl dose for Au on W being 2x10^{14} whereas in the case of Ag on Si the quoted dose is 5x10^{15}). This again might be expected since the density of ionisation will be less in the case of lower Z material, as the stopping power is mainly the result of interaction with the atomic electrons. Hence less intense ionisation would be expected to lead to higher doses being required, as is indeed observed.

One of the first groups to reproduce some of the Caltech observations was that based at Upssala University in Sweden (Jacobson 1983). Irradiations were performed using O, S and I ions with energies of 12, 12, and 70 MeV respectively. The systems studied included metal/ceramic, metal/metal, ceramic/ceramic and metal/polymer. Film adhesion was assessed using scotch tape and scratch testing methods. For gold on glass, irradiation produced adhesion exceeding the tape test threshold for doses above 10^{12} ions cm^{-2}. For copper films on aluminium substrates the effect of the native oxide layer, as well as irradiation was investigated. They found that irradiation to doses in excess of 10^{14} ions cm^{-2} was effective in improving adhesion where a native oxide layer was present, but when a sputter etching step was introduced prior to copper deposition to remove the native oxide layer, the as deposited adhesion was as good as for the irradiated non sputter etched samples, and no further improvement was observed after irradiation. Elemental depth profiling using scanning Auger spectroscopy showed the absence of interfacial oxygen in the case of the sputter etched samples, but failed to see any difference between irradiated and non irradiated samples. For metal films on polymer substrates, adhesion enhancement occurred at
low doses (typically $10^{12}$ ions cm$^{-2}$), and deteriorated at much higher doses due to breakdown of the substrate material.

The group at the Royal Melbourne Institute of Technology in Australia were also active at this time, and performed a number of irradiations using 2 MeV helium ions (Mitchell 1984a, 1984b, Sood 1984, Sood 1985) and samples of various metal films on semiconductor and dielectric substrates. These results are summarised in table 2.2 which shows that, in general, higher doses are required than in previous observations of the effect on similar systems as might be expected from the lower ionisation density that will be produced by a 2 MeV helium ion when compared to the heavier ions used by other groups.

In several film/substrate combinations (e.g. Au/Si, Au/glass, Pt/glass) no threshold was found, presumably due to the threshold either being higher than the highest dose used (approximately $5 \times 10^{16}$ ions cm$^{-2}$) or due to some threshold ionisation density effect.

Table 2.2 Summary of RMIT observations of ion enhanced adhesion (Mitchell 1984a, 1984b, Sood 1984, Sood 1985).

<table>
<thead>
<tr>
<th>Material</th>
<th>Threshold dose for Q-tip adhesion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt on ZrO$_2$</td>
<td>$2 \times 10^{14}$</td>
</tr>
<tr>
<td>Pt on Al$_2$O$_3$</td>
<td>$1 \times 10^{14}$</td>
</tr>
<tr>
<td>Pt on glass</td>
<td>$4 \times 10^{16}$</td>
</tr>
<tr>
<td>Pt on Si</td>
<td>$1 \times 10^{15}$</td>
</tr>
<tr>
<td>Sn on GaAs</td>
<td>$1 \times 10^{15}$</td>
</tr>
<tr>
<td>Al on glass</td>
<td>$1 \times 10^{14}$</td>
</tr>
</tbody>
</table>

The work performed at the State University of New York (Berkowitz 1985) used modest velocity ions from carbon to phosphorus and gold films on silicon and glass substrates. In this case adhesion enhancement was only observed for silicon substrates, and even then only at high doses (around $10^{16}$ ions cm$^{-2}$). This is in
conflict with the results above where adhesion enhancement has been observed for Au on glass, but the complex behaviour of the substrate material under irradiation must be borne in mind. Cracking and compaction of the irradiated areas of the glass was observed. For silicon substrates, although the general level of adhesion was improved, the irradiation gave rise to the formation of 1-10 μm diameter blisters in the gold film, which appeared to be due to the release of gas into the interfacial region. The same effect could be produced by heating non irradiated samples, and was thus attributed to the desorption of surface contaminant species such as CO, O₂, N₂, H₂O which were trapped in the interfacial region during the deposition of the gold layer.

2.3 Stopping power dependence

One of the important parameters of the radiation enhanced adhesion process is the dose of ionising radiation required to produce an effect. In many cases the adhesion appears to increase dramatically at some threshold dose, above which the adhesion is either stable, or in some cases, further irradiation leads to a fall in adhesion due to some competing deleterious effect. It may well be that by studying the way this threshold dose varies for different combinations of film and substrate, or different types of ionising radiation, we may gain some insight into the mechanism of the effect. At the very least, any theory for the effect should seek to explain the observed variations in threshold doses.

Unfortunately there has been little systematic work of this kind on the effect; the majority of the observations are of the "thrash it and see" variety. The exception to this is the work by two groups on the ion enhanced adhesion of gold films on tantalum. The Caltech group measured the threshold dose of ions to produce scotch tape adhesion of gold films on tantalum substrates (Mendenhall 1983) using ions from 1 MeV protons up to 107 MeV krypton. In all cases a threshold irradiation dose to produce scotch tape adhesion was found, which varied from 3x10¹⁶ ions cm⁻² (protons) to 5x10¹² ions cm⁻² (krypton). When the data for threshold dose (D₉₀) is
plotted against the ion stopping power \((dE/dx)\) on a log/log plot a straight line fit produced the result that the threshold dose was quite well described by the formula

\[
D_{th} = 4.2 \times 10^{14} (dE/dx)^{-1.65}
\]

The same system of film and substrate was investigated some three years later (Stokstad 1986) using ions of constant velocity \((2.85 \text{ MeV/amu})\) from carbon to nickel. Again, the threshold dose for scotch tape adhesion was measured for a range of ions. When a straight line fit through their data was attempted the result was in this case

\[
D_{th} = 10^{17} (dE/dx)^{-3.0}
\]

Hence the second result found not only a different (higher) dose of each ion was required when compared to the previous measurement, but that the exponent of the stopping power dependence was also quite different. These results are compared in figure 2.1. There are only two obvious differences in the experimental procedures capable of explaining this discrepancy. The first is the different sample preparation procedure, which in the case of the measurements of Stokstad et al included a glow discharge cleaning step prior to the deposition of the gold film. However, in the original paper, it is stated that samples prepared without the glow discharge cleaning step did not require different threshold doses. The other significant difference is the velocity of the ions used for the irradiations, which was approximately 1 MeV per nucleon in the work of Tombrello et al compared to some 3 MeV per nucleon in the measurements of Stokstad et al.

The second measurement also included data on the way in which the threshold dose varied as a function of the incident angle of the ion. The threshold dose decreases as the ion impinges at a more acute angle to the surface, the dose being well fitted by \(D_{th} \propto \cos \theta\), which is in line with the behaviour of the sputtering yield
Figure 2.1: The published results of radiation enhanced adhesion measurement for the system of gold film on tantalum (Mendenhall 1983, Stokstad 1986). The least squares fit through observed threshold doses as a function of ion stopping power is shown. Note that the discrepancy between the two measurements is some two orders of magnitude in ion dose for ions with a stopping power of 1 MeV mg$^{-1}$ cm$^{-2}$. 
for low energy ion bombardment. The same publication also reported measurements of gold films on silicon substrates (all the above with native oxide layer). In this case the threshold dose was found to have an even stronger dependence on ion stopping power and to require yet higher doses. The threshold dose was well described by the formula

$$D_{th} = 6 \times 10^{18} (dE/dx)^{-4.1}$$

The lack of agreement between the two measurements on the gold on tantalum system is rather alarming, since if this were a general feature of experimentation in this field then it would appear to cast serious doubt on the use of threshold dose behaviour as a tool in furthering the understanding of the mechanism of the effect.

### 2.4 Other ionising radiations

The principle advantage of MeV ions for the investigation of irradiation enhanced adhesion is the extremely intense nature of their energy deposition into electronic processes. In the case of a 20 MeV chlorine ion the electronic energy loss exceeds 3400 eV per atomic diameter while passing through gold. At the interface between a thin film and a solid, such intense excitation can only be produced by MeV ions as they are the only form of intensely ionising radiation capable of reaching the interface.

Many groups have chosen, however, to investigate the effects of other forms of ionising radiation such as electrons beams, UV photons and gamma rays. The group at RMIT were the first to attempt experiments using electron and UV irradiation rather than MeV ions (Mitchell 1984a, Mitchell 1984b, Sood 1985). They found that a wide variety of metal films deposited onto silicon and glass substrates showed adhesion improvements after high dose keV electron (typically $10^{17}$ to $10^{18}$ cm$^{-2}$) or UV irradiation. The fact that such sources produce an effect was attributed to
there being a common electronic origin to the radiation enhanced adhesion phenomena. Interestingly, some irradiations were performed with an electric field across the interface, which resulted in a further enhancement of the adhesion level, which occurs independently of the polarity of the bias. This was attributed to an increased flux of low energy secondary electrons across the interface (generated in the material by the primary irradiation electrons), producing a higher degree of interfacial excitation.

Adhesion enhancement for gold films on teflon was observed due to keV electron and gamma irradiation by the group at Harwell (Sofield 1984). The dose of electrons required was somewhat lower (approximately $10^{16}$ cm$^{-2}$) as might be expected on a polymer substrate. Higher doses ($10^{18}$ cm$^{-2}$) were later found to be effective for films of NaCl on glass (Sofield 1987). Other workers report electron (2 keV) enhanced adhesion of gold films on silica (Battaglin 1986) at doses of around $10^{18}$ cm$^{-2}$.

One of the most interesting results of electron irradiation experiments concerns observations of gold adhesion on silicon both with and without a native oxide layer, prepared under Ultra High Vacuum (UHV) conditions (Dallaporta 1986). They found that irradiation by electrons of 1-3 keV energy and doses of $6 \times 10^{17}$ cm$^{-2}$ were effective in improving the adhesion of gold on a native oxide sample. If the gold is deposited on an atomically clean silicon surface (as verified by in-situ Auger Electron Spectroscopy [AES]), the gold shows good adhesion, and no evidence for improvement after subsequent electron irradiation. The electron irradiation is responsible for breaking up the native oxide layer, as observed by AES analysis of a native oxide sample both with and without monolayer gold coverage. Thus the adhesion improvements are attributed to the formation of gold/silicon bonds which are suppressed by the presence of a native oxide layer.
2.5 Observations of chemical changes

Only in a limited number of cases have changes in the atomic bonding arrangement at the sharp film/substrate interface been observed directly. Observations at Harwell using X-ray Photoelectron Spectroscopy (XPS) (Sofield 1984) to examine an irradiated gold/teflon interface showed enhanced adhesion to be accompanied by changes in the carbon and gold spectral lines attributed to formation of Au-C-F ternary complexes at the interface, no doubt driven by the release of fluorine radicals due to radiation damage of the teflon.

XPS has also been used in studies of the adhesion of gold films on gallium arsenide substrates (Wie 1988). In this case the adhesion enhancement from MeV ion irradiation was found to correlate well with the breakup of interfacial water vapour contaminants to form gallium hydroxide. The formation of such species at an exposed GaAs surface has been reported by other workers (Bardin 1988). In a further study, changes in the bonding of interfacial copper atoms on glass substrates following irradiation by 6 MeV silicon ions was observed using XPS (Chen 1989). Irradiated samples showed interfacial copper atoms to have a high degree of Cu(I) bonding compared to the Cu(0) bonding of the bulk film. Such Cu(I) bonding was absent in non irradiated samples.

Another technique which has been employed for observing chemical changes is Conversion Electron Mossbauer Spectroscopy (CEMS). The use of depth selective CEMS and metal films rich in $^{57}$Fe on glass substrates (Carbucicchio 1986) enabled not only the adhesion enhancement due to $10^{16}$ 100 keV protons cm$^{-2}$ bombardment to be measured, but the change in the local bonding environment of the interfacial $^{57}$Fe to be assessed in parallel. In this case a decrease in a feature attributed to Fe-C bonding was observed to correlate with the increased adhesion. This was attributed to breaking of bonds between the iron film and carbon containing contaminants at the interface, in favour of stronger direct bonding between film and substrate species. In a second study (Ingemarsson 1987), the adhesion of $^{57}$Fe films on teflon was investigated. It was found that irradiation by some $10^{13}$ 16 MeV sulphur ions cm$^{-2}$
produced a strong bond, which coincided with the appearance of CEMS spectral features which could be attributed to the formation of Fe-C and Fe-F bonds at the interface. In this study, the same features were observed for irradiated iron films on PVC, even though irradiation produced no adhesion enhancement for PVC substrates. Hence for polymer substrates, the formation of chemical bonds between film and substrate atoms does not necessarily lead to better adhesion.

A novel way to investigate interfacial rearrangement produced by MeV ion bombardment is the use of transmission ion channeling. In these measurements (Headrick 1985) the number of non-registered silicon atoms at the interface between a silicon single crystal and a metal overlayer was measured as a function of ion dose. In the absence of a metal layer no increase is observed, whereas for a silver film, disorder is produced at a rate of 0.078 atoms per ion and for a gold film 0.11 atoms per ion. This disordering is not due to direct primary nuclear collisions at the metal/silicon interface as it could not account for the observed efficiency, but were thought, by the authors, to perhaps be consistent with damage produced by recoil metal atoms being implanted into the silicon by a collision cascade process.

2.6 Effects of interfacial contamination

The large discrepancies between experimental results on nominally identical systems may well be attributable to variations in the contaminant species present in the interfacial region, which will inevitably be present in all samples prepared in other than Ultra High Vacuum (UHV) conditions. Such contaminants may take the form of native oxide layers (present on the surfaces of most metals) or adsorbates such as carbon monoxide and water vapour.

The power of such interface contaminants to completely dominate adhesion behaviour was illustrated by the experiments of John Baglin's group at IBM (Baglin 1985b). Alumina substrates were prepared by means of thermal and sputter cleaning followed by exposure to clean oxygen, purified water or ethanol.
This would be expected to result respectively in a clean oxygen terminated surface, a surface with adsorbed water vapour and a surface with adsorbed hydrocarbon. Deposition of copper films was followed by peel testing with and without an intermediate heat treatment and/or irradiation by helium and neon ions. The results are given in table 2.3. Note how the samples exposed to ethanol show negligible adhesion, even after irradiation or heat treatment. The preferred surface was oxygen terminated alumina, but again note how heat treatment produced dramatic improvements in the interfacial adhesion.

Table 2.3 Effects of interfacial contamination on adhesion of copper films on alumina (Baglin 1985b)

<table>
<thead>
<tr>
<th>Substrate preparation</th>
<th>Peel strength (arbitrary units)</th>
<th>not heated</th>
<th>450 degrees 1 hour</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>as deposited</td>
<td>Ne</td>
<td>as deposited</td>
</tr>
<tr>
<td>O₂</td>
<td>3.5</td>
<td>6.4</td>
<td>13.5</td>
</tr>
<tr>
<td>water</td>
<td>0.9</td>
<td>4.1</td>
<td>5.3</td>
</tr>
<tr>
<td>ethanol</td>
<td>0.0</td>
<td>0.0</td>
<td>2.2</td>
</tr>
</tbody>
</table>

Similar results have been reported for aluminium films on soda glass (Collins 1969) where differences in threshold dose were observed depending on whether the final surface treatment was a rinse in water or alcohol.

Most chemical treatments are done with the intention of providing a "clean" substrate surface. There is, however, a large volume of evidence that such procedures only serve to alter the type and level of contamination left on the surface. An example is provided by work on chemical cleaning of soda glass and fused quartz substrates (Carbucicchio 1986) in 10% HF followed by HCl:H₂O₂:H₂O (1:1:5) and ultrasonic rinsing in trichloroethene, acetone and ethanol. Even this extensive treatment resulted in surfaces with some 4x10¹⁵ atoms cm⁻² of carbon on the surface, indicating total coverage by a hydrocarbon layer.
2.7 Comparison of irradiation before and after deposition

One of the questions that arises in radiation enhanced adhesion is the relative roles of the small degree of mixing that may be produced at the interface, compared with the chemical effects due to ionisation induced excitation (breakup of bonding to contaminant species, etc). In an attempt to clarify the roles of such competing mechanisms, the relative efficiency of MeV ion irradiation before and after the deposition of a metal film has been investigated (Ingemarsson 1988). In these experiments the adhesion of gold films deposited in a good vacuum ($10^{-8}$ mbar) irradiation chamber either immediately before or after irradiation by $10^{12}$ to $2 \times 10^{15}$ chlorine ions cm$^{-2}$ at an energy of 20 MeV was examined. The substrates were alumina, silicon, silicon dioxide on silicon and fused quartz. In the case of dielectrics, the ability of MeV ions to induce sputtering of the surface from electronic excitation is well known. The sputtering yield is strongly dependent on the material properties in ways which are not yet understood. It was thus expected that irradiation prior to gold film deposition would be, to a greater or lesser extent, effective in producing a "clean" surface.

The results did not fit a simple pattern however, as is shown in table 2.4. For gold films on alumina, pre-deposition irradiation was found to be more efficient than post-deposition irradiation whereas for silicon and silica substrates the opposite was true. In the case of fused silica substrates, irradiation prior to deposition leads to films which preferentially fail in the irradiated areas, i.e. the adhesion is made worse by irradiation. No correlation with the previously observed electronic sputtering yields was found. The results were tentatively attributed to the fact that pre-deposition irradiation mainly results in some removal of contaminant species from the surface and perhaps a degree of surface enrichment in one of the species which may or may not be beneficial. Post-deposition irradiation was thought to lead to improved adhesion by the production of new interfacial chemical species involving film and substrate atoms. This chemical approach was supported by the fact that silver films behaved differently to gold films on silicon and silica substrates. Silver adheres better
to a surface containing oxygen, whereas gold adheres better to clean silicon. This is attributed to the fact that silver forms compounds with oxygen whereas gold does not, and evidence for gold-silicon bond formation has been found in some cases (Bauer 1980).

Table 2.4 Threshold doses for irradiation of gold films performed both pre and post deposition (Ingemarsson 1988)

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Pre-irradiated threshold dose (ions cm$^{-2}$)</th>
<th>Post-irradiated threshold dose (ions cm$^{-2}$)</th>
<th>Erosion yield (atoms/ion)</th>
</tr>
</thead>
<tbody>
<tr>
<td>alumina</td>
<td>2x10$^{13}$</td>
<td>2x10$^{14}$</td>
<td>&lt;0.22</td>
</tr>
<tr>
<td>silicon</td>
<td>2x10$^{14}$</td>
<td>2x10$^{13}$</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>fused silica</td>
<td>de-adhesion</td>
<td>1x10$^{15}$</td>
<td>2.9</td>
</tr>
<tr>
<td>silica on Si</td>
<td>5x10$^{14}$</td>
<td>5x10$^{14}$</td>
<td>-</td>
</tr>
</tbody>
</table>

2.8 Adhesion degradation observations

In almost all studies that have been reported in the literature, the effect of irradiation is to improve adhesion of any thin film. In many cases the improvement is modest though very significant, perhaps a factor of 2 to 5. In some cases a greater factor has been reported. The cases where irradiation proves detrimental to adhesion are few, but are indicative of the fact that this is not a simple phenomenon, and numerous competing mechanisms are often at work.

As briefly mentioned in section 2.2, irradiation of gold films on glass has been observed to give rise to blistering (Berkowitz 1985). As stated previously, the blisters were assumed to be due to the release of interfacial contaminant species, and could be reproduced just by heating to temperatures above 350 Celsius. In the study of the irradiation induced adhesion of gold films on Al$_2$O$_3$ it has been observed that 10$^{14}$ to 10$^{17}$ 1 MeV nitrogen ions cm$^{-2}$ gives rise to the formation of dome shaped blisters of up to one micron size for sapphire substrates, but not for Al$_2$O$_3$ grown on aluminium.
by anodic oxidation (Daudin 1988).

We have also observed bubbles produced by MeV ion irradiation of gold films on deposited tantalum pentoxide which contained some 10% atomic hydrogen (Sugden 1990). The effect was avoided by a pre-deposition anneal step in air or vacuum, which was shown to completely remove the hydrogen contaminant. Sequential Elastic Recoil Detection Analysis measurement using a 30 MeV $^{35}$Cl$^{6+}$ beam also proved that hydrogen was indeed released from the substrate material by irradiation, at a rate consistent with the observation of bubbles formed by the release of such hydrogen into the gold/substrate interface.

### 2.9 Summary

As we have seen, there is a significant body of published experimental work on the effects of radiation on thin film adhesion. The effect appears to be universal, in that almost all systems studied to date show beneficial effect from irradiation. The observations suggest a common electronic origin for the effect, since it is observed with not only high energy ions, but also with electron, gamma and UV irradiation. For this reason we should not seek to explain the effects observed in ion irradiated samples solely on the basis of nuclear stopping. This should not, however, rule out contributions from nuclear recoil mixing, but in the high energy ion regime, where electronic stopping is dominant, such effects are likely to be of secondary importance in the dose range of interest.

In a few cases, changes in chemical bonding arrangements have been observed at the film/substrate interface which would support a radiolysis type mechanism.

The observation of threshold doses as a function of film and substrate species is, in general, in line with the expectation that primary energy loss processes are important (high stopping power leads to low threshold dose). Assorted measurements have highlighted the important influence of sample preparation (and in particular surface contaminants) on the observed behaviour, suggesting that the structure and
composition of the interface region has a dominant effect on the adhesion behaviour of thin films.
CHAPTER 3

Theory

The observation that high energy particles and other irradiation processes can produce significant improvements in thin film adhesion is relatively recent, and hence has received scant attention from the theorist community. One of the goals of any comprehensive theoretical approach must be to explain the observed trends of threshold doses for adhesion improvement with different irradiation species, and with different couples of film and substrate. A major handicap has to be the poor reproducibility of the experiments performed to date, which in many cases report discrepancies of greater than an order of magnitude, in experiments on nominally the same system. Although in many cases this may be attributable to variations in sample preparation methodologies, some of the variability must be due to the inherent short comings of commonly applied adhesion tests.

The theories to explain the phenomena, such as they are, fall basically into two categories; those which seek to explain improved adhesion in terms of radiolytically induced atomic bonding rearrangements in the excited ion wake (chemical theories), and those which consider the contributions from image charge interactions with near interface charged defects or mixing produced by MeV sputtering to be the most important (structural theories). The latter is applicable only in the case of metal films on insulator (or to a lesser extent semiconductor) substrates. The current status of these approaches is reviewed briefly in the following sections.

3.1 Interface chemistry theories

Rather than a simple single theory, interface chemistry encompasses a range of non equilibrium phenomena which may occur in the excited wake of any form of ionising radiation. As stated previously, the principle effect of such radiations is the disruption of the initial electronic configuration, leaving the atoms at the interface
between film and substrate in an excited state, which may lead to a variety of epithermal processes. In the case of MeV heavy ions, such excitation may extend many atomic diameters (Kobetich 1968) from the path of the ion, which of course makes them particularly efficient at producing the observed effects.

The main concept in such interface chemistry theories is radiolysis, i.e. the ionisation induced bond breaking and rearrangement which must occur to some extent in the excited region of the ion wake. Such "hot chemistry" may perhaps be thought of as breaking up the weak bonding between the substrate surface and contaminant species such as water, hydrocarbons and the like which will be present at all interfaces (except those formed in Ultra High Vacuum (UHV) conditions). The substrate atoms may then be inclined to form new bonds involving the film species atoms, perhaps forming ternary compounds with any radical species formed from the ionisation of the contaminants. It is certainly the case, that in interfaces produced in conventional coating equipment, where no in-situ surface cleaning is done prior to film deposition, it is quite typical for one or two monolayers of hydrocarbon to be present at the film/substrate interface (Carbucicchio 1986). Such hydrocarbon layers, when present on the surface, have been shown to decompose under irradiation, and indeed in some cases, chemical changes involving carbon contaminant species at a film substrate interface have been observed (Carbucicchio 1986, Ingemarsson 1987).

If interfacial contaminant layers were the key to the radiation enhanced adhesion phenomenon then one would expect the effect to occur for all combinations of film and substrate, where a limiting contaminant layer exists. The corollary of this, of course, is that an atomically clean interface should show no benefit from irradiation. Experiments using UHV preparation techniques would thus be expected to cast considerable light on the validity of such arguments.
3.2 Image charge interaction theory

This theory, put forward by Stoneham and Tasker, seeks not only to explain the radiation enhanced adhesion phenomenon for metal films on dielectrics, but the adhesion of such films in general (Stoneham 1985). It relies on the elegant concept of image charges induced in the metal layer by the fixed charges in the near surface of the insulator.

The concept of image charges is well established. Across any boundary between materials of different dielectric constants $\varepsilon_1$ and $\varepsilon_2$, any fixed charges in the insulator will polarise the adjacent metal atoms, an interaction which can most readily be imagined in terms of an induced image, of opposite polarity, at a position which is a mirror image using the boundary as a reflecting plane, as illustrated in figure 3.1. The electrostatic attraction between a charge $Q$ and its classical image a distance $z$ from the boundary results in a lowering of the interfacial energy by an amount $U(z)$, given by,

$$U(z) = \frac{Q^2}{2z\varepsilon_1} \left( \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + \varepsilon_2} \right)$$

which in the case of a dielectric with $\varepsilon=10$, and unit charge located one atomic diameter from the interface with a metal gives a reduction in the interfacial energy of approximately 0.2 eV, or in other words, a contribution of the same order as Van der Waals forces. For a simple ionic crystal, such as sodium chloride, the images in any metal overlayer will simply tend to continue the existing lattice of charges, resulting in a lowering of the interfacial energy by an amount close to the free surface energy of the unrelaxed crystal.

This model has received experimental support from trends in such processes as the wetting of oxide surfaces by unreactive liquid metals (a property which can be related to adhesion) (Stoneham 1985). Analysis has shown that such wetting phenomena are very poorly described by Van der Waals interactions, and is independent of the liquid metal providing the metal does not react chemically with the
Figure 3.1: A schematic representing the image charge mechanism of thin film adhesion. Fixed charges in the dielectric substrate induce classical images in the metal film close to the film/substrate interface. The interaction produces a net attraction, and a corresponding lowering of the interfacial energy.
insulator. A correlation with the dielectric constant of the insulator was noted, which allowed the criterion for wetting to be established as a static dielectric constant exceeding 25 or the ability to change ion valence. The former gives enhanced image interaction directly from the formula above, the second from the fact that the image term is not linear with Q, and hence $2M^{2+}$ going to $M^{1+}$ and $M^{3+}$ will result in a 25% increase in electrostatic attraction.

This theory also seeks to explain the enhancement of adhesion by irradiation, since the damage produced in the dielectric region close to the metal will include charged defects, with associated images in the metal layer (Stoneham 1987). Such additional image charge contributions have been shown to be fully consistent with the observed increases in adhesion assuming significant but reasonable concentrations of near surface defects.

It is important to note that this mechanism is only relevant to metal on insulator systems, and to a lesser extent, metal on semiconductor and will not be a factor in metal on metal adhesion. In all but a few cases, however, experimental limitations on substrate preparation result in significant contamination of metal substrate surfaces with native oxide and other light element containing layers, and hence in many practical situations metal on metal adhesion may still involve image charge effects. From the above it is quite straightforward to calculate the beneficial effect of a single charged defect close to the dielectric/metal interface. The problem, however, is to determine the concentration and distribution of such defects in the interfacial region, which is rather more difficult experimentally. In the case of MeV ion irradiation, for example, the majority of charged defects produced in a dielectric result from poorly understood collective electronic excitation phenomena. In cases where suitable analytical tools have been brought to bear on the problem, such as the transmission channelling work of Headrick and Seiberling (Headrick 1985), the increase in non-registered silicon at the metal non-metal interface could be interpreted in more than one way. The increase in disorder could either be a direct result of irradiation, producing the secondary benefit of improved adhesion from image charge
interactions or, alternatively, the increase could be due to chemical reaction between lattice silicon atoms and the metal layer, moving them from their initial lattice sites.

3.3 Mixing produced by electronic sputtering

With low energy ions, a large fraction of their energy deposition directly produces atomic displacements, leading to collision cascades and the phenomenon of sputtering. For high energy ions, the probability of such atomic collisions is small, and relatively few atomic displacements are produced by this mechanism. Hence the ability of low energy ions to produce mixing at the interface between a film and substrate is all but absent for MeV ion irradiation, and the interface remains abrupt, even at quite high doses (Mendenhall 1983).

Sputtering has been observed, however, in the case of MeV ion irradiation of dielectrics, at a rate far exceeding what one would expect on the basis of direct atomic collision interactions (Tombrello 1984). Such sputtering is the result of electronic excitation of the material, which gives rise to a highly ionised region in the ion wake which, due to the long electronic relaxation time of dielectric materials, is able to give rise directly to the formation of atomic displacements. When such displacements meet the surface the result is sputtering. The effect has been studied by various groups with the surprising observation that the sputter yield varies dramatically from material to material in ways that are not understood. It also depends on the form of the material. For example, the yield differs greatly for SiO$_2$ in the form of a thick thermally grown oxide on silicon when compared to SiO$_2$ in quartz and borosilicate glass (Qiu 1983). Yields as high as 50 atoms per ion have been observed in the case of SiO$_2$ on silicon (Sugden 1991), but are vanishingly small for semiconductors, such as silicon, or metals (Tombrello 1984). The energy distribution of the sputtered particles has been measured in some cases, and has been found to have a Maxwellian distribution with a characteristic temperature of a few thousand Kelvin (Griffith 1980).

The reason this electronic sputtering has relevance to radiation enhanced
adhesion is that should such processes occur in a dielectric substrate material coated with a metal layer, one might expect the atomic rearrangements due to recoiling species to produce some degree of mixing at the abrupt film/substrate interface. The energy of the recoils would be such that very little penetration would occur, and hence such processes would only lead to mixing at the level of a monolayer or two. This would still be sufficient to produce beneficial effects on adhesion, particularly if it lead to the disruption of an interfacial contaminant layer.

This approach has much in common with the image charge interaction case since it would be valid only when a dielectric layer is present, but as stated above this is not very limiting since in many systems of film/substrate a native oxide layer may be present on the substrate surface.

A major problem with such an explanation is the dramatic variation of the sputtering yield from material to material, which is generally not reproduced in the threshold dose observations. This is particularly true in the case of native oxide and thermal oxides of silicon. For a 20 MeV chlorine ion incident on a thermal oxide the sputter yield is approximately 3 whereas for a native oxide on silicon the yield is less than 0.01. The observed threshold doses for adhesion enhancement for gold films on these two substrates are found to be comparable, which does not support such electronic sputtering as being the prime factor in the adhesion modification of these systems. Another factor against such a theory is the observation highlighted above, that sputtering is suppressed in the case of native (i.e. thin) oxides of silicon. This is believed to be due to electron injection from the substrate, which is able to quench the highly ionised region around the ion trajectory before atomic motion occurs. If this is the case, we would also expect such electron injection to occur from a metal overlayer on a dielectric substrate, which would also act to quench the atomic motions, which might otherwise lead to mixing at the abrupt metal/dielectric interface.
CHAPTER 4

Experimental approach and method

In this chapter we will briefly highlight the most important conclusions reached from study of the published observations of the radiation enhanced adhesion phenomenon, and explain our chosen course of investigating the effect through performing certain key experiments under precisely controlled conditions.

4.1 Conclusions from published material

The basic aim of this project is to further the understanding of the effect of radiation enhanced adhesion. It was our hope that with the available range of facilities at the Harwell Laboratory, in both the thin film and radiation effects areas, that significant progress would be possible by the pursuit of certain key experiments, with precise control of the most important experimental parameters.

From a thorough examination of the dozens of published observations two things become clear. Firstly, despite the wide variety of systems studied (film/substrate combinations) the effect would appear to be universal, in that in virtually all systems investigated irradiation produces some tangible benefit to film adhesion. In some cases the improvement is modest though significant; in others the force to peel the film increases by as much as two orders of magnitude, and the evidence suggests this to be a property of the particular film/substrate combination. This universality is despite the wide variety of irradiation species utilised which have included ions, electrons, gamma rays and UV photons. In a very limited number of cases, a degradation in adhesion has been observed which is attributable to a dominant deleterious effect, often involving adsorption or incorporation of light element species which are released into the interface region between film and substrate causing bubbles to be formed.

The second, less promising, observation is the large discrepancy in threshold
doses for adhesion enhancement in observations by different groups on the same system of film and substrate. This is most strikingly illustrated in the work of Tombrello et al (Mendenhall 1983) and Stokstad et al (Stokstad 1986) on the MeV ion adhesion modification of gold films on tantalum. In each case the threshold dose to produce scotch tape adhesion for a range of ions was measured in order to ascertain whether any universal dependence of the effect on ion stopping power (dE/dx) existed. Their results were dramatically different both in terms of the threshold doses and the dependence on dE/dx as shown in figure 2.1. At the lighter ion end the difference in observed threshold dose was some two orders of magnitude, which in all but cosmological fields would be regarded as a large difference indeed! As stated at the time, the discrepancy is most likely due to a systematic difference in the experiments. The prime candidates are the glow discharge cleaning step in the preparation procedure, or the higher velocity ions used by Stokstad et al.

4.2 Experimental approach

Other factors which shaped our course on the experimental front were the difficulties involved in making appropriate measurements of what exactly was occurring at the crucial film/substrate interface as a consequence of the irradiation. Ideally one would like to observe chemical and/or structural changes in the interface region, but the majority of techniques which are sensitive to such changes either sample too large a depth (XRD, RAMAN, etc) to be sensitive to the interfacial monolayers or sample too small a depth (XPS, AES, etc) to be of use in studying the interface between a continuous thin film and the underlying substrate. Perhaps the most promising techniques for study of interface structure are those of Transmission Electron Microscopy (TEM) and Scanning Tunnelling Microscopy (STM). The ability of TEM to produce near atomic resolution of interface structure has proved beneficial in the development of epitaxial film growth processes in the semiconductor industry (Bean 1984), as well as the study of radiation damage processes in single crystals.
(Sato 1980). The key problems which precluded its use in the present work were firstly the very time consuming and often low yield of the sample preparation procedures involved, and secondly concerns that such procedures would alter the very interface structures we were hoping to observe. A common method of thinning samples to the type of dimensions necessary for TEM work (< 50 nm) is to mechanically section the sample followed by etching using a low energy ion beam. As stated in the experimental review chapter, such ion beams have been shown to produce the very effects we seek to observe, and hence any technique which relies on such processes can be ruled out as being destructive in the present context. The second technique highlighted in that of Scanning Tunnelling Microscopy. The atomic resolution of such instruments suggest them to be ideal tools in the investigation of structure on the atomic scale. There are, however, several obstacles which must be overcome before such tools may be successfully applied to the study of radiation enhanced adhesion. Firstly, the STM is only appropriate to the investigation of conducting samples, and thus severely limits the range of systems which may be investigated. The technique also suffers from sensitivity to surface cleanliness which precludes its use on the contaminated surfaces which form the basis of the majority of film/substrate interfaces. The ability of STM’s to investigate interface properties either by in-situ sectioning of samples (Feenstra 1986) or by looking at electron injection into the underlying substrate (Hallen 1991) are still very much in their infancy. It is possible that the new generation of atomic resolution instruments under development which sample alternative surface properties (lead currently by the Atomic Force Microscope) may well be appropriate tools in the future.

It was thus decided that rather than look directly for the changes produced by irradiation, we would attempt to gain an understanding of the important parameters which determine the efficacy of the process. Once the important parameters were isolated, the hope was that an objective appraisal of these parameters would itself suggest the most likely mechanism, or at the very least, severely limit the range of credible mechanisms.
Such an experimental approach relies heavily on the ability to produce reliable and reproducible adhesive behaviour. The discrepancy, highlighted above, in the results of two methodical studies of the MeV ion enhanced adhesion of the same film/substrate combination was thus of great concern. It was therefore decided to investigate this discrepancy by repeating the measurements on this system of gold on tantalum, to ascertain whether the differences in the results represented some fundamental limitation in the reproducibility of such experiments (which would obviously make progress by experimental means all but impossible) or due to some systematic difference between the two measurements, in for example sample preparation, or the velocity of ions used in the irradiations.

4.3 Experimental method

Initial experiments were thus performed on the system of gold film on tantalum substrates (with native oxide) using conventional sample preparation equipment, closely mimicking the experiments performed by the other groups. These measurements are described in detail in chapter 5.

Our deduction at that time that sample preparation was likely to be the key to the whole question lead us, in parallel, to develop a unique Ultra High Vacuum (UHV) sample preparation system at Harwell known by the acronym SURF, which is described in some detail in the appendix section.

This system contains a unique combination of surface processing stages all contained within a single UHV envelope with a base operating pressure of $2 \times 10^{-10}$ mbar. The system consists of the following functional units:

- Sample introduction via load-lock
- 0-30 keV ion source (differentially pumped)
- Oxidation furnace
- Metal film deposition
In-situ analysis (Low and Medium Energy Ion Scattering)

- vacuum transfer to MeV analysis and irradiation facilities

In *SURF* we have the capability to control surface and hence interface composition and crystallinity, and to deposit films at pressures which ensure the interface to be virtually free of contaminant species. Vacuum transfer to our MeV irradiation facilities was developed to eliminate any possible effects from atmospheric exposure prior to irradiation. With such control, a positive insight into the role of such factors as native oxide and contaminant layers, adsorbates, image charges and the like should be possible.

In the chapters which follow the experimental work performed in the current project is described in detail. Initial experiments were performed on the radiation enhanced adhesion of gold films deposited onto polished tantalum discs performed in conventional coating and irradiation facilities, with conventional modest vacuum of the order of $10^{-6}$ mbar. The adhesion of the films was assessed using both the scotch tape and scratch testing methods, both with and without irradiation by a range of MeV ions. The work on the gold on tantalum system was then repeated and extended in the UHV sample preparation facility *SURF*, utilising the vacuum transfer to a UHV irradiation chamber. The work on tantalum, with and without native and thermal oxide layers, provides an example of both metal on metal and metal on insulator systems. To extend our understanding to systems of metal film on semiconductor we then performed experiments on the gold film on silicon system, both with and without native and thermal oxide layers. Finally, the effect of the film species was investigated by performing a limited number of experiments using silver films on silicon/silica substrates.
CHAPTER 5

Gold film on tantalum (conventional vacuum)

The system of gold film on tantalum was chosen for the reasons outlined above, namely to investigate the discrepancy reported in the dependence of threshold adhesion dose with ion stopping power in the two published studies of Tombrello et al (Mendenhall 1983) and Stokstad et al (Stokstad 1986). Both groups found the threshold doses to have a power law dependence on ion stopping power dE/dx, i.e.

\[ D_{th} \propto (dE/dx)^n \]

but reported dramatically different exponent values of n=1.6±0.2 and n=3.0±0.2. It was our aim to repeat this measurement to see if the discrepancy could be attributed to a systematic difference in the experimental methods of the two groups. From their descriptions these were essentially the same other than a glow discharge cleaning step used prior to gold film deposition, and the higher ion velocities in the work by Stokstad et al. The sample preparation procedure followed here closely follows that of Tombrello et al, i.e. no glow discharge cleaning step.

5.1 Experimental procedure

5.1.1 Sample preparation

The tantalum samples were 25 mm diameter discs cut from 99.9% purity tantalum sheet and mechanically polished in conventional metallographic polishing equipment using 14 μm diamond paste in order to achieve a uniform surface finish. Samples were then degreased in an ultrasonic bath filled with a 1:1 aqueous solution of RBS25 detergent, rinsed in water and then etched in a 1:1 aqueous solution of nitric acid followed by a final rinse in distilled water prior to loading into the vacuum coater,
an Edwards E306. The nitric acid etch is intended to remove the native oxide layer but in practice was found to have little effect, since tantalum will readily re-oxidise. The step was retained however, for consistency with the previous measurements. Gold was evaporated from a molybdenum boat, by resistive heating, to a thickness of 50 nm at 0.5 nm s⁻¹ at a pressure of 3x10⁻⁶ mbar. The film thickness was determined by a quartz crystal oscillator adjacent to the samples. The samples were then stored in air until required for irradiation.

5.1.2 Irradiation

The irradiations were performed on the Harwell tandem accelerator in a chamber pumped by a liquid nitrogen baffled diffusion pump with a typical operating pressure of 5x10⁻⁶ mbar. The beam in each case was collimated to an area of 4 x 4 mm some 0.5 m upstream of the target. The true irradiation dose was calculated from the measured area of the remaining gold on samples passing the scotch tape adhesion test. Although the beams used were not scanned, the uniformity of the beam across the exposed area is estimated at no worse than a factor of two from consideration of the observed adhesion threshold behaviour.

Table 5.1 Detail of ions used in sample irradiations.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Machine energy (MeV)</th>
<th>Energy at interface (MeV)</th>
<th>Stopping power in gold Electronic (MeV mg⁻¹ cm²)</th>
<th>Stopping power in gold Nuclear (MeV mg⁻¹ cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>¹H</td>
<td>5.0</td>
<td>4.99</td>
<td>0.028</td>
<td>0.0001</td>
</tr>
<tr>
<td></td>
<td>1.2</td>
<td>1.19</td>
<td>0.059</td>
<td>0.0001</td>
</tr>
<tr>
<td>⁴He</td>
<td>15.0</td>
<td>14.99</td>
<td>0.132</td>
<td>0.0001</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>1.97</td>
<td>0.339</td>
<td>0.0005</td>
</tr>
<tr>
<td>¹²C</td>
<td>30.0</td>
<td>29.87</td>
<td>1.316</td>
<td>0.0011</td>
</tr>
<tr>
<td>¹⁶O</td>
<td>31.0</td>
<td>30.78</td>
<td>2.285</td>
<td>0.0025</td>
</tr>
<tr>
<td></td>
<td>9.0</td>
<td>8.76</td>
<td>2.451</td>
<td>0.0068</td>
</tr>
<tr>
<td>¹⁹F</td>
<td>10.0</td>
<td>9.72</td>
<td>2.817</td>
<td>0.0091</td>
</tr>
<tr>
<td>³⁵Cl</td>
<td>18.0</td>
<td>17.43</td>
<td>5.720</td>
<td>0.0321</td>
</tr>
<tr>
<td>⁸¹Br</td>
<td>40.0</td>
<td>38.97</td>
<td>9.955</td>
<td>0.1323</td>
</tr>
</tbody>
</table>
The irradiation dosimetry was performed by monitoring the fraction (some 10%) of the beam scattered into a surface barrier detector by a gold coated rotating blade beam chopper just upstream of the target. This detector was calibrated against a well suppressed Faraday cup for each beam species immediately prior to irradiation to an accuracy of a few percent. The irradiations comprised four doses on each sample along the centre line in a logarithmically increasing sequence as shown in figure 5.1 which shows a sample irradiated by 20 MeV chlorine ions after the scotch tape test. The beams used are summarised in table 5.1, and ranged from 5 MeV protons at the fast light ion end up to 40 MeV bromine at the slower heavy ion end. The table also gives the electronic and nuclear components of the ion stopping power in a gold film, which clearly demonstrates the dominance of electronic processes at these high ion energies.

### 5.1.3 Adhesion assessment

The techniques employed in the present studies are the scotch tape and scratch adhesion tests. In the scotch tape test, scotch pressure sensitive tape is applied to the sample surface and rubbed using a blunt instrument. The tape is then pulled, perpendicular to the surface, and the deposited film, in this case gold, is either removed with the tape (fail) or remains on the substrate (pass). It is an example of a threshold adhesion test and is capable of surprisingly reproducible results, but has the disadvantage of being a rather weak test of adhesion since only modest adhesion is required to pass. It is worth noting that as deposited gold films on most substrates, or most films on inert substrates such as teflon, will in general fail the scotch tape test. A sample subjected to this test is shown in figure 5.1. A pass was only awarded if the entire beam spot survives the test intact as that shown at the bottom of the figure.

In the scratch test a modified Revetest micro-hardness tester was used with a Rockwell C profile 100 µm diameter diamond dragged across the surface at a constant
0.5 mm s\(^{-1}\) with loads from 0 to 500 g. Examination of the tracks produced under a microscope enabled the critical load to remove the gold film to be determined. In the case of gold films this was easy to observe, as a clear colour change occurs as the underlying substrate is revealed. The advantage of scratch testing is that the load can be varied to obtain some quantitative estimate of the degree of adhesion (Benjamin 1960), although relating a critical load to any useful quantity is all but impossible since the details of the precise failure mode during film stripping varies from system to system (Bull 1988). The test is however very useful as a ranking test to determine the relative effectiveness of alternative preparation schemes. The details of the mechanics of these two adhesion tests and a brief description of other techniques used to quantify adhesion are given in appendix A1.

5.2 Results

Unirradiated samples mostly failed the scotch tape test indicating poor as deposited adhesion and requiring a scratch test load of approximately 20 g to initiate film stripping. Irradiation with 5x10\(^{13}\) chlorine ions cm\(^{-2}\) improved the adhesion of the gold film as shown in figure 5.1 such that the scotch tape test was passed and scratch testing required some 200 g load to remove the gold film. Similar improvements were observed with the other ion species but with progressively higher doses being required of the lighter ions. The threshold doses to pass the scotch tape test are given in table 5.2, for each ion species, along with the dose required to pass the 200 g load scratch test for comparison purposes. The data for threshold doses are plotted against ion stopping power in the gold overlayer in figure 5.2, which also has the data reported by Tombrello and Stokstad. The data we obtained are well fitted by a power law dependence on the stopping power \((dE/dx)\) with least squares fitting giving a threshold dose of 4.8x10\(^{14}\)(dE/dx\(^{1.42+0.11}\) (scotch tape test) and 4.5x10\(^{14}\)(dE/dx\(^{1.48+0.12}\) (scratch test 200 g load). The data obtained is thus in reasonable agreement both in terms of
Figure 5.1: A typical scotch tape test sample after testing. The sample has been irradiated with four distinct doses of $20 \text{ MeV } ^{35}\text{Cl}$ ions which were a)$5 \times 10^{12}$, b)$1 \times 10^{13}$, c)$2 \times 10^{13}$ and d)$5 \times 10^{13}$ ions cm$^{-2}$ respectively. A pass is only awarded when the entire beam spot survives the tape test intact, as in d) above.
observed power law dependence and absolute doses with that obtained previously by the Caltech group (Mendenhall 1983). Consistent results were also obtained with both of the adhesion test method used.

Table 5.2  Threshold dose to pass the scotch tape and scratch adhesion tests, for gold films on tantalum substrates.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Energy at interface (MeV)</th>
<th>Threshold dose (ions cm$^{-2}$) Scotch tape</th>
<th>Threshold dose (ions cm$^{-2}$) Scratch test</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1$H</td>
<td>4.99</td>
<td>$1 \times 10^{17}$</td>
<td>-</td>
</tr>
<tr>
<td>$^4$He</td>
<td>14.99</td>
<td>$8 \times 10^{15}$</td>
<td>$8 \times 10^{15}$</td>
</tr>
<tr>
<td>$^{12}$C</td>
<td>29.87</td>
<td>$1 \times 10^{14}$</td>
<td>$5 \times 10^{14}$</td>
</tr>
<tr>
<td>$^{16}$O</td>
<td>30.78</td>
<td>-</td>
<td>$2 \times 10^{14}$</td>
</tr>
<tr>
<td>$^{19}$F</td>
<td>8.76</td>
<td>$4 \times 10^{14}$</td>
<td>$1 \times 10^{14}$</td>
</tr>
<tr>
<td>$^{35}$Cl</td>
<td>17.43</td>
<td>$2 \times 10^{13}$</td>
<td>$5 \times 10^{12}$</td>
</tr>
<tr>
<td>$^{81}$Br</td>
<td>38.97</td>
<td>$2 \times 10^{13}$</td>
<td>$5 \times 10^{12}$</td>
</tr>
</tbody>
</table>

5.3 Sample preparation differences

At the time these experiments were performed, the fact that we reproduced the result of the Caltech group was taken as being very significant since the result of Stokstad et al immediately became an anomaly attributable to the key sample preparation difference, namely the use of a glow discharge cleaning step. Glow discharge cleaning involves making the substrate the cathode of an argon ion discharge at typically a few hundred volts, and is thus a crude form of sputter cleaning. The process will tend to disrupt the native oxide layer that is inevitably present on the surface of the tantalum prior to deposition, despite the preceding preparation steps, due to the ability of tantalum to readily form a thin surface oxide layer upon exposure to air at room temperature. This confirmed our suspicion that
surface preparation was the key to understanding the effect of irradiation enhanced adhesion, and lead us to proceed to experiments under conditions where the substrate surface composition in terms of native oxide layers, surface contaminants and adsorbates, could be controlled.

Quite how such surface pre-treatment could account for the observations is rather less clear. Why should glow discharge cleaning make subsequent radiation processing less efficient? Changes in the thickness and nature of interfacial contaminants could result in different levels of as deposited adhesion, and might also explain why the difference in threshold dose for a particular ion, since the system (film/contaminant/substrate) would be different in each case. What is more difficult to explain is the significantly different slope of the stopping power dependence, i.e. $n=1.42\pm0.1/1.48\pm0.1$, $n=1.6\pm0.2$ (our measurements and Tombrello et al) and $n=3.0\pm0.2$ (Stokstad et al). This suggest more of a systematic difference in the mechanism of adhesion enhancement itself. The only other difference, other than sample preparation methods, is the ion velocities used. Both our initial experiments, described above, and those of Tombrello et al, used a range of ion velocities, which average some 1 MeV per nucleon. The irradiations performed in the work of Stokstad et al used ions of one velocity, corresponding to an energy of 2.85 MeV per nucleon, which is significantly higher. Since the results are plotted against the ion stopping power ($dE/dx$) then if process has some intrinsic physical dependence on the stopping power then the velocity of the ion should not be of primary importance, providing the primary interaction processes are the same (i.e. electronic stopping). If the velocity of the ion were an important factor, it would immediately call in to question the validity of looking at stopping power dependence in isolation. This doubt regarding the importance, or otherwise, of ion velocity was a factor in deciding to carry out all subsequent ion irradiations at a common ion velocity at the film/substrate interface of 0.04c, or roughly 0.75 MeV per nucleon.
Figure 5.2: Results of measurements of threshold ion dose to pass both the scotch tape and scratch adhesion tests, as a function of ion stopping power. The fits to the data, and those to the previously reported measurements by Tombrello et al and Stokstad et al are also shown. Note that the two adhesion tests produce almost identical results, which are in reasonable agreement with those of Tombrello et al.
CHAPTER 6

Gold film on tantalum prepared in UHV

As stated in the preceding sections, the SURF preparation facility was built in order to perform experiments on the adhesion of unreactive thin films and the effect of MeV ion irradiation. The first step of this programme was to repeat the measurements previously performed (i.e. gold film on tantalum substrate) but with Ultra High Vacuum (UHV) preparation techniques. In the experimental description which follows, only the most important aspects of the SURF system are described; for a fuller description refer to appendix section A3.

In the experiments which follow, the adhesion of gold films deposited on tantalum substrates, both with and without native and thermal oxide layers, has been investigated. The effects produced by MeV ion irradiation using beams from the Harwell Tandem accelerator have also been assessed. Much use is made in the following sections of the terms "clean" and "dirty" in relation to substrate preparation state. It is important to understand that these terms are being used for convenience, and are not intended as an accurate or exhaustive description of the substrate surface, in terms of freedom from adsorbates, etc. The terms merely indicate whether any pre-treatment, or cleaning, of the substrate occurred in UHV prior to deposition of the metal film.

Hence in this context:

"dirty" = put through chemical cleaning procedures prior to loading

"clean" = treated in UHV in an attempt to obtain a clean surface

Many papers testify to the inability of chemical techniques to produce clean surfaces (Henrich 1985, Carbucicchio 1986, Pronko 1984). All claims made for
cleaning procedures should be viewed sceptically unless supported by evidence from in-situ analysis techniques, which can show the surface to be free from native oxide layers, adsorbed water vapour, hydrocarbons, adsorbates and the like. Hence in the current context, the terms "dirty" can also be defined as most probably contaminated, and "clean" as quite possibly contaminated.

6.1 Experimental procedure

In the work described in this section, the substrate consists of 15 x 15 mm tantalum sheet sections with various pre-treatments. Firstly, tantalum sheet with a native oxide layer, with precisely the same pre-treatment as in the previous conventional vacuum experiment. Secondly, tantalum with a thick thermally grown oxide layer on the surface. The third substrate type is atomically clean tantalum, achieved by low energy argon sputtering. Finally, the adhesion of gold to UHV cleaned thermal tantalum oxide was investigated.

6.1.1 Sample preparation

All the tantalum samples were produced by cutting 15 x 15 mm sized sections from 99.9% pure tantalum sheet. The size of sample is determined by the UHV preparation system, which is designed to work with bare samples, i.e. without carriers, and hence the various treatment and analysis stations, as well as the transport between them, rely on a uniform sample size. The tantalum samples were not polished in any way, as the lengthy, and sometimes unproductive, metallographic polishing step was found unnecessary; the adhesion assessment techniques working almost as well on the original sheet as on carefully polished specimens.

In the case of the native oxide samples, the procedure was to degrease in a 1:1 solution of RBS25 detergent, rinse in water and then etch in a 1:1 solution of nitric acid, followed by a final distilled water rinse, prior to loading into SURF via the load
lock system. This is essentially the same procedure as used in the previous conventional vacuum study. The acid etch step is designed to dissolve the native oxide layer from the surface, but in practice this quickly regrows such that a native oxide layer of approximately 5 nm thickness is observed on the surface (see the results section). Evacuation of the load lock takes of the order of one hour, by which time the load lock pressure will reach $5 \times 10^{-7}$ mbar. The samples in the load lock are then loaded into the main drive carrier of SURF, which transports samples linearly between a preparation chamber, the deposition station and the in-situ analysis chamber. Once transferred, the gate valve to the load lock can be closed, and the pressure recovers typically to $2 \times 10^{-10}$ mbar in one hour. The pressure recovery is aided by the introduction of only the fresh sample material, with no carriers or mounts, and hence the minimum possible unbaked surface area is added. In the case of "dirty" native oxide samples, no further treatment is given prior to deposition of the gold film.

For "dirty" thermal oxide samples the source tantalum material is the same, and is given the same degreasing and acid etch. The distilled water rinse is followed, in this case, by oxidation in laboratory air within a resistively heated quartz walled furnace at 550 degrees Celsius for a period of 1 hour. This results in the growth of an oxide layer approximately 150 nm thick, with a composition close to that for stoichiometric tantalum pentoxide. After cooling to room temperature, the samples were then loaded into SURF using the load lock procedure previously described. Once again, no further pre-treatment is given prior to the gold film deposition.

For "clean" metal substrates, samples prepared as described above in the native oxide section, were sputtered using an argon ion beam from the SURF diplasmatron ion source at an energy of 9 keV. The area sputtered was approximately one centimetre in diameter, the beam current approximately 5 μA and the sputtering dose used some $6000 \, \mu\text{C cm}^{-2}$. Assuming a sputter yield of unity, this should be sufficient to remove some 9 nm of oxide, and hence is more than enough dose to completely remove the native oxide layer, although this does not guarantee a clean metal surface as the final result. The pressure during sputtering was $5 \times 10^{-10}$ mbar due
to the low gas load from our ion source design, and the two stages of differential pumping between source and sample.

During such a sputtering run, which takes of the order of 20 minutes, the residual gas spectrum in the sample chamber would typically be as shown in table 6.1.

Table 6.1 Typical residual gas constituents in sample chamber during sputtering

<table>
<thead>
<tr>
<th>Component</th>
<th>partial pressure (10⁻¹⁰ mbar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>0.5</td>
</tr>
<tr>
<td>H₂O</td>
<td>1.0</td>
</tr>
<tr>
<td>CO</td>
<td>1.0</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.5</td>
</tr>
<tr>
<td>Ar</td>
<td>3.0</td>
</tr>
</tbody>
</table>

After sputtering to remove the native oxide layer, the metal film deposition would be performed quickly, typically within five minutes, to preserve the sample cleanliness.

Finally, the "clean" thermal oxide substrates were prepared exactly as for the "dirty" thermal oxide samples, with the addition of a sputter cleaning step prior to gold film deposition. The sputtering was performed to the same dose in the same way, again quickly followed by deposition of the metal film. In the case of compound materials, the use of sputter cleaning has the draw-back that the chemical composition of the near surface region may well be altered, since it is quite likely that sputtering will lead to enhanced loss of one of the species. For many oxides, sputtering leads to a surface reduced in oxidation state in comparison with the bulk structure due to enhanced loss of oxygen.

Deposition of the gold film was performed from a resistively heated alumina coated molybdenum boat to a thickness of 50 nm at a rate of 0.5 nm s⁻¹. The SURF deposition chamber consists of a sample chamber, separated from the deposition
equipment by a liquid nitrogen cooled baffle plate with only a small hole for the evaporant material to emerge. Each side of the chamber is pumped by a 4000 l s\(^{-1}\) cryopump to cope with the considerable gas load involved. The pumping and baffling arrangement are efficient enough to maintain a pressure in the sample chamber of \(1 \times 10^{-9}\) mbar, or better, throughout a deposition. The film thickness is monitored using twin quartz crystal film thickness monitors, mounted adjacent to the sample. Ex-situ analysis of gold films produced show the thickness to be accurate to some 5% which is quite adequate for the present purpose.

### 6.1.2 Irradiation

As described more fully in the appendix section, SURF has the capability for samples to be transferred under vacuum to our MeV ion irradiation and analysis facilities. This is accomplished by loading up to eight samples onto a target ladder introduced through the load lock. The ladder may then be withdrawn into a vacuum transfer vessel, which can be detached from SURF and connected onto the UHV irradiation chamber. The ladder is equipped with a bayonet fitting to enable it to be transferred to the irradiation chamber manipulator. The transfer procedure takes around 30 minutes, and although the transfer vessel is not pumped during transfer, the pressure whilst isolated from any pumping system remains some \(10^{-3}\) mbar.

The irradiation chamber has a base pressure of \(1 \times 10^{-9}\) mbar, and also has facilities for performing near surface materials analysis using the Rutherford Backscattering (RBS) and Elastic Recoil Detection Analysis (ERDA) techniques. The beam line is pumped by ion pumps, and is separated from the accelerator by a liquid nitrogen cooled restriction. The chamber is pumped by cryopump, and together these measures provide not only good vacuum, but a low level of surface hydrocarbon build up during irradiation. This is illustrated in figure 6.1, which shows the surface carbon and hydrogen peaks observed during ERDA analysis of thermally grown silicon.
Figure 6.1: Variation of measured carbon and hydrogen surface impurities as a function of measurement dose using 30 MeV $^{35}$Cl ions in an ERDA geometry in both conventional and Ultra High Vacuum (UHV) analysis chambers. Note the UHV analysis (which utilised a vacuum sample transfer system) is some factor of 10 cleaner, and deposits far less material from the residual vacuum. As a rough guide, $1 \times 10^{15}$ atoms cm$^{-2}$ represents a single monolayer coverage.
Figure 6.2: Pattern of sample irradiation in the Ultra High Vacuum (UHV) irradiation chamber. The sample is mounted on a computer controlled manipulator, with dosimetry also under computer control, enabling the pattern shown above to be accomplished without intervention from the experimenter. The irradiation doses increase in a roughly logarithmic series covering a dose range of a factor of 200.
dioxide films produced in SURF as a function of analysis dose. Since the Harwell implementation of the ERDA technique uses a 30 MeV $^{35}\text{Cl}^+$ beam, the effect of ionisation at the surface encourages the deposition of hydrocarbons from the residual gas of the analysis chamber. In the figure, note that the initial amount of hydrocarbon present is some ten times lower in the case of a sample transferred under vacuum, when compared with our more conventional analysis chamber, in which samples are loaded from atmosphere. Also note that the build up of further hydrocarbon occurs much more quickly in the case of the conventional analysis chamber which is pumped by diffusion pump and operates typically at $10^{-6}$ mbar.

The irradiations were performed using five different ion species with velocities of 0.04 of that of light. The choice of a constant velocity was made, in part, to facilitate modelling calculations (discussed in chapter 9). The species were $^4\text{He}$, $^{12}\text{C}$, $^{19}\text{F}$, $^{35}\text{Cl}$ and $^{81}\text{Br}$ with the energies and stopping powers detailed in table 6.2. The sputter ion source of the Tandem permits rapid species changes, enabling three beams to be used in a single accelerator shift. The beam was collimated to 3 x 3 mm some 100 mm upstream of the target, and the dose used determined by the counts in a semiconductor detector facing a rotating chopper blade, which intercepts some 5\% of the beam. The counts in this detector were calibrated against a well suppressed Faraday cup for each species. Up to eight doses were used on each 15 x 15 mm sample by use of computer control of both the sample motion and the irradiation dosimetry. An example irradiation pattern is shown in figure 6.2, showing eight doses in a roughly logarithmic series, covering a dose range of a factor of 200.
Table 6.2 Detail of ions used in UHV sample irradiations. Note that the energies selected are such that the ion velocities are all equal at the interface of interest, with a value 4% of the speed of light.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Machine energy (MeV)</th>
<th>Energy at interface (MeV)</th>
<th>Stopping power in gold (MeV mg⁻¹ cm⁻²)</th>
<th>Stopping power in gold (MeV mg⁻¹ cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>electronic</td>
<td>nuclear</td>
</tr>
<tr>
<td>^4He</td>
<td>3.01</td>
<td>3.0</td>
<td>0.290</td>
<td>0.0003</td>
</tr>
<tr>
<td>^12C</td>
<td>9.19</td>
<td>9.02</td>
<td>1.676</td>
<td>0.0030</td>
</tr>
<tr>
<td>^19F</td>
<td>14.57</td>
<td>14.28</td>
<td>2.955</td>
<td>0.0068</td>
</tr>
<tr>
<td>^35Cl</td>
<td>26.94</td>
<td>26.30</td>
<td>6.473</td>
<td>0.0233</td>
</tr>
<tr>
<td>^81Br</td>
<td>62.11</td>
<td>60.87</td>
<td>12.488</td>
<td>0.0938</td>
</tr>
</tbody>
</table>

6.1.3 Adhesion assessment

After irradiation, the samples were removed from the vacuum system and stored in sealed sample boxes until required for testing. Some were tested quite soon (within 24 hours) after irradiation, others were stored for up to three months before testing. In the present work, no evidence of significant ageing phenomena has been found.

Adhesion testing once again relied on the quick and simple scotch tape test, for a rapid qualitative assessment, and in the case for poorly adhering films the technique was used to determine the threshold dose for radiation enhancement. Scratch testing using the procedure described previously, was also performed to give a quantitative measure of the adhesion in both as deposited and irradiated cases.

6.2 Results

The same series of irradiations and testing was performed in each of the substrate cases outlined in the sample preparation section. The results, in each case, are described below.
6.2.1 "Dirty" native oxide substrates

As stated earlier, the preparation procedure does not eliminate the native oxide layer, which quickly regrows to some 5 nm thick as shown by the ERDA data of figure 6.3. The light elements, hydrogen, carbon and oxygen are clearly resolved. The oxygen content, signified by a peak centred around channel 300, is consistent with a native oxide thickness of some 2 nm. This conclusion is reached by iterative comparison between the observed spectrum and the results of our Ion Beam Analysis simulation package SIMBA. The surface carbon peak is consistent with a small level (some one monolayer) surface hydrocarbon contaminant (C_nH_{2n}).

As deposited films had poor adhesion and failed the tape test. A scratch load of 20-50 g was sufficient to completely strip the gold film from the substrate. This result is shown in figure 6.4 (a), where the results for the as deposited film are indicated by a cross in the box for the scotch tape test, indicating failure, and a bar whose ends represent the loads for 10% and 90% film removal. In each case a minimum of two samples were tested.

Irradiation was observed to improve adhesion to a level where the tape test was passed, which coincides with a significant increase in the scratch test load to produce stripping to the order of 50-100 g. The threshold doses to produce scotch tape adhesion for each ion are also indicated and ranged from some 2x10^{13} ions cm^{-2} for ^4He to 5x10^{13} ions cm^{-2} for ^{81}Br. It should be noted that this behaviour and the values of threshold doses are entirely consistent with the observations of the radiation enhanced adhesion of gold films on tantalum (native oxide) reported in chapter 5 where preparation techniques were entirely conventional.
Figure 6.3: Elastic Recoil Detection Analysis (ERDA) spectrum obtained from a chemically cleaned tantalum surface. Note that despite treatment with nitric acid, the surface contains a significant surface oxide layer.
Gold film on Tantalum/Tantalum Oxide

(a) Native oxide "dirty"

- Scratch load (g)
- Scotch tape result

(b) Thermal oxide "dirty"

(c) "clean" metal (sputtered)

(d) "clean" oxide (sputtered)

Figure 6.4: Results of radiation enhanced adhesion experiments on the gold film on tantalum system. The results are for a) "dirty" native oxide substrates, b) "dirty" thermal oxide substrates, c) "clean" metal and d) "clean" oxide. The left hand box in each case shows the performance of the as deposited film, with the other boxes indicating the effect of irradiation. The circles contain the result of the scotch tape test in each case. The boxes indicate the scratch test load required to strip the film. Note the bottom of the bar represent the load to strip 10% of the film area, the top represents 90% stripping. Where no threshold was found, the data is for the highest dose tried.
6.2.2 "Dirty" thermal oxide substrates

Once again, as deposited films failed the tape test, and stripping was initiated at modest scratch test loads. In the case of thermal oxide tantalum substrates, the substrate surface was considerably roughened by the oxidation process, which has the effect of making total gold removal in the scratch test all but impossible. Hence the scratch load bars extend to high loads even though the majority of the film is stripped at quite modest loads.

Irradiation was again observed to produce tangible benefits, with the doses shown giving rise to scotch tape adhesion, and considerable increase in the scratch load. In the case of $^4$He, no threshold was found although irradiations were performed up to $1 \times 10^{16}$ ions cm$^{-2}$. Other than the result for $^4$He irradiation, and the anomalously low threshold for $^{81}$Br, these results are in reasonable agreement (with a factor of two in threshold dose) with those for native oxide substrates as described above.

6.2.3 "Clean" metal substrates

In this case the intention was to deposit gold onto atomically clean tantalum metal. The as deposited gold film passed the scotch tape test, and required a load of in excess of 50 g to initiate stripping.

Irradiated samples also passed the tape test, and although there was considerable variation in the scratch loads required, there is no evidence from these samples of any further adhesion enhancement in irradiated areas.

6.2.4 "Clean" oxide substrates

In a similar fashion to the "clean" metal substrates above, the as deposited films passed the tape test for "clean" oxide substrates. In this case, the scratch loads to strip the film were somewhat higher, at some 200 g.

Irradiation produced no observable benefit in the case of gold films on "clean"
oxide substrates, and scratch loads were at a similar high level.

6.3 Effect of UHV preparation and surface cleanliness

From the above results, three important conclusions can be drawn.

Firstly, the results for gold films on native oxide tantalum substrates are identical for samples prepared in \textit{SURF} to those obtained in the previous study, where only conventional modest vacuum preparation equipment was used. It would seem that depositing gold films onto such substrates in ultra high vacuum does not, in itself, provide any benefit in terms of adhesion.

Secondly, the results for "dirty" native and thermal oxide substrates follow a broadly similar pattern, indicating that the thickness of the oxide layer is not critical provided it is greater than 5 \text{nm}.

The most important conclusion comes from the two "clean" substrate cases. Not only do the as deposited films have good adhesion (as good or better than the "dirty" case after irradiation), but there is no evidence that irradiation of these "clean" interface samples provides any additional benefit. It would appear that we have evidence that radiation enhanced adhesion requires the presence of an interface containing significant amounts of interface contaminant species, in the form of native oxides, adsorbates, hydrocarbons, and the like.
CHAPTER 7

Gold film on silicon prepared in UHV

Analogous to work described in the preceding section, the SURF preparation facility was also used study the adhesion of gold films deposited on silicon and silicon dioxide substrates, with various pre-treatments. Silicon has several advantages as a substrate material in studies of thin film adhesion. Firstly, silicon wafers are a readily available source of high purity optically flat material on which to deposit films for testing. The flatness is of advantage when adhesion testing, since the mechanical interlocking of structures which occurs for rough surfaces is totally absent, with a consequent improvement in reproducibility. The optically flat surface also leads to more reproducible results in scratch testing, since the contact area between diamond and substrate remains constant, leading to constant loading at the point where failure is initiated. The use of silicon as a substrate material makes better use of the preparation facilities in SURF since oxides can be grown in-situ, and perhaps more importantly, an atomically clean silicon surface can be produced by solely thermal means. The native oxide of silicon is not thermally stable, and can be removed by heating silicon to 950 Celsius in ultra high vacuum. At these temperatures, SiO is volatile, and is desorbed from the surface until only an atomically clean surface remains.

7.1 Experimental procedure

In the work described in this section, the substrate consists of 15 x 15 mm sections of silicon cut from 2 inch n-type 4-6 Ω cm<sup>-1</sup> <100> wafers. In no case was any chemical pre-treatment prior to loading into the SURF system given, since any attempt at cleaning prior to loading was found only to increase the levels of surface contamination. Once again, the substrates used divide into four convenient groups; native oxide, thermal oxide, clean silicon and clean oxide.
7.1.1 Sample preparation

All the silicon samples were produced by cutting 15 x 15 mm sized sections from 2 inch <100> wafers using an automated diamond cutting machine. Samples were loaded through the load-lock into the SURF preparation system, and in the case of the native oxide samples, no further treatment is given prior to deposition of the gold film. Such samples are referred to as "dirty" native oxide, since no treatment in UHV is given to produce a clean surface. The resulting gold/native oxide interface can thus be expected to contain significant levels of contaminants, such as hydrocarbons and adsorbed species like water.

For thermal oxide samples the material was transferred in SURF to the oxidation furnace, which consists of a resistively heated quartz tube furnace with supplies of ultra pure dry oxygen (both natural and isotopic $^{18}$O). Oxides were grown at 950 degrees Celsius for a period of 24 hours at a pressure of 100 mbar, after first removing the native oxide by heating in the furnace hot zone to 950 degrees Celsius in UHV for 5 minutes. This results in the growth of an oxide layer approximately 100 nm thick, with a composition which agrees well with that for stoichiometric silicon dioxide. After removing the samples from the furnace hot zone, the oxidising gas was pumped away and the oxide substrates returned to the deposition chamber. In the case of gold on "clean" oxide, the deposition followed within 30 minutes of removing the samples from the furnace system.

For gold films on "dirty" oxide substrates, contamination of the oxide surface was achieved simply by removing oxide samples produced by the above procedure from SURF through the load-lock system, storing them overnight in laboratory air before returning them to SURF through the load-lock system the following day.

For "clean" silicon substrates, sections of wafer, complete with native oxide layer, were sputtered using an argon ion beam from the SURF duo-plasmatron ion source at an energy of 9 keV. The area sputtered was approximately one centimetre in diameter, the beam current approximately 5 μA and the sputtering dose used some 6000 μC cm$^{-2}$. As stated in the tantalum preparation section, this dose should be...
sufficient to remove approximately 9 nm of oxide, and hence is ample dose to completely remove the native oxide layer. Once again, the pressure during sputtering was some $5 \times 10^{-10}$ mbar. After sputtering to remove the native oxide layer, the metal film deposition was performed quickly, typically within five minutes, to preserve the sample cleanliness.

The efficacy of the sputter cleaning process is illustrated by the Elastic Recoil Detection Analysis data of figure 7.1. The upper part of the figure gives the observed spectrum of recoiled particles from the near surface of a gold on "dirty" native oxide sample under bombardment by 30 MeV $^{35}$Cl$^{6+}$ ions. Peaks are observed due to the oxygen of the 2 nm thick native oxide layer, accompanied by carbon and hydrogen peaks corresponding to some 2 monolayers of hydrocarbon contaminant at the gold/native oxide interface. If this is compared with the lower figure, which is identical data for a sample of gold on "clean" silicon obtained by argon ion sputtering, we observe that the oxygen signal is much reduced, as is the signal from carbon and hydrogen interface contaminants. From this spectrum, the upper limit on oxygen at interface is $1 \times 10^{15}$ atoms cm$^{-2}$, and those for interfacial carbon and hydrogen $0.3 \times 10^{15}$ cm$^{-2}$ and $0.5 \times 10^{15}$ cm$^{-2}$ respectively (note $1 \times 10^{15}$ represents roughly one monolayer). Thus we have clear evidence that the sputter cleaning is reasonably effective in removing the native oxide layer, although the sensitivity of the ERDA technique leaves something to be desired in terms of determining if this is truly atomically clean.

Deposition of the gold film was once again performed from a resistively heated alumina coated molybdenum boat to a thickness of 50 nm at a rate of 0.5 nm s$^{-1}$ utilising the differentially pumped deposition system within SURF as described in chapter 6.
Figure 7.1: Elastic Recoil Detection Analysis (ERDA) spectra obtained from samples of 50 nm thick gold film on silicon. The upper spectrum was obtained from a sample with no in-situ cleaning of the silicon surface prior to gold deposition, and the oxygen signal due to the native oxide layer is clearly resolved. The lower spectrum is for a sample sputtered with 9 keV argon ions prior to gold deposition, and the native oxide layer has been removed. Note also the dramatic drop in interface hydrogen.
7.1.2 Irradiation

Samples were transferred, under vacuum, to the UHV irradiation and analysis chamber on the Harwell 7 MV Tandem accelerator, prior to irradiation by the same range of ion beams at the common velocity of 0.04c, again collimated to an area of 3 x 3 mm, with up to eight doses per sample in a logarithmically increasing sequence to determine the threshold dose.

7.1.3 Adhesion assessment

After irradiation, the samples were removed from the vacuum system and stored in sealed sample boxes until required for testing. Some were tested quite soon (within 24 hours) after irradiation, others were stored for up to three months before testing. In the present work no evidence of significant ageing phenomena has been found.

Adhesion testing once again relied on the quick and simple scotch tape test, for a rapid qualitative assessment, and in the case for poorly adhering films the technique was used to determine the threshold dose for radiation enhancement. Scratch testing using the procedure described previously, was also performed to give a quantitative measure of the adhesion in both as deposited and irradiated cases.

7.2 Results

The same series of irradiations and testing was performed in each of the substrate cases outlined in the sample preparation section. The results, in each case, are described below.

7.2.1 "Dirty" native oxide substrates

As deposited films had poor adhesion and failed the tape test. A scratch load of around 10-20 g was sufficient to completely strip the gold film from the substrate. This result is shown in figure 7.2 (a), where the results for the as deposited film are
indicated by a cross in the box for the scotch tape test, indicating failure, and a bar whose ends represent the load for 10% and 90% film removal. In each case a minimum of two samples were tested.

Irradiation was observed to improve adhesion to a level where the tape test was passed for all cases except \(^4\)He, which coincides with a small but significant increase in the scratch test load to produce stripping, to the order of 20-50 g. The threshold dose to produce scotch tape adhesion for each ion are also indicated and ranged from some \(1 \times 10^{16}\) ions cm\(^{-2}\) for \(^{12}\)C to \(1 \times 10^{14}\) ions cm\(^{-2}\) for \(^{81}\)Br. No threshold was found for irradiation with \(^4\)He ions despite doses as high as \(4 \times 10^{16}\) ions cm\(^{-2}\). It should be noted that the threshold doses observed are some one order of magnitude higher than those observed for the radiation enhanced adhesion of gold films on tantalum (native oxide) reported in chapters 5 and 6, which might well be expected in the light of the lower ion stopping power in silicon.

To establish the importance, or otherwise, of the adsorbed water vapour that is inevitably present on any surface which has not been cleaned in UHV, a pair of native oxide samples were heated in the UHV furnace to 300 degrees Celsius immediately prior to the gold film deposition. This temperature is high enough to desorb the majority of the water vapour from the surface, but is too low to have any effect on the native oxide itself. This gave rise to the result in the box on the left of figure 7.2 (a), which indicates that such modest temperature pre-treatment has no effect on subsequent film adhesion.

### 7.2.2 "Dirty" thermal oxide substrates

Once again, as deposited films failed the tape test, and stripping was initiated at modest scratch test loads.

Irradiation was again observed to produce tangible benefits, with the doses shown giving rise to scotch tape adhesion, and a considerable increase in the scratch
Gold film on Silicon/Silicon Oxide

(a) Native oxide "dirty"
therm. 300°C

(b) Thermal oxide "dirty" (room air 24 hrs)

Scratch load (g)
Scotch tape result

(c) "clean" silicon (sputtered)
therm. 950°C sputt.+ air

(d) "clean" oxide (sputtered)
therm. 600°C sputt. sputt.

Figure 7.2: Results of radiation enhanced adhesion experiments on the gold film on silicon system. The results are for a) "dirty" native oxide substrates, b) "dirty" thermal oxide substrates, c) "clean" silicon and d) "clean" oxide substrates. The centre box indicates the performance of the as deposited film, with the other boxes indicating the effect of irradiation or alternative production methods (e.g. thermal cleaning). Where no threshold was found, the data is for the highest dose tried. Note that thermal cleaning of the silicon at 950 degrees Celsius in UHV produces adhesion far in excess of any other processing method.
load. Once again, in the case of \(^4\)He no threshold was found although irradiations were performed up to \(4 \times 10^{16}\) ions cm\(^{-2}\). These results are observed to be largely consistent with those for native oxide substrates as described above.

### 7.2.3 "Clean" silicon substrates

In this case the intention was to deposit gold onto atomically clean silicon. The as-deposited gold film passed the scotch tape test, and required a load of 20-50g to initiate stripping. This is not very much higher than in the "dirty" substrate cases above, but the adhesion is obviously sufficient to pass the scotch tape test consistently.

Irradiated samples also passed the tape test, and the small variability in the scratch loads shows there is no evidence from these samples of any further adhesion enhancement in irradiated areas.

In addition, the effect of two further preparation routes was investigated. Firstly, a pair of samples was given the same sputtering pre-treatment to obtain a "clean" silicon surface, but was temporarily removed to atmosphere through the load-lock system prior to deposition of the gold film. Thus the surface could be expected to be free from a significant native oxide layer (since atmospheric exposure was short), but would be saturated with species such as water and hydrocarbons. The adhesion in this case was still sufficient to give scotch tape adhesion, and scratch loads were similar to samples without the atmospheric exposure test. Another alternative pre-treatment was to prepare a "clean" silicon surface by thermal cleaning rather than sputtering. This was achieved by heating samples to 950 degrees Celsius in the UHV furnace for 30 minutes prior to deposition of the gold film. Such thermal cleaning is generally accepted as being the best route to obtaining an atomically clean silicon surface. In this case, dramatically better gold film adhesion was observed, passing the tape test with ease and requiring much higher scratch loads (of the order of 500-1000 g) than any other gold on silicon/silica sample.
7.2.4 "Clean" oxide substrates

From the preceding sections a clear picture was beginning to emerge. In all cases where films had been deposited onto "clean" substrates good adhesion had been observed, which did not show any further benefit from irradiation. This pattern was to be spoiled by the observations made of gold films deposited on nominally "clean" thermal oxide samples. Here the as deposited films failed the tape test and stripped with loads of 10-20 g. Irradiation of such samples was found to be beneficial, with the pattern of threshold doses being quite close to those observed for the two "dirty" silicon oxide substrates (native and thermal).

The data suggested that if previous observations were correct, then these oxide samples must be "dirty" in some way. This is indeed the case, as the procedure for growing oxides in the SURF system will tend to leave a significant level of oxygen adsorbed onto the surface, which subsequently contaminates the gold/oxide interface. This comes about from the oxidation procedure, in which the sample is removed from the furnace hot zone whilst still in the oxidising gas. As the sample cools, the gas will adsorb onto the surface, and some of this will remain when the sample is returned to the UHV environment of the deposition chamber.

To confirm that adsorbed oxygen was responsible for the observed poor adhesion, samples were prepared with additional treatment steps prior to gold film deposition. First of all, sputtering with argon to the full 6000 µC dose was tried as shown in the figure, which had some effect, taking the adhesion to a level approximately the same as that required for the tape test. If the sputtering treatment was followed by atmospheric exposure prior to deposition, the adhesion was very poor. The most elegant and most successful way of removing the adsorbed oxygen is to heat in UHV. This was performed in the furnace system at a temperature of 600 Celsius which should easily be high enough to desorb the oxygen without in any way effecting the thermal oxide layer, which is quite stable at this temperature. This thermal treatment was indeed effective, passing the tape test and requiring scratch loads of some 50-100 g to strip the gold film.
7.3 Important observations

Several important observations need to be highlighted from the above. Firstly, in the case of "dirty" native and thermal oxide samples, irradiation by MeV ions is found to have beneficial effects as it was for tantalum substrates. In this case the threshold doses were considerably higher, which is what one would expect, as the lighter atomic number of silicon/silica substrates will reduce the intensity of the electronic excitation at the film/substrate interface, making ion irradiation less efficient.

Secondly, in the case of gold on "clean" silicon, although sputter cleaning in UHV produced improved adhesion, thermal cleaning is observed to be much more effective. This has important implications in terms of adhesion mechanisms for this system. If the adhesion were the result of image charge type interactions one would expect sputter cleaning to be more effective than the thermal method since this will give rise to a high surface defect density. The reverse is observed to be the case.

Finally, the observations on the "clean" thermal oxide system indicate that the surface chemistry is important in these systems. The small level of adsorbed oxygen present before deposition is sufficient to dominate the adhesion behaviour of the gold film. Thermal cleaning is again observed to be more effective than ion sputtering, which is perhaps indicative of the inability of ion sputtering to produce a truly "clean" surface.
CHAPTER 8

Silver film on silicon prepared in UHV

To investigate the effect of film species, a limited programme of work was performed using silver films deposited on silicon, both with and without a thermal oxide layer. Silver is another relatively unreactive metal, but has a somewhat more extensive chemical repertoire in comparison with gold. Silver will form an oxide, and hence there might be a possible reaction with an oxide substrate. Silver is also known to form stable compounds with silicon, at least in the case of silver on an atomically clean silicon surface (Porter 1988).

8.1 Experimental procedure

The same 15 x 15 mm n-type silicon sections were used as substrate material, with only three surface types and a limited number of irradiation species. Once again, all sample preparation was performed in the SURF facility.

8.1.1 Sample preparation

The three substrate classes in this case were native oxide (no pre-treatment prior to deposition), "clean" silicon prepared both by sputtering to 6000 μC with 9 keV argon ions and by a thermal clean in UHV at 950 degrees Celsius for 5 minutes. Finally the adhesion of silver onto thermally cleaned oxide was investigated.

Depositions were performed using the same alumina coated molybdenum boats used previously for the deposition of gold films. This was accomplished without breaking vacuum by the ability to re-load source material into the deposition system in UHV. Fresh source material is loaded into the system in the form of short sections cut from 1mm thick wire, contained in an open box capable of being loaded through the load lock system, and from there into the sample transport rack and sample positions. The top of the liquid nitrogen cooled cryoshield includes a funnel, onto which such source material may be carefully dropped, with a high probability that the material
will come to rest in the dished centre of the molybdenum boat. A single load is sufficient for depositing some 3 to 6 films in the current context, and provided the boat is run at a high enough temperature to evaporate all the volatile material, a reasonably clean change over of evaporant species can be achieved. This is particularly true when switching to a lower melting point material (e.g. from gold to silver) since the second material may well evaporate at temperatures below the melting point of the first.

A Rutherford Backscattering spectrum obtained from an 40 nm thick silver film deposited on silicon is shown in figure 8.1. The presence of a small degree of contamination from gold is observed, but by comparison with the simulated spectrum (solid line) the gold level is estimated at some 0.25% atomic of the film which is small enough to have little influence on the adhesive behaviour, since it is dispersed throughout the film.

8.1.2 Irradiation

Samples were transferred under vacuum to the UHV irradiation facility, and a more limited investigation of the MeV ion modification behaviour carried out using only $^{19}$F and $^{81}$Br ion beams.

8.1.3 Adhesion assessment

Scotch tape and scratch testing was performed on as deposited films, and films subject to irradiation.
Figure 8.1: Rutherford Back-Scattering (RBS) spectrum obtained from a 50nm thick silver film on sputtered silicon substrate. Note the logarithmic vertical scale of detected counts permits us to see the small peaks due to argon trapped in the silicon near surface, and a low level (0.25%) gold contaminant in the silver film.
8.2 Results

8.2.1 "Dirty" native oxide substrates

The results for silver films deposited onto "dirty" native oxide are shown in figure 8.2. The as deposited films showed poor adhesion, and failed the tape test. Scratch testing removed the film at low loads of only 10-20 g. As observed for gold films, the adhesion was improved by irradiation to a level above the threshold for scotch tape adhesion, but in reality the adhesion was still quite poor, only requiring some 20-30 g to scratch the film from the substrate even after irradiation.

8.2.2 "Clean" silicon substrates

For silicon without a continuous native oxide layer, the picture is rather different. Silver films adhered well to both sputter cleaned and thermally cleaned silicon samples, with the highest adhesion observed in any film substrate combination in the present work. The tape test was easily passed, and loads to produce stripping in the scratch test were at a level where damage to the wafer sections was common (turning the scratch tester into a somewhat slow diamond wafer cutter). No further adhesion enhancement upon irradiation by F and Br ions was observed, but considering the strong adhesion observed in the as deposited case this was not surprising.

8.2.3 "Clean" oxide substrates

As shown in figure 8.2, only the adhesion of silver deposited onto thermally cleaned oxides was investigated. The thermal treatment was simply to heat the thermal oxide (grown by the procedure described in section 7.1.1) in the furnace hot zone to 600 degrees Celsius for 15 minutes in UHV in order to remove adsorbed oxygen from the oxide surface. This was done immediately prior to deposition of the silver film.
Silver film on Silicon/Silicon Oxide

(a) Native oxide "dirty"

Scratch load (g)
Scotch tape result

(b) "clean" silicon
therm. 950°C

(c) "clean" thermal oxide
therm. 600°C

As dep. F Br

>4E15 1E14

1000 500 200 100 50 20 0

1000 0

Figure 8.2 : Results of radiation enhanced adhesion experiments on the silver on silicon system. The results are for a) "dirty" native oxide substrates, b) "clean" silicon, and c) "clean" thermal oxide. Note in this case only two ion species were used and that in general the adhesion observed is far greater than for the equivalent gold film.
Films prepared in this way showed good adhesion, passing the tape test and requiring loads of around 500 g under scratch testing. The effect of ion irradiation was not assessed in the case of silver films on oxide substrates.

8.3 Important observations

From comparison of the above results with those for gold films it is quite clear that silver films deposited in UHV onto "clean" silicon/silica surfaces have significantly better adhesion than their gold counterparts. Since the preparation routes are identical, this can only be the result of the more reactive film species. Hence we have clear evidence of chemical effects in the adhesion of thin films to semiconductor and dielectric surfaces.
CHAPTER 9

Discussion

In the sections which follow, the important results of the previous experimental sections will be discussed, and the development of a semi-empirical model of the radiation enhanced adhesion phenomenon will be presented.

9.1 Effect of UHV Processing

Over the past 20 years there has been a continuous trend towards improved vacuum for thin film processing systems. The main aim of such developments is improved reproducibility and hence reliability of process conditions. As already stated, adhesion is a fundamental parameter for any thin film process and hence the impact of improved vacuum technology on film adhesion is a subject worthy of attention.

The factors which give rise to film adhesion were outlined in the opening chapter and are of chemical, electrostatic and mechanical origin. In all practical systems, however, the interface will be far more complex than the idealised one of film atoms on an atomically clean and flat substrate. Factors such as the presence of interfacial contaminant species which include water vapour, hydrocarbons, and native oxide layers may well dominate the adhesion behaviour. This has been a factor in the development of the many ion assisted deposition technologies. Such technologies all involve near surface energy deposition by low energy ions in some form (Harper 1984, Hirsch 1978, Franks 1979), which will produce sputtering of material from the surface. The poor quality of the vacuum conditions of the majority of thin film processing equipment (typically $10^{-6}$ mbar) precludes the use of such ions as a practical cleaning pre-treatment, as the surface will rapidly become re-contaminated at such pressures (a partial pressure of $10^{-6}$ mbar is sufficient for a monolayer of gas species to arrive at an exposed surface every second). Hence such techniques only
achieve partial and dynamic cleaning, requiring the deposited film species to accompany the ion bombardment process. Careful fine tuning of the relative arrival rates between film species and ions is often required in order to produce the optimum film characteristics (Hoffman 1980, Cuomo 1982).

In some cases, alternative approaches to producing reliable adherent thin film coatings may be possible. These include high energy irradiation and UHV processing.

High energy irradiation is of course the subject of this dissertation, and has been shown to be an effective way of producing technologically useful adhesion between film and substrate, in systems were adhesion is traditionally poor. The use of high energy ions may well be ruled out in all but the highest value added cases on cost grounds, due to the expensive nature of the required accelerator hardware. However, the same or at least similar effects have (as stated in chapter 2) been observed due to irradiation by much more accessible electron and UV photon beams. The present understanding of such phenomena is still poor (although my hope is that this dissertation will represent a significant step forward) and hence we are some way from being able to exploit such processes.

The use of UHV processing techniques for microelectronics fabrication has grown in recent years due to the wide spread use of techniques such as Molecular Beam Epitaxy (MBE) for thin film growth (Bean 1980), where Ultra High Vacuum process chambers are a prerequisite. Other new fabrication and inspection technologies are developing (such as Ion Beam Deposition (Appleton 1987) and Scanning Tunnelling Microscopy (Binnig 1983)) in which UHV pressures are required. Further factors include the drive towards larger wafer sizes and smaller device sizes. Larger wafers mean bigger plant, and hence ever more expensive fabrication lines with their plethora of expensive to maintain clean rooms. An alternative philosophy for fabrication facilities is to dispense with the clean room and built a continuous process system, where the wafer spends the majority of its time in a UHV or ultra pure gas environment, with automated lithography stages where required, thus eliminating the majority of the handling and transportation stages.
currently employed. Such "cluster tools" exist as research scale systems at present (Burggraaf 1989).

Smaller device sizes in microelectronics has lead to increased importance in precise control of process parameters, because of the increased sensitivity of smaller devices to small flaws in fabrication due to contamination. Hence UHV techniques are generally perceived as being beneficial in terms of better control over process parameters.

The work presented in chapters 5 and 6 has an important bearing on such technologies. The preparation of gold films on tantalum (with native oxide) substrates in both conventional and Ultra High Vacuum systems gave rise to identical results, not only in terms of as deposited adhesion, but also in the way in which adhesion was modified by heavy ion irradiation. These results clearly show that UHV deposition of thin films does not, in itself, produce any observable benefit. The principle difference between conventional and UHV deposition on these samples will be the purity of the deposited film. At a typical conventional deposition pressure of 10^-6 mbar, the arrival rate of water vapour (the main residual gas at such pressures) will be approximately one monolayer per second. A typical deposition rate for gold in the present studies is 0.5 nm per second or approximately 2 monolayers per second. Hence gold atoms and water vapour molecules arrive at the surface of the substrate in the ratio 2:1, and in the worst case we would expect the film to be characterised by a large degree of contamination by such species. In the UHV case, the pressure during deposition is typically better than 10^-9 mbar, and thus the ratio in arrival rates becomes 2000:1 or in other words 0.05%. It would be surprising to find such a low level of contamination having any significant effect on the adhesion properties of a thin film.

In the case of gold films, the above paints a rather black picture. Although the arrival rates are as stated, an important factor missing from the above is the relative probabilities that the arriving species will stick to the surface rather than be reflected back into the vacuum, the so called "sticking coefficient". During the deposition of a gold film, the sticking coefficient for gold arriving at the fresh gold covered surface
may well approach unity, whereas water vapour molecules will have far less affinity for the relatively inert gold surface. This is borne out by the fact that gold films relatively free from bulk contaminants may be deposited in modest vacuum conditions.

Such contamination by species present in the residual gas of the vacuum system are more likely to be of significance in the deposition of reactive metals and semiconductors, which react spontaneously with air at room temperature to form oxides.

As stated above, the cleanliness of the vacuum primarily effects the purity of the deposited film. The fact that our experiments produced identical results with conventional and UHV sample preparation clearly indicates that the film purity does not play a major part in determining the adhesion behaviour of the film/substrate system in this case. This suggests, as one might expect, that the adhesion is dominated by properties of the interfacial region.

We conclude, therefore, that film deposition in Ultra High Vacuum has no observable advantage over conventional vacuum deposition, unless the substrate surface is subject to some pre-treatment which alters the composition of the region which will eventually form the film/substrate interface. What UHV techniques do produce is an environment whereby a clean sample surface may stay that way for a useful period of time, allowing the effectiveness of various pre-treatment processes to be assessed in a reproducible fashion. The environment also allows the use of surface analysis techniques such as Low Energy Ion Scattering, Scanning Tunnelling Microscopy or X-ray Photoelectron Spectroscopy to be applied in a meaningful way to the analysis of the surface composition and structure of samples given these various pre-treatments.
9.2 Effect of interface cleanliness

As stated in the section on experimental approach in chapter 4, the present work was undertaken, in part, to ascertain the role of sample preparation in the phenomenon of radiation enhanced adhesion, and particularly the importance of interfacial cleanliness.

All the cases studied to date show that adhesion is considerably improved if the film is deposited onto a surface which has been cleaned in UHV, with further evidence for the superiority of thermal cleaning over sputtering. Secondly, no improvement in adhesion was observed due to ion irradiation in any system with an interface free from significant levels of contamination.

Both of these observations are clear evidence of the way in which contaminant species present at the film/substrate interface completely dominated the observed adhesion behaviour.

The observations in chapter 7 of gold films on "clean" silicon oxide substrates were particularly interesting as they show adhesion behaviour which is dramatically effected by relatively small amounts of adsorbed oxygen, which remain on the surface at the end of the oxidation process. Simply by heating to 600 degrees Celsius to remove these adsorbates prior to deposition we may improve the adhesion by perhaps a factor of three.

The absence of radiation induced adhesion enhancement in the case of samples prepared with clean interfaces is clear evidence for interfacial contaminants being involved in the radiation enhanced adhesion process, which will be discussed in more detail in a following section.

The process by which such interfacial contamination leads to premature film failure is rather less clear. It could simply be the case that such intervening contaminant layers act as a barrier to the formation of direct bonding between film and substrate atoms. This may be an important factor in systems of film and substrate which would not be expected to react strongly, i.e. where the driving force for a reaction is not strong, as evidenced in our results for gold films on thermally cleaned
silicon. It may perhaps be that the presence of contaminant species acts as some form of catalyst agent in the film failure process during testing, akin to the Westwood-Rebinder type (chemo-mechanical) effects (Sofield 1991), in which the presence of species such as hydrogen have been found to have a strong influence over a variety of macroscopic materials properties.

9.3 Comparison of sputtering and thermal cleaning

The results described in chapter 7 for the adhesion of gold films on "clean" silicon are also interesting as they highlight the relative merits of alternative techniques for the preparation of a clean surface; namely low energy ion bombardment (sputtering) and thermal cleaning in Ultra High Vacuum. Thermal processing alone is a viable method for producing an atomically clean silicon surface due to the fact that the native oxide decomposes to form volatile SiO at temperatures above 900 degrees Celsius in UHV, leaving behind an atomically clean substrate surface.

Although sputtering with a large dose of 9 keV argon ions prior to gold deposition was observed to be successful at removing the majority of the oxygen initially present in the native oxide, the adhesion of such films was found to be far inferior to films deposited onto clean silicon prepared by a thermal route. The adhesion of gold films on thermally prepared silicon far exceeded that observed by any other preparation route, including high energy heavy ion irradiation.

The most likely explanation for these observations is that the sputtering process is not capable of producing an atomically clean surface. The large dose of argon ions would be expected to remove some 9 nm of silicon dioxide, which far exceeds even conservative estimates of the thickness of a native oxide layer on silicon (approximately 2 nm). Low energy ion sputtering is far from being a simple process however, and some of the species present on the original surface would be expected to be recoil implanted into the near surface by nuclear collisions. Thus although the original surface oxide layer is completely removed, the final surface composition may
well include some of the species present in this original layer, with oxygen being the most likely as it constitutes the most common species in the original surface layers. As stated in chapter 7, the ERDA analysis of gold films on sputtered silicon substrates puts an upper limit on the oxygen present at the gold/silicon interface of some $1 \times 10^{15}$ atoms cm$^{-2}$, which represents a level of less than one monolayer. Thus the analysis does not rule out the presence of significant levels of oxygen contamination at the gold/sputtered silicon interface.

A more sensitive technique for the analysis of the contaminant species on surfaces is Low Energy Ion Scattering. Data obtained from a freshly sputtered and a thermally cleaned silicon surface are compared in figure 9.1. We observe that the sputtered silicon surface still shows some sign of contamination with oxygen, despite the high sputtering dose.

Thermal treatment to produce a clean silicon surface has the advantage that the native oxide is removed by the natural volatility of SiO at elevated temperatures, and one would not expect significant levels of contaminant species on a silicon surface prepared in this way.

This result suggests that good adhesion of gold films on silicon can be achieved provided that gold and silicon atoms can be brought into intimate contact at the interface, i.e. without interference from contaminant species such as adsorbates, hydrocarbons and even small amounts of oxygen.

The superiority of thermal cleaning over ion sputtering is reinforced in the observations of gold films on the "clean" thermal oxide. In this case adhesion of as deposited films was poor due to traces of oxygen adsorbed on the substrate surface due to an oversight in the initial preparation procedure. The adhesion was improved far more effectively by the introduction of a thermal treatment (600 degrees Celsius in UHV) than by sputtering prior to deposition. This indicates that, once again, the oxygen contaminant was removed far more completely by thermal treatment than by sputtering alone.
Figure 9.1: Low Energy Ion Scattering (LEIS) data for freshly sputtered and thermally cleaned silicon surfaces. Note that the sputter cleaned sample still shows an oxygen contaminant to be present, and a smaller silicon peak, indicating a contaminated surface.
9.4 Film species

The comparison of silver and gold films on silicon substrates prepared under identical conditions is of great interest, as the effect of chemical species should become evident. In this case the chosen film species are examples of relatively inert metals and neither would be expected to react strongly with silicon or its oxide. The results were described in chapters 7 and 8. On native oxide substrates, where no pre-treatment was given prior to film deposition, both gold and silver films showed poor adhesion of a similar level. This was modestly improved by heavy ion irradiation (sufficient to pass the scotch tape test). On sputter cleaned silicon substrates the behaviour of the two film species is diametrically different. Gold films show only modest adhesion, requiring a scratch test load of some 20 g to induce film stripping, whereas silver films on samples prepared in the same way proved impossible to remove by scratch testing, even with loads of 1000 g.

The above is clear evidence of adhesion behaviour with a strong dependence on film species. Silver is more chemically reactive than gold, forming an oxide at room temperature and thus the fact that silver produces a stronger interaction with a "clean" sample is not so unexpected. It is surprising, however, that the observed difference in adhesion between gold and silver is so dramatic; the silver film requiring some 50 times the load to remove the film from the surface in a scratch test.

The data for thermally cleaned silicon, which as stated above should be totally free from any surface contaminant species, show similar excellent levels of adhesion, with the silver once again superior to the gold. These results suggest that a good adhesive interface is attainable for both metals provided that the initial substrate surface is totally free of contaminants. The silver films would appear to be far less sensitive to small levels of contamination present at the initial surface, perhaps due to the ability of silver to react chemically with oxygen.

Data was also obtained for gold and silver films on a freshly cleaned silicon oxide surface (produced by heating an oxidised sample to 600 degrees Celsius in UHV). Once again, the adhesion of a silver film is found to be significantly better than
that of a gold film on substrates prepared in an identical fashion.

All the above are evidence of film adhesion being strongly dependent on the chemical species of the film, even though the systems studied were films of relatively inert metals.

### 9.5 Semi-empirical model of threshold dose observations

In the following sections, the development of a model of the radiation enhanced adhesion process is developed, using semi-empirical methods to calculate the resultant radial energy distribution around the path of a fast heavy ion. The model is compared with the experimental observations made by ourselves, and those previously reported by other groups.

#### 9.5.1 Why a dependence on stopping power (dE/dx)?

We have seen strong evidence for the radiation enhanced adhesion phenomenon to be closely linked with the presence of contaminant species at the film substrate interface, as we observed no effect when films were deposited onto clean surfaces. Beneficial effects were still observed, however, for all systems where interfacial contaminants were present, and the variation of the threshold dose to pass the scotch tape adhesion test was noted for a variety of ion species at a constant velocity of 0.04c.

As stated several times throughout this dissertation, the ion dose required to produce radiation enhanced adhesion effects, and the way in which such doses vary between different ion species, should be of interest as this may cast some light on the type of mechanism which is operating. As stated in chapter 2, where many of the published data on this effect were briefly described, there is considerable evidence for an increase in threshold dose with decreasing atomic number for film and substrate, and also an increase in dose as the ion stopping power decreases.
Both these trends might be expected, since both result in a lower density of electronic excitation at the interface, which would intuitively require larger doses to produce equivalent effects. Only in a very few cases has the stopping power dependence of the radiation enhanced adhesion phenomenon been measured. In these cases a power law dependence on ion stopping power \((dE/dx)\) has been suggested, i.e.

\[ D_{th} \propto (dE/dx)^n \]

No universal pattern has been established, with reported exponent values varying between \(n=1.4\) and \(n=4.0\). If one were being cynical, one might suggest that the power law dependence originates from the fact that most workers have presented their threshold dose versus stopping power data on log/log graphs, with error bars such that drawing anything other than a straight line through the data points was unjustified. This approach of using a single parameter (i.e. the stopping power) to model the effect did not appear to be producing useful insights into the phenomenon, nor indeed was it likely to give any predictive capability.

A new approach is required, which takes into account the two dimensional nature of energy loss processes. This is illustrated in figure 9.2 which shows the energy deposition of two ions in gold. The ions are 6 MeV \(^{12}\)C and 1 MeV \(^{35}\)Cl and have identical stopping powers of 1.72 MeV mg\(^{-1}\) cm\(^{-1}\). As can be seen from the figure, although the energy lost per unit distance travelled is the same in each case, the way in which that energy is distributed is rather different. The heavier ion travels more slowly and produces a large number of modest energy excitations which provide excitation (by secondary processes) over a small region close to the ion trajectory. The faster, lighter ion on the other hand will produce fewer interactions, but with a mean energy per event which is higher than for the heavy ion. This has the result of spreading the excitation energy over a wider region, since the secondary processes will be capable of transferring energy over a larger distance (Kobetich 1968).
Figure 9.2: Schematic diagram representing the differing spatial distribution of excitation energy around a fast ion (left) and a slow ion (right) with the same linear energy deposition rate ($dE/dx$). The faster ion will produce fewer but higher energy electronic primary excitations, giving rise to a wider excitation zone as depicted in the figure.
9.5.2 Spatial energy distribution around ion trajectories

This spatial distribution of excitation energy around an ion trajectory is of direct relevance to a large number of ion induced phenomena, as described in more detail in appendix section A4. If one imagines the passage of an ion to produce some effect which requires a threshold energy $e_0$, then the number of atoms effected, per ion, depends not on the stopping power ($dE/dx$), but on the spatial distribution, $E(r)$, around the trajectory as shown in figure 9.2. In this case, we see that although both ions have the same stopping power, the zone which exceeds the threshold excitation energy is significantly larger for the fast ion than the slow ion. Thus it is inconceivable that any model based on ion stopping powers alone could ever be expected to provide a thorough description of such radiation effects.

The modelling results presented here are the result of calculations based on the work of Kobetich and Katz, who successfully applied this radial energy distribution approach to the explanation of a variety of ion/solid interaction phenomena in the 1960's (Kobetich 1968). The method, and its applications, are more thoroughly described in the appendix section and only the principles will be presented here.

The model uses semi-empirical relations for primary excitation and secondary electron transport to calculate the expected radial distribution, $E(r)$, of excitation energy for a given ion in a given material. To apply this approach to effects at the interface of a film and substrate, the distributions were calculated for both film and substrate and the average distribution used as a guide to the excitation present at the interface. This is a valid approximation, since the main energy transport process at these ion energies are electron/electron collisions, which will rapidly give rise to an energy distribution along the ion path which is isotropic over short distances. The distribution does fall dramatically as one moves out radially from the ion trajectory however. If one assumes a given energy threshold, $e_0$, for the adhesion modification process (whatever its origin), then one can calculate the effected zone as being that where this energy threshold is exceeded.

The area of the effected zone will thus be given by $A=\pi r_0^2$, where $e_0$ is the
energy threshold, and \( r_0 \) is the corresponding effected radius. Since one might expect a process to reach some degree of saturation at a dose \( D_{\text{sat}} \), when each area of the interface had been effected once (on average) given approximately by

\[
D_{\text{sat}} = \frac{1}{\alpha}
\]

then one might expect some correlation between these calculated saturation doses and the observed threshold dose for radiation enhanced adhesion. In such a model the only parameter which is varied is the threshold energy \( e_0 \), and hence if good agreement between model and data is obtained, the value of this threshold energy might well give an insight into the mechanism responsible for the effect.

### 9.5.3 Comparison with experiment

The calculations outlined above were carried out for all the film/substrate combinations described in the experimental sections (chapters 5 to 8) and for all ions from \( z=1 \) to \( z=40 \) at the velocity used in the present work of 0.04c, and assuming threshold energies of 0.1, 0.2, 0.5, 1.0, 2.0, 5.0 and 10.0 eV per atom. The result of these calculations for gold film on tantalum substrate (with native oxide) are shown in figure 9.3. The figure shows the expected saturation dose plotted against the ion atomic number. The experimentally observed threshold doses for such samples are shown plotted on the same figure, and the observations appear to be largely consistent with a threshold energy for the adhesion enhancement process of the order of 5 eV.

The calculations for gold films on silicon substrates (again with native oxide) are shown in figure 9.4. In this case the saturation doses for a given energy and ion are considerably higher, reflecting the lower atomic number of the substrate material, which reduces the energy loss rate. The observed threshold doses, although typically a
Figure 9.3: Comparison of model predictions for saturation dose with experimentally observed threshold doses for irradiation enhanced adhesion of gold films on tantalum (with native oxide). The model predictions have been calculated with assumed energy thresholds of 0.1, 0.2, 0.5, 1.0, 2.0, 5.0 and 10.0 eV. Note that all but the 4He ion observation show excellent agreement with the model prediction based on an energy threshold for adhesion of 5 eV.
Figure 9.4 : Comparison of model predictions for saturation dose with experimentally observed threshold doses for irradiation enhanced adhesion of gold films on silicon (with native oxide). The model predictions have been calculated with assumed energy thresholds of 0.1, 0.2, 0.5, 1.0, 2.0, 5.0 and 10.0 eV. Note that all observations show reasonable agreement with the model prediction based on an energy threshold for adhesion of 5 eV. No threshold was observed for He irradiation although doses up to 4x10^{16} ions cm^{-2} were tried.
Figure 9.5: Comparison of model predictions for saturation dose with experimentally observed threshold doses for irradiation enhanced adhesion of a) gold on "dirty" tantalum thermal oxide, b) gold on "clean" silicon oxide, c) gold on "dirty" silicon thermal oxide and d) silver on "dirty" native oxide silicon samples. The model predictions have been calculated with assumed energy thresholds of 0.1, 0.2, 0.5, 1.0, 2.0, 5.0 and 10.0 eV. Note that the majority of observations show reasonable agreement with the model prediction based on an energy threshold for adhesion of 5 eV. No threshold was observed for $^4$He irradiation although doses up to $4 \times 10^{16}$ ions cm$^{-2}$ were tried.
factor of three higher than for the gold/tantalum case, are once again found to be broadly consistent with an energy threshold of around 5 eV. Calculations were performed for the four other systems in the present work where threshold doses were measured, and the comparison between calculated saturation doses and observed threshold dose is made in the composite figure 9.5. Once again, the threshold doses are found to be broadly in line with an energy threshold of the order of 5 eV.

The model also provides a reason for the lack of any observed effect for ⁴He irradiation in several systems. As can be seen from the figures, the saturation (and hence threshold) doses rise dramatically as the Z of the ion decreases, such that for many systems the expected threshold for adhesion enhancement would exceed 10¹⁷ ions cm⁻², which is a higher dose than performed in the current programme of irradiations.

The correlation between the observed threshold doses and the saturation doses calculated from the model must be considered further. In a practical situation, the experimental measurement gives the dose of ions required to pass a particular mechanical adhesion test, such as the scotch tape test. If the effect of each ion is the individually effect, or "stitch", a microscopic region at the interface, there is no reason to believe that the dose at which the scotch tape threshold is exceeded should be that at which all areas of the interface are effected. It might be, for example, that effecting 10% of the interface might be sufficient to produce scotch tape adhesion. Data obtained by Baglin (Baglin 1985a) and other workers, on the variation in adhesive strength as a function of ion dose indicate that a roughly linear increase in adhesion is roughly linear with dose in the appropriate range, and reaches a plateau at some dose, dependent on the combination of ion, film and substrate. This plateau dose is precisely that which should be compared with the saturation doses which result in the model calculation, as these are the doses at which every point at the interface has been effected. In our observations of scratch test load, and its variation with ion dose, we have found that the scotch tape threshold lies typically at some 50% of the plateau dose. Thus for consistency, we should really compare the dose to effect 50% of the
interface area with the experimental observation. The steep slope of the calculated curves of saturation dose for ions of different atomic number mean that errors in irradiation dose of a factor of two do not greatly influence the comparison between model and data.

9.5.4 The data of Stokstad et al and the apparent discrepancy

As was pointed out in chapters 2 and 4, the reported discrepancy in threshold dose dependence of the ion enhanced adhesion of gold films on tantalum, reported by Tombrello et al and Stokstad et al was a factor in determining the direction and approach of the studies reported in this dissertation. Our initial observations were found to be largely consistent with those of Tombrello et al, whose sample preparation and irradiation methodologies we closely followed. While the differences in sample preparation (i.e. glow discharge cleaning prior to gold deposition) used by Stokstad et al will have an effect, it is difficult to explain why such a process would render ion irradiation some two orders of magnitude less efficient for light ions. The other significant difference between the experiments of the two camps is the velocity of the ions used. Our data, shown in figure 9.3, used ions of a common velocity of 0.04c which corresponds to some 0.75 MeV per nucleon. The experiments of Stokstad used substantially higher velocity ions, with energies of 2.85 MeV per nucleon, or in other words velocities of approximately 0.08c. To see if the apparent discrepancy in results could be explained purely by the difference in ion velocity (and hence the spatial distribution of electronic excitation) we have performed calculations of expected saturation dose for gold films on tantalum with ion velocities of 0.08c, and threshold energies of 0.1, 0.2, 0.5, 1, 2, 5, and 10 eV. The result of these calculations is compared with the experimentally observed scotch tape adhesion thresholds of Stokstad et al in figure 9.6. Note that despite the previously apparent disagreement between our observations, we observe both to be consistent with an excitation threshold of 5 eV.
Figure 9.6: Comparison of model predictions for saturation dose with the experimental observations of threshold doses made by Stokstad et al for irradiation enhanced adhesion of gold films on tantalum. In this case the calculations are made for an ion velocity of $0.08c$, corresponding to the ion energies of 2.85 MeV per nucleon. The model predictions are shown for assumed energy thresholds of 0.1, 0.2, 0.5, 1.0, 2.0, 5.0 and 10.0 eV. Note that despite the previous apparent discrepancy between our results and those shown above, both are consistent with the model prediction based on an energy threshold for adhesion of 5 eV.
The apparently higher doses of ions required by Stokstad et al to bring about scotch tape adhesion for gold films on tantalum can thus be entirely explained in terms of the different (less dense) excitation distribution around the higher velocity ions, and underlines the futility of attempting to find an explanation or model of the process based solely on stopping powers.

9.5.5 Summary of modelling results

The process of modelling the radial energy distribution has thus proved to provide a useful tool in understanding the observed variations in threshold doses for the ion induced adhesion effect. We have seen that, in all cases where adhesion enhancement was observed, the threshold dose was consistent with a threshold energy of excitation of approximately 5 eV. This value appears to be independent of the film/substrate species, and suggests a common origin for the adhesion enhancement mechanism.

The modelling process has successfully resolved the apparent discrepancy between the results of different groups for the radiation enhanced adhesion of gold films on tantalum as being entirely explainable in terms of the different ion velocities, and hence spatial excitation distributions. Although the sample preparation routes used in the two cases also differed, the inclusion of glow discharge cleaning prior to gold film deposition is likely only to alter the levels and nature of the interfacial contaminants, rather than eliminate them.

The 5eV value of this excitation threshold is of interest since it would be expected to give some insight into the processes which might be occurring at the film/substrate interface. The value observed is considerably higher than that for the majority of chemical bond strengths (up to 1-2 eV) but much less than the energy required for atomic displacements in single crystals (around 20-50 eV). Although the significance of this value remains unclear, one possible scenario might be that the process involves the disruption of weak substrate/adsorbate bonding, in the presence of significant excitation energy such that the formation of ternary complexes involving
film/adsorbate/substrate atom becomes possible.

9.6 Evidence for interfacial chemistry mechanism

As stated in chapter 3 the proposed mechanisms for the radiation enhanced adhesion phenomenon fall neatly into two distinct camps. Some propose that the enhanced adhesion is produced by electrostatic interactions from charged defects close to the film/substrate interface, induced by the passage of the radiation (the so called "image charge" mechanism). A larger number support theories which propose the interaction to be rather more direct, with the electronic excitation at the interface giving rise to the formation of altered bonding in favour of a stronger more adherent arrangement.

Our observations, both of radiation enhanced and as deposited adhesion, are entirely consistent with a mechanism which involves chemical changes at the film/substrate interface, with particularly strong evidence from the following:

1. For silicon substrates prepared under identical conditions, we observe silver to adhere far more strongly than gold. This strongly suggests interface chemistry is dominant in determining adhesion for these systems.

2. In the case of gold films on silicon we observe thermal cleaning of the substrate to produce much more adherent films than sputtering. This is the opposite to what one would expect if image charge interactions were responsible for adhesion, since sputtering with low energy ions will produce a great deal of near surface damage, resulting in a high level of near surface defects. Thermal cleaning in UHV, on the other hand, will produce a clean surface with low levels of near surface defects, since any defects will tend to anneal out at the elevated temperatures used to remove the native oxide (approximately 950 degrees Celsius). The observations are consistent with interfacial cleanliness being critical to good adhesion.
3. In the case of dielectric substrates prepared with clean interfaces we observed no benefit from subsequent irradiation. This would not be the case if image charge interactions were responsible for the effect, since such interaction would be expected to produce a significant additional contribution irrespective of the cleanliness of the interfacial region. The absence of any effect in the absence of interfacial contaminants is once again evidence of interface chemistry as playing a major role.

4. For gold films on "dirty" silicon oxide substrates we observe identical adhesion enhancement for both thin native oxide and thicker thermal oxide substrates, even though the production of atomic displacements by electronic excitation is quite different in the two cases. Our group, and others, have observed efficient sputtering to occur when silicon dioxide is bombarded by MeV heavy ions, provided the thickness of the oxide is greater than the native oxide thickness. Such atomic displacement phenomena could well give rise to a large concentration of defects, and even a significant mixed interfacial region for bombarded metal films on silica but not for a film on a native oxide substrate. It may well be the case that such MeV sputtering mechanisms will be suppressed anyway, by electron injection from the metal overlayer.

All the above provide evidence that interface chemistry plays a dominant role in not only the radiation enhanced adhesion phenomenon, but the observed adhesion behaviour in general.
CHAPTER 10

Conclusion

In this investigation of the radiation enhanced adhesion of thin metallic films we have developed the ability to produce well characterised samples with controlled interfacial composition. This ability has lead not only to insights into the radiation enhanced adhesion effect, but also to adhesion phenomena in general. The important conclusions will be summarised in the following chapter, with particular emphasis on progress toward our original goal.

10.1 UHV processing and adhesion

As stated in the previous chapter, the modern trend is for thin film fabrication equipment to aim for better and better vacuum. The present study has shown that for one of the system studied, that of gold films on tantalum substrates, there is no difference in as deposited adhesion whether the films are deposited in vacuum of \(10^{-6}\) mbar or \(10^{-9}\) mbar. Thus any claims that UHV processing will produce any benefits for properties such as adhesion should be viewed with scepticism. UHV on its own will produce a cleaner film, but as we have shown it is the interfacial cleanliness which matters for adhesion. This can only be improved by appropriate pre-treatment techniques which are capable of changing the substrate surface composition in a beneficial way.

For such pre-treatment techniques to produce a reliable end product, it may be necessary, however, to employ UHV processing to achieve the required degree of process reliability.
10.2 Interfacial cleanliness and adhesion

The main driving force for building the UHV sample preparation facility was the investigation of the role of interfacial contaminants in the radiation enhanced adhesion phenomenon. As a by product of this we have seen the effect of interfacial cleanliness on film adhesion in the absence of radiation. The basic conclusion is that "clean" interfaces give rise to adherent films, whereas "dirty" interfaces do not. In this context "dirty" refers to any system where the substrate surface is anything less than atomically clean.

The work on silicon and thermal oxide silicon substrates has shown that the adhesion of gold films, which in general would be regarded as quite chemically inert, are sensitive to even small levels of interfacial contamination as evidenced by the poorer adhesion of films deposited onto sputtered (oxygen contaminated) as opposed to thermally cleaned (oxygen free) samples.

The fact that gold films deposited onto thermally cleaned silicon show excellent adhesion, far in excess of anything that can be produced even by high energy ion irradiation, is indeed surprising and provides strong evidence for interfacial cleanliness as being of primary importance in the production of adherent films.

10.3 Sputtering as a surface cleaning technique

Another aspect of thin film fabrication technology which has been highlighted in the present study is the inability of sputtering, with low energy ions, to produce a truly clean surface. We have seen that gold film adhesion is significantly better on silicon and silicon oxide substrates where thermal rather than sputter cleaning procedures were used. This is attributed to the inability of sputtering to completely remove oxygen, present as either a recoiled impurity (native oxide) or surface adsorbate (thermal oxide).

Although the energy of argon ions used in the present work (9 keV) is higher than those used in most ion enhanced deposition processes (typically a few hundred to
a few thousand eV), the basic interaction processes will be the same, other than the higher energy tending to produce mixing effects over greater depths. The conclusion must be that although low energy ion sputtering definitely alters the composition of the near surface, and this may well be of benefit to the adhesion of some subsequently deposited films, to say that the effect of the ion beam is to "clean" the surface is an unjustified over simplification and somewhat of a misnomer.

10.4 Radiation enhanced adhesion effects and interfacial contamination

The main aim of building the UHV sample preparation facility, as stated above, was to investigate the role of interfacial contaminants in the radiation enhanced adhesion phenomenon. As was highlighted in the section dealing with our experimental approach, it was suspected that sample preparation differences lay at the heart of the dramatic discrepancies between the results of different experimental groups reported in the open literature. If this were the case, and the contaminant species present at the interface were important in determining the observed efficiency of irradiation, then one would naturally be lead to ask if these contaminant species were playing an essential part in the entire process.

This has indeed proved to be the case in the systems we have studied. In these systems, which included metal on metal, metal on semiconductor, and metal in insulator. Irradiation produced no beneficial effects for samples prepared with atomically clean interfaces. This provides strong evidence that the primary adhesion promoting mechanism in the high energy irradiation of film/substrate interfaces is the disruption of interfacial contaminant containing layers in favour of stronger chemical bonding across the interface, thus reducing the interfacial energy and increasing the energy of adhesion.

A radial energy distribution model of energy deposition has been successfully applied to our observations and found to be consistent with a process with an energy
threshold of some 5 eV per atom, which is perhaps indicative of the breaking up of weak chemical bonds in the interfacial region involving contaminant species such as adsorbate, hydrocarbons and the like. The model has also explained the apparent discrepancy between measurements made of the threshold dose dependence on ion stopping power previously reported. The observations may be entirely explained by the difference in ion velocities used, and hence the difference in the electronic excitation distribution. All the observations are consistent with threshold excitation energies of the order of 5 eV.

10.5 Direction of future work

The precise mechanism involved in radiation enhanced adhesion phenomena may well vary from system to system, but there is strong evidence in the cases studied here that the effect is primarily due to radiolytic effects on interfacial contaminant species present at the film/substrate interface. A definitive answer to the mechanism involved will only be obtained if some form of analysis sensitive to chemical bonding or structural rearrangement can be performed before and after irradiation. This should detect the changes which results, and can correlate such changes with the observed changes in film adhesion. Unfortunately, suitable techniques such as Raman IR Spectroscopy, X-ray diffraction, etc, lack the necessary depth resolution to be able to analyse a buried interface. Very near surface techniques such as X-ray Photoelectron Spectroscopy and Auger Electron Spectroscopy have the required sensitivity but would require very thin films (<2 nm) in order to be sensitive to interface bonding. Such thin films would require the deposition, high energy irradiation and surface analysis system to be within a single UHV environment to avoid unacceptable changes due to atmospheric exposure. To the knowledge of the author, such a system has yet to be built.

The radial energy deposition model shows promise as a predictive tool, not only for the radiation enhanced adhesion effect, but for all effects where electronic
energy deposition is the driving force. With the addition of a Scanning Tunnelling Microscope to the SURF facility, various opportunities for verifying the spatial distribution of effects around an ion trajectory become apparent. Firstly, one could consider the study of the spatial distribution of damage around ion trajectories on semiconductor surfaces or even insulating surfaces (with appropriate techniques to overcome their inherent unsuitability for STM work). Cross-sectional STM work at a film/substrate interface is also a possibility worthy of investigation. Reports of electron injection STM work, where electrons are injected through a film into an underlying conducting substrate, are of interest since a chemically modified interface (by irradiation) might well be expected to show fluctuations in injection probability in areas around each ion trajectory. A further possible application of STM work to this field is the study of the effect of various surface preparation techniques on wetting and film nucleation phenomena. As has been mentioned, wetting is closely correlated to adhesion, and one might expect the surface preparation processes used in the present work (e.g. sputter and thermal cleaning of silicon) to yield results which reinforce the adhesion observations.
APPENDIX

A1 Adhesion testing methods

One of the many problems in experimentation in the field of adhesion phenomena is the lack of reproducible tests for the quality of the adhesive bond between a thin film and the underlying substrate (Mittal 1978). Many of the tests are of a threshold nature, and provide a simple pass or fail result. Others attempt to measure the force required to separate the film from the substrate, while another approach is to look at more fundamental aspects such as the substrate surface energy and wetting.

One of the shortcomings of all the available adhesion tests is that they are incapable (with very limited exceptions) of giving data which can be converted to a quantitative value for the energy of adhesion (the energy required to separate unit area of film and substrate). It is precisely this energy which varies between one system and another, and although some tests may prove effective at ranking films according to the adhesion strength, putting a figure to the energy of adhesion is much more difficult. As a general guide, however, since surface free energies are of the order of 1 J m\(^{-2}\), the adhesion energy of a perfectly bonded interface (i.e. one with negligible interfacial energy and bond strengths of the order of 6 eV), the energy of adhesion will be approximately 2 J m\(^{-2}\). In very weakly bonded films, where most of the adhesion results from Van der Waals contributions, the rather weak energy of such bonding results in adhesion energies of the order of 0.1 J m\(^{-2}\). The majority of deposited thin films lie in the middle ground between these two extremes (Neugebauer 1970).

In the sections which follow a brief description of the commonly applied adhesion tests will be given, with particular emphasis on their respective strengths and weaknesses. The majority of the techniques are illustrated by the schematic diagrams in figure A1.1.
Figure A1.1: Schematic diagram illustrating some of the most commonly applied mechanical film adhesion test methods.
A1.1 Scotch tape test

This a very simple example of a threshold adhesion test, and although crude, is capable of surprisingly reproducible results (Strong 1945, Bateson 1952). The basis of the test is simple; scotch tape (3M pressure sensitive tape) is placed on the surface of the film, and is rubbed with a blunt instrument. The film is then pulled at right angles to the substrate, and if the film remains on the substrate the result is a pass, if the film is removed with the tape the result is a fail. The main drawback is that this test has a threshold which corresponds to fairly weak adhesion, and hence is only of use in poorly adhering systems such as noble metal films or substrates such as teflon.

One of the perceived problems with the test is that it tests the film/substrate interface by applying a further film, and hence generating yet another interface. The adhesion of the tape to the film is not, in general, observed to be particularly sensitive to the surface quality of the film. This cannot be said, however, for the surface roughness of the substrate, since the contact area of the tape with the film depends directly on the surface roughness, as the tape is not in general able to follow the surface contours of a rough surface. This may result in patchy or incomplete film removal on surfaces with poor surface finish, hence the popularity of silicon and glass substrates in reported experiments.

A1.2 Q-tip or cotton bud test

This test follows on naturally from the scotch tape test, as it is again a threshold adhesion test. It involves rubbing the surface of the film with a cotton bud (or for those from the other side of the Atlantic, what is known as a Q-tip), to test whether the film can be removed. The test is slightly more severe than the scotch tape test, but again is hardly a test of excellence, since films which may be removed by rubbing with a cotton bud are not likely to be technologically useful. The test is rather subjective, since no two people are likely to carry out such a test in exactly the same way. The somewhat feeble construction of the test implement does, of course, limit
the range of loadings that may be applied.

A1.3 Peel test

The peel test is, in many ways, a quantitative version of the scotch tape test. It involves attaching a stripe of film, of known width, to a balance and measuring the force required to peel the film from the substrate at right angles to the surface (Baglin 1984). This would appear to be the ideal test as it comes closest to measuring the types of quantities needed for a quantitative study of adhesion strength. There are drawbacks, however, such as the fact that the film will, in general, inelastically deform as it is pulled from the surface, which will obviously have an effect on the measurements. The test also requires a film of sufficient thickness for the strip to remain intact, which precludes the use of very thin films (<1 μm). This is more of a limitation than it might at first appear, in that in many combinations of film and substrate tensile or compressive stresses build up as the film thickness is increased, leading to spontaneous failure of the interface at micrometre type thicknesses.

In some cases, finite-element analysis of the peeling process has been performed resulting in a "universal" dimensionless plot for the steady state peel force against the energy of adhesion (Kim 1985). Providing parameters such as the Youngs modulus, Yield strength and thickness of the film are known, this enables a quantitative estimate of the adhesion energy. The analysis which has been made has also proved useful in identifying the way in which measured parameters, such as peel force, are effected other parameters of the system such as film thickness.

With the above comments taken into account, it is probably still the case that, subject to further improved analysis of the failure process, the peel test represents the best hope for an adhesion test capable of providing quantitative information on adhesion energies.
A1.4 Pull test

The pull test involves attaching a cylindrical pin of known area to the film surface, either using a glue or solder layer, and then measuring the peak force required to pull the pin from the substrate, complete with film (Sofield 1984). The main objections to such a test are the use of the joining layer of glue, or worse still solder, since such processes are likely to perturb the film/substrate adhesion, particularly in the case of thin films where diffusion processes are more likely. A more fundamental objection arises when one considers what is actually being measured. When such a pin test is conducted, the film will invariably fail by initiation at some weak point, which then propagates across the pin area. The common practice of quoting adhesion in terms of force per unit area of test is thus fatally flawed. The test is used principally as a mimic of the types of mechanical loads that practical thin film products may be subjected to in applications such as semiconductor device packaging.

The principle difference between this test and the peel test is that the pull test is dominated by failure initiation, whereas the peel test is dominated by the propagation of such failure, which more closely related to the adhesive properties of the film as a whole.

A1.5 Scratch test

In the scratch test, a diamond stylus or steel ball is dragged across the surface of the film with a precisely known load (Carbucicchio 1986, Kikuch 1985). Often the samples are mounted on motorised stages such that the speed of the stylus movement across the film is precisely controlled. The accumulation of shear stress in front of the moving stylus will ensure that once a critical load is reached, the film will be removed leaving a clear channel. In general, microscope examination of such scratches is used to assess the onset of film removal, which is aided by the film and substrate being different colours (e.g. gold on silicon). The test is semi-quantitative, in that it enables samples of the same materials to be ranked in terms of their resistance to interfacial
failure. There is not, however, any universal way of relating the critical failure load to any parameter such as energy of adhesion, except in a very limited cases where the precise details of the failure mode (which may well vary from system to system) has been modelled (Bull 1988).

A1.6 Contact angle test

In stark contrast to the above mechanical adhesion tests, the contact angle test provides a direct measurement of the energy of adhesion, $E_{ad}$ at the substrate surface. As illustrated in figure A1.2, the test involves measuring the equilibrium angle of contact $\Omega_c$ between a liquid drop of the film material and the surface of the substrate material A.

In equilibrium it has been shown that

$$E_{ad} = \gamma_{s(A)} (1 + \cos \Omega_c)$$

where $\gamma_{s(A)}$ is the surface free energy of material A (Murr 1975). Hence for a perfectly adhering interface, where $E_{ad}$ is of the order of $2\gamma$, the contact angle will be close to zero and the film will wet the surface well. For a poorly adhering film, the energy of adhesion will be very small, and hence the contact angle will be large, approaching 180 degrees, and the film will form beads as shown in the figure. A contact angle of 90 degrees would occur in the case of an interface with an adhesion energy equal to the surface free energy of the substrate.

This technique has received little attention from experimentalists in the adhesion field, partly because it is so far divorced from the practical mechanical failure criteria, which determine the technological usefulness of a coating. The technique also requires knowledge of, and perhaps even more difficult, control of the surface energy of the substrate. Surface energies are known only for a limited number of single crystal materials, and are critically dependent on the precise state of the
surface in terms of reconstruction and perturbations due to adsorbates. The technique should be of interest, however, to those working in the field of surface science where Ultra High Vacuum techniques should permit control of such surface parameters.
Figure A1.2: Schematic diagram of the contact angle adhesion test.
A2 Harwell facilities for MeV ion irradiation and analysis

Throughout the work described in this dissertation, extensive use has been made of the MeV accelerator facilities of the Harwell laboratory. In the current context this includes the 5 MV Van der Graaff and 7 MV Tandem accelerators, operated by the Accelerator Applications Department of M&MT, Intec, a part of AEA Technology. The two machines provide a variety of ion species, used in both research and applied programmes. The facilities made use of in the present work are described in the following sections.

A2.1 Irradiation facilities

In the initial experiments using conventional preparation techniques (described in chapter 5) the irradiations were performed in modest vacuum (10^{-6} mbar), using a chamber designed for Ion Beam Analysis of samples by techniques such as Rutherford Backscattering (RBS), and Elastic Recoil Detection Analysis (ERDA). It contains the essential elements of sample manipulation (using a seven position target ladder), variable collimation and accurate dosimetry, using a rotating blade beam chopper system calibrated against a well suppressed Faraday cup.

The majority of the experiments made use of a Ultra High Vacuum (UHV) irradiation facility on the 7 MV Tandem accelerator commissioned for this study. A photograph of this facility is shown in figure A2.1. The chamber comprises a 1 metre diameter stainless steel cylinder pumped by a CTI Cryogenics CT-8 cryopump, producing a base pressure of 10^{-9} mbar without bake-out. The chamber is equipped with a Vacuum Generators HPLT-150 precision XYZ and theta manipulator, for use with a bayonet mounted eight position target ladder. The target ladder can be loaded using a wobble-stick in the preparation system SURF, and transferred under vacuum using the transportable load-lock facility, which can be seen attached to the lid of the irradiation chamber. Although the load lock system is not pumped, the pressure when isolated from any host vacuum system is still approximately 10^{-3} mbar, and hence
Figure A2.1: Photograph of the Ultra High Vacuum (UHV) irradiation facility of the Harwell Tandem accelerator. Note the vacuum transfer vessel attached to the chamber lid, which enables a ladder containing up to eight samples to be transferred from the sample preparation system (SURF) without atmospheric exposure.
although not capable of maintaining an atomically clean sample surface, it does
dramatically reduce the level of contamination due to atmospheric exposure, which
would otherwise occur. The design of the load lock transfer system permits eight
samples to be loaded from SURF onto a target ladder, the load lock uncoupled
complete with target ladder, and the ladder loaded into the irradiation chamber within
one hour. The load lock system allows the pressure of the system to recover to its base
value within minutes of loading a ladder assembly.

The beam is steered and focussed down the beam line, de-coupled from the
accelerators diffusion pumped vacuum system by a liquid nitrogen cooled restriction
to prevent oil backstreaming. The line itself is pumped by ion pumps to eliminate
hydrocarbons. The beam area is determined by a collimator on a geneva mechanism
containing six alternative sizes including 3 x 3 mm and 4 x 4 mm for irradiations, and
2 x 1 mm for ERDA analysis. The collimator is located only 100 mm upstream of the
target. The dosimetry of this chamber once again makes use of a rotating blade coated
with 200 nm of gold, which intercepts some 5% of the incident beam, scattering a
small fraction into a semiconductor particle detector. This detector is calibrated
against an electrically suppressed Faraday cup immediately prior to irradiation, such
that irradiation fluences should be accurate to a few percent. The UHV nature of the
irradiation system made use of a conventional DC motor to drive the chopper blade
impossible, and hence a UHV compatible stepper motor, running continuously at
approximately 2 Hz was used instead.

As well as the chopper semiconductor detector, the chamber is equipped with
two further particle detectors. These were located at 160 degrees for detecting
backscattered particles for sample analysis using the RBS technique (using both He
and heavier ions), and 30 degrees for detection of recoiled target light elements with
the sample in a geometry for ERDA analysis, described further in the sections below.
A2.2 Rutherford Backscattering (RBS) analysis

The technique of Rutherford Backscattering is one of the most well established uses of high energy particle accelerators, and is commonly used as a diagnostic tool in high technology process development. The analysis technique makes use of nuclear scattering of high energy particles, typically helium, by the atomic nuclei of the atoms in the near-surface. The energy with which a helium projectile is backscattered depends on the mass of the target atom, the scattering angle and (due to energy loss) the depth at which the scattering event took place. Hence the technique can give quantitative depth resolved information on the masses present in the first micron of a sample. The scattering cross section increases with the mass of the target making the technique particularly sensitive for heavy elements. A spectrum from the scattering of 2.0 MeV $^4$He from a sample of 50 nm gold on silicon is shown in figure A2.2. The use of a simulation code such as SIMBA, developed at Harwell, enables the expected spectrum from a best estimate of the sample composition to be calculated, and the true composition determined by comparison of the experimentally obtained data with the simulation. This simulation process can thus yield quantitative information on film thickness and composition. An example of the sensitivity of the technique is given in figure A2.3, which shows the RBS spectrum using 2.0 MeV $^4$He ions on a sample which is supposedly 50 nm of silver on silicon. The boat used for the evaporation of the silver, however, had previously been used to deposit gold films, and hence a gold contaminant is clearly resolved. In many cases, such data was obtained as a by product of the irradiation experiments, since the vast majority of irradiations were performed in a geometry suitable for RBS analysis, and hence the RBS spectra were recorded as a matter of course.
Figure A2.2: Rutherford Back-Scattering (RBS) spectra obtained from identical 50 nm gold films on native oxide silicon (top) and sputter cleaned silicon (bottom) substrates. Note the presence of implanted argon from sputtering in the lower spectrum.
Figure A2.3: Rutherford Back-Scattering (RBS) spectra obtained from a 50nm silver film on sputter cleaned silicon substrate. Note the presence of implanted argon from sputtering and the small level of contaminant gold in the silver film (some 0.25%).
A2.3 Elastic Recoil Detection Analysis (ERDA)

The Elastic Recoil Detection Analysis (ERDA) technique is complementary to RBS in that it is a way of obtaining quantitative depth profiles of the light elements, including hydrogen. As applied at Harwell, the technique uses a 30 MeV $^{35}\text{Cl}^{6+}$ beam at an incident angle of 20 degrees to the surface, and detects the light target atoms which recoil from nuclear collisions at a scattering angle of 30 degrees using a semiconductor detector equipped with a foil to arrest the elastically scattered chlorine ions. This absorber foil restricts the sensitivity of the technique to elements lighter than fluorine. A spectrum obtained from a thin (23 nm) $^{18}\text{O}$ oxide layer grown on silicon is shown in figure A2.4. Markers are given at energies corresponding to surface recoils of the elements hydrogen, oxygen and carbon.

In the figure, the hydrogen and carbon peaks observed on a sample transferred from SURF under vacuum is compared with those observed in a sample from the same batch of oxides, but this time analysed in our conventional ERDA facility, with the inevitable exposure to laboratory air. In the first case (UHV) the hydrocarbon contamination is equivalent to some 20% of a monolayer, whereas in the latter the coverage with hydrocarbon is some 2 monolayers, which is typical of samples exposed to atmosphere.

A2.4 Nuclear Reaction Analysis (NRA) and RBS Channelling

The 5MV Van der Graaff accelerator is equipped with a UHV chamber for Nuclear Reaction Analysis (NRA) and RBS channelling. In the case of NRA, the ability of particles to initiate characteristic nuclear reactions is used to give quantitative information on the species present. The prompt reaction products, usually particles but occasionally gamma rays, are detected and the technique made quantitative by reference to standards for particular elements. RBS channelling is essentially the same as RBS described above, but with the additional information that can be obtained by aligning the incident beam with a primary axis of a single crystal
Figure A2.4: Elastic Recoil Detection Analysis (ERDA) spectra from a 23 nm thick silicon oxide thermally grown in isotopic $^{18}\text{O}_2$, as measured in our conventional ERDA chamber (top) which requires exposure of the sample to atmosphere for loading, and in our Ultra High Vacuum analysis chamber (bottom) which uses vacuum transfer. Note the far lower levels of surface hydrocarbon contaminant in the UHV case.
target. Such a process leads to a dramatic reduction in the probability of nuclear scattering, and hence can be used to assess crystal quality, damage distributions or investigate epitaxy.

The chamber has the capability for transfer from the SURF preparation facility, and a base pressure of $5 \times 10^{-8}$ mbar. The system uses a semiconductor detector in backscattering geometry with interchangeable collimators, with and without absorbers, to detect either reaction product particles or backscattered projectiles. The sample is mounted on a 2 axis goniometer for use in channelling analyses. The commonly applied nuclear reactions are $(d,p)$ for the simultaneous measurement of carbon, oxygen and nitrogen levels, and $^{18}O(p,\alpha)$ and $H(\text{^{15}N},\gamma)$ resonant reactions for sensitive depth profiling of $^{18}O$ and hydrogen respectively. In the case of resonant nuclear reaction profiling, the particle energy is varied under computer control, to vary the depth at which the resonant particle energy is reached, thus allowing the concentration variation of the particular nuclear species with depth to be obtained.
A3 The Harwell UHV Sample Preparation Facility: SURF

A3.1 Introduction

As discussed previously, to perform meaningful experiments in the vast field of surface and interface phenomena it is essential to have precise control of surface cleanliness and crystallinity. For the majority of materials this leads directly to a requirement for Ultra High Vacuum (UHV) sample processing, since conventional high vacuum systems result in unacceptable levels of surface contamination by adsorbates and hydrocarbons. In a research environment this is not difficult to achieve since sample sizes can be small, and throughput and ease of use are of only secondary importance.

The system currently under development at Harwell, known by the acronym SURF (Surface Ultra high vacuum Research Facility), encompasses a range of facilities, enabling its use in a wide variety of fields. It has specifically been used, to date, in studies of silicon oxidation mechanisms and radiation effects on the adhesion of thin metal films.

A3.2 System Description

A3.2.1 General Principles

At a pressure of $10^{-6}$ mbar, which is common place in a wide variety of high vacuum equipment such as ion implanters and deposition systems, gas molecules arrive at any exposed surface at a rate of some $1 \times 10^{15}$ cm$^{-2}$ per second which is equivalent to roughly one atomic layer per second. Thus if we wish to perform meaningful experiments with reactive surfaces (e.g. silicon), it is imperative that the partial pressures of reactive species, such as H$_2$, O$_2$, CO, be reduced to a level whereby atomically clean surfaces can be maintained for useful periods. This requirement is satisfied in the case of UHV pressures ($1 \times 10^{-10}$ mbar), which can be
achieved routinely provided considerable attention is paid to selection of materials in a system subjected to only moderate bake-out (130 degrees Celsius for 48 hours). Within SURF, samples of a standard size of 15 x 15 mm are handled without stubs or holders, such that a minimum of material is introduced through the load lock. Sample transport throughout relies on magnetically coupled linear/rotary motion drives, with wobble stick loading and unloading. A schematic diagram of the current system is shown in figure A3.1. The beam from the ion source may be used in any of the three main chambers which are configured for sample preparation, metal deposition and in-situ analysis respectively. The furnace chamber is equipped with a quartz hot-wall furnace and isotopic $^{16}$O and $^{18}$O gases for labelled oxide experiments. The system also permits vacuum transfer of samples to UHV ion irradiation and analysis facilities on our 5 MV Van de Graaff and 7 MV Tandem accelerators.

The individual parts of the SURF system are described in the following sections.

A3.2.2 Ion Source

The ion source is of the duo-plasmatron type, and is connected to research grade supplies of $D_2$, He, Ne, and Ar gas for rapid beam switching, which can be achieved in around 2 minutes. The source provides extracted currents of up to 1 mA and the energy can be varied from 0.5 to 20 keV. The UHV requirement in the specimen chambers necessitates two stages of differential pumping of the ion source, which is achieved by using a 200 l s$^{-1}$ diffusion pump on the source chamber and a 2000 l s$^{-1}$ cryopump on an intermediate chamber separated by a 15 degree analysing magnet. The differential pumping apertures restrict target currents to a maximum of around 5 $\mu$A cm$^{-2}$, which is accompanied by a pressure rise in the target chamber of as little as 2x10$^{-10}$ mbar. Under these conditions the majority of the pressure rise is due to ions rather than gas molecules, which may be verified by monitoring the gas load in the UHV system on turning off the analysing magnet.
A Schematic of SURF

1 Ion Source
2 PUMPING Station
3 15° magnet
4 PUMPING Station
5 Sputtering Chamber
6 Deposition Chamber
7 LEIS/MEIS Chamber
8 Magnetic Drive
9 Oxidation Vacuum System
10 Oxidation Furnace
11 Load Lock
12 Bake out Jacket

Figure A3.1: Schematic diagram of the SURF sample preparation facility.
Figure A3.2: Photograph of the current configuration of the SURF sample preparation facility.
A3.2.3 Load lock and Preparation chamber

The preparation chamber allows introduction of samples from atmosphere through a load lock. Transfer occurs at a pressure of typically $1 \times 10^{-8}$ mbar which recovers to less than $2 \times 10^{-10}$ mbar within 1 hour. Sample cleaning can be performed using Ar$^+$ sputtering at 3-15 keV and current densities of up to $5 \mu$A cm$^2$ which typically removes some 2 monolayers per minute of SiO$_2$.

A3.2.4 Deposition chamber

The deposition chamber allows metal layers 0.1-200 nm thick to be deposited at rates up to 1 nm per second. It comprises of 4 alumina coated molybdenum boats on a rotary drive, separated from the substrate area by a liquid nitrogen cooled baffle, with only a small hole for evaporant material to pass through. Each half of the deposition system has a 4000 Ls$^{-1}$ cryopump to cope with the considerable gas load during deposition. The chamber has an RF quadrupole for residual gas analysis. Twin quartz crystal oscillators on the sample holder are used to monitor film thickness.

After prolonged out-gassing, it is possible to deposit gold or silver films from this system in an ambient pressure of $1 \times 10^{-9}$ mbar. Since the deposition rate is typically some 2 monolayers per second, the vacuum can be seen to be adequate to ensure that it is possible to produce essentially atomically clean interfaces with such a system.

A3.2.5 Oxidation chamber

This chamber consists of a quartz hot wall furnace equipped with supplies of dry natural and isotopic $^{18}$O enriched gas, attached to a chamber with a base pressure of $1 \times 10^{-10}$ mbar. The furnace magnetic drive is made entirely of quartz to eliminate metallic contamination of the hot zone. The pressure of the furnace during oxidation is monitored using a capacitance manometer in the pressure range of 1 to 1000 mbar.
Water vapour, within the oxygen, is less than 5 ppm and any water vapour formed by 
\( \text{H}_2 \) diffusion through the hot furnace wall is trapped on an arm of the tube which is 
submerged in liquid nitrogen. The gas can be sampled through a differentially pumped 
residual gas analyser.

### A3.2.6 In-situ Analysis

An important ability in any UHV processing facility is the ability to characterise the structures produced in-situ, since atmospheric exposure will, in most cases, result in irreversible changes. Surface and near-surface analysis are performed in \textit{SURF} using the techniques of Low and Medium Energy Ion Scattering (LEIS and MEIS). The techniques use the same experimental arrangement of ion beam and a 50 
mm diameter Hemispherical Electrostatic Analyser (HEA) at a fixed scattering angle 
of 90 degrees as shown schematically in figure A3.3. Particles which undergo binary 
collisions with near surface atoms of the sample pass around the analyser, without 
retardation, and are detected by a channeltron electron multiplier. The HEA is driven 
under computer control, and has a resolution \((\delta E/E)\) of approximately 4\% at present. 
The scattering angle of 90 degrees is particularly convenient for two reasons. Firstly, 
the angle results in the elimination of energetic sputtered particles, since at an angle of 
90 degrees to the beam these will have very small energies, and secondly because the 
kinematics of binary collisions result in a very straight forward expression for the 
resultant energy of the scattered projectile. The projectile energy after the binary 
collision \(E\), between a projectile mass \(m\) and target mass \(M\), is given by

\begin{equation}
E = E_0 \frac{(M-m)}{(M+m)}
\end{equation}

where \(E_0\) is the projectile energy prior to scattering. The collection of energy 
distributions requires that the analyser be set with appropriate positive (outer 
hemisphere) and negative (inner hemisphere) voltages for each scattered energy, and
A diagram of the ion scattering facility.

The scattering angle is fixed at 90°.

Figure A3.3 : Schematic diagram of the in-situ analysis using the ion scattering techniques of Low and Medium Energy Ion Scattering (LEIS and MEIS). In the current system, typical analysis beams are 1.5 keV $^4$He (LEIS) and 10 keV $^2$H (MEIS). Electrostatic analysis of the scattered particles ensures only those scattered as ions are detected.
hence data are collected by scanning the analyser through the selected range of energies, counting for a preset accumulated charge on the target for each data point. The sample is mounted on a two axis goniometer to enable the investigation of surface or near surface channelling phenomena.

In the case of Low Energy Ion Scattering, beams of inert gas ions, typically 1.5 keV He, are used to give information on the species present on the surface of the sample. The surface specific nature of the LEIS technique arises from the rapid neutralisation of inert gas ions at low energies. Hence the projectile particle will only be scattered as an ion if the collision occurs with a target atom in the surface monolayer. Since analysis makes use of an electrostatic analyser, only those particles scattered as ions will be detected, and hence the surface specificity. An example spectrum for the scattering from clean and contaminated silicon surfaces with partial gold coverage is given in figure A3.4. In contaminated case, the deposition of the gold was accompanied by a significant burst of carbon monoxide from the deposition system components and hence we observe carbon and oxygen, as well as silicon and gold. Features are observed which correspond to binary collisions between He and C (E/E_0 = 0.5), He and O (E/E_0 = 0.60), He and Si (E/E_0 = 0.75), and He and Au (E/E_0 = 0.96).

Quantification of LEIS data is notoriously difficult, as the intensity of the observed peaks is critically dependent on the probability of the projectile being scattered as an ion. Even for true surface scattering this is less than one and dependent on the precise state of the surface, including the presence of contaminant species such as adsorbates. Hence the technique is only of practical use when used on clean surfaces, in which case it gives a useful qualitative guide to which species are present on the surface.

Medium Energy Ion Scattering, in this context, uses 10 keV D^+ ions with analysis currents of typically 100 nA, to give a depth resolved picture of the near surface (1-100 nm). For these energies of D^+, the probability of neutralisation is smaller, and hence particles scattered over a range of depths are detected. Since the
Figure A3.4: Low Energy Ion Scattering (LEIS) data obtained from silicon surfaces with a partial coverage with gold. The top data is for a sample with a significant level of carbon monoxide as a surface contaminant, whereas the data for the second sample reveals only silicon and gold to be present on the surface.
particles lose energy in a well defined way, the depth at which the scattering event took place can be estimated from the detected energy. With MEIS, the ability to align the analysis beam with a primary axis of a single crystal target can yield useful information on crystallinity, since under such conditions, the probability for nuclear scattering is much reduced. This results from the steering forces of the atomic rows, which tend to keep the projectiles within the open lattice channels. As an example of the MEIS scattering technique we present data from a silicon sample with a native oxide layer of approximately 2 nm in figure A3.5. In channelling alignment, peaks are clearly resolved corresponding to the Si and O incorporated in the amorphous native oxide layer, and the background silicon signal is well suppressed. The spectrum obtained with the beam striking the sample in a random direction is also shown. To a lesser extent, MEIS also suffers with problems of quantification since the technique relies on the detection of charged scattered particles in situations where the neutralisation probability is not precisely known. However, with careful cross comparison with other more quantitative techniques such as Rutherford Backscattering or Nuclear Reaction Analysis it is possible to produce quantitative results.

### A3.2.7 Vacuum transfer

Up to 8 samples may be loaded onto a target ladder, connected via a bayonet fitting, to a linear/rotary drive which may optionally be attached in place of the load lock system. The ladder can then be removed, under vacuum, for transfer to our UHV chambers on either our 5 MV Van de Graaff accelerator for Nuclear Reaction Analysis (e.g. $^{18}$O profiling) or our 6 MV Tandem for ion irradiation experiments or Rutherford Backscattering or Elastic Recoil Detection Analysis. At present the transfer flask is not pumped and hence the pressure in the flask rises to around $10^{-3}$ mbar during transfer which takes around 30 minutes.
Figure A3.5: Medium Energy Ion Scattering (MEIS) data obtained by channelling a 10 keV deuteron beam in a native oxide silicon sample. Note the dramatic reduction in yield from the single crystal substrate silicon when the analysing beam is aligned with a principle axis of the sample, leaving only the peaks from non-registered surface silicon and oxygen.
A3.2.8 Ion Beam Deposition

Various laboratories are experimenting with depositing materials by an ion beam route such that the arriving ions, which form the film, have precisely controlled energies usually in the range of 1-500 eV. To produce technologically useful deposition rates such systems are usually based around ion implantation machines. We have experimented with a small deceleration lens, within the current system, as a means of developing lens technology for a future machine to be based on an implanter. Carbon ions can be extracted from the duo-plasmatron and current densities of up to 1 µA cm\(^{-2}\) over a 5 mm diameter area obtained. With the current lens, which is a miniature design some 100 mm long and 50 mm diameter, current densities are maintained down to around 50 eV. Further refinement of the design to include substrate heating is currently in progress.

A3.2.9 Scanning Tunnelling Microscopy

The imaging capabilities of the Scanning Tunnelling Microscope (STM) has had a dramatic impact in the field of surface science. To further enhance the capabilities of our system we are currently accommodating the addition of a commercial STM system, designed by Omicron in West Germany, within the same vacuum environment. The requirement that the STM system be able to accept the bare 15 x 15 mm samples from the rest of SURF has necessitated the design of our own custom chamber, with facilities for loading samples onto tantalum holders in-situ, as well as load lock and electron beam heating for stand-alone operation. Since the instrument is required to work whilst attached to the existing equipment of SURF, the isolation of the STM from rather high levels of both acoustic and mechanical vibration is of prime importance. For this reason we have selected a design which uses magnetic damping of the microscope stage rather than conventional viton stacks.

This may well be the most difficult operating environment that an STM has so far encountered and hence the STM chamber has been designed to be detachable from the main system for the highest resolution imaging work.
A4 The Kobetich-Katz Model of MeV ion effects

The appendix section which follows describes a modelling framework, used to extract some useful information on the radiation adhesion effect produced by MeV ions. The model dates back to the late sixties, when it was shown that it was of benefit in the understanding of several effects produced by MeV ions, such as the formation of etchable damage tracks, and the response of inorganic scintillators to heavy ions.

A4.1 General approach

The range of interactions of fast heavy ions with solid materials are many and complex. A precise mathematical description of such processes is still some way off, as it is only during recent years that reliable descriptions of the much simpler low energy ion beam effects have evolved. At low energies, almost all of the projectile energy is lost to nuclear collision processes. Hence a reasonable approximation of the atomic potential leads directly to an ability to predict the final result of the passage of a slow ion through a solid, provided enough care is taken over following the history of each and every displaced atom.

In the case of MeV ions, the situation is somewhat different. The majority of energy deposition is lost to the atomic electrons, and it is the subsequent dissipation of this excitation energy which leads to the considerable range of observable phenomena. Since such phenomena are critically dependent of the electronic properties of the material, it would seem that any model which aims to treat the effects of MeV ions in a rigorous fashion would need to contain a detailed description of electronic excitation phenomena, as well as details of the electronic properties of the materials of interest. Fortunately, it is possible to make useful predictions based on a much simpler approach to electronic excitation phenomena, developed by Kobetich and Katz of the University of Nebraska.

In their work of the late 1960's, the newly developed semi-empirical range-energy relationships and formulae for transmission probabilities of energetic electrons
in matter were combined with expressions for the energy distribution of primary
electronic excitations, to provide a method of calculating the transverse energy
distribution around the trajectory of a fast heavy ion.

A4.2 Semi-empirical relations

The model is based on three semi-empirical relations, that for the production of
energetic primary electrons, that for the range energy relationship for the energetic
electrons, and that for the transmission probability of the electrons.

The first of these, for the production of primary excitations, arises as follows.
The effective charge $z_e$, of an ion of atomic number $Z$, moving through matter at a
velocity $v=\beta c$, has been shown to be approximated by the expression

$$z_e = Z[1 - \exp(-125\beta Z^{2/3})]$$

The number $dn/d\omega$ of energetic electrons per unit ion path having energies between
$\omega$ and $\omega + d\omega$ liberated from matter having $N$ free electrons per unit volume by a
passing ion of effective charge $z_e$ is given by

$$dn/d\omega = 2\pi N z^2 e^4/mv^2\omega^2[1 - \beta^2/\omega/\omega_m + \pi\beta z/137(\omega/\omega_m)^{1/2}(1-\omega/\omega_m)]$$

where $\omega_m = 2mc^2\beta^2/\gamma^2$ and $e$ and $m$ are the electron charge and mass respectively.
To account for the initial electron binding energy, the kinetic energy of the electron
$\omega$ is related to the total energy imparted to the electron $\omega$, by the average
ionisation potential of the material $I$, by the expression

$$\omega = w + I$$

The most energetic electrons result from the closest impacts, but are relatively
uncommon. The vast majority of the electrons result from larger impact parameter events, and give rise to less energetic electrons which will deposit most of their energy close to the ion trajectory. It is these electrons which give rise to the intense excitation close to the ion trajectory. From classical kinematics, it can be shown that electrons of energy $\omega$ are ejected at an angle $\varphi$ to the path of the moving ion given by

$$\cos^2\varphi = \omega/\omega_m$$

For electrons with ranges much less than those of electrons with an energy $\omega_m$, it becomes sufficient to consider that all electrons are emitted perpendicular to the ion trajectory, and hence the energy dissipation process to be cylindrically symmetric.

The second semi-empirical relation is that of the range-energy relations of the primary excitation electrons. The relation

$$r = A\omega[1-B/(1+C\omega)]$$

has been shown to give a reasonable description of the range $r$ of monoenergetic electrons of energy $\omega$ between 0.3keV and 20MeV using a value $A=5.37\times10^{-4}$ g cm$^{-2}$ keV$^{-1}$, $B=0.9815$ and $C=3.123\times10^{-3}$ keV$^{-1}$.

The final relation is that for the probability of electron transmission. A simple expression for the fraction $\eta$ of electrons of incident energy $\omega$ and practical range $r$ through an absorber of thickness $t$ is

$$\eta = \frac{1+\exp(-gh)}{1+\exp[g(\omega r-h)]}$$

where $g$ and $h$ are characteristics of an absorber of atomic number $Z$ and mass
number \( A \), given by

\[
g = 9.2Z^{0.2} + 16Z^{2.2} \\
h = 0.63Z/A + 0.27
\]

For compound materials, \( Z \) and \( A \) are replaced by their average values weighted over the mass fractions.

The two empirical relations given for the electron transport are combined to give a quantitative description of the radial energy distribution around the trajectory of a fast heavy ion by considering the energy flux dissipated in a series of cylindrical shells. The results of such calculations can be expressed in a form independent of the \( Z \) of the projectile ion for ions of a constant velocity, which is particularly convenient in the present work. The radial energy distribution around ions passing through gold are given in figure A4.1, for ion velocities from 0.04c to 0.99c. Note that the energy density in the centre of the effected zone decreases with increasing ion velocity, since 0.04c (around 1MeV/nucleon) roughly corresponds to the peak in the ion stopping power. Also note, that as the ion velocity increases, the corresponding increase in the mean energy of primary excitations leads to a considerable widening of the effected zone radius.

**A4.3 Applications**

In the next section, a brief description of the application of this approach to the modelling of MeV ion effects is given, with particular reference to the production of etchable damage tracks in dielectrics and the response of inorganic scintillators to MeV ions.
Figure A4.1 : Radial distribution of excitation energy around the path of ions travelling through gold for ions with velocities from 0.04 to 0.99 of the velocity of light (Kobetich 1968).
A4.3.1 Formation of etchable damage tracks

The observation in 1959 that fast heavy ions (in particular fission fragments) produce tracks in dielectrics such as mica has lead to considerable experimental and theoretical investigation into this aspect of radiation effects. The tracks have been used to develop quantitative radiation detection techniques, as well as being of importance in geology. Fast heavy ions, as stated previously, lose most of their energy in electronic excitation phenomena, giving rise to a considerable flux of secondary electrons in the vicinity of the ion track. The resultant damage leaves the material around the ion track more susceptible to dissolution by appropriate etching media. An etchable track is formed if the damaged region is of sufficient diameter to freely permit the etchant to pass along the damage trail and into the bulk of the material. The prediction of which ions will produce etchable damage tracks in a given material is difficult, but the model described above has been applied with some success. What was considered was the ionisation energy density at a distance of the order of 2 nm from the ion trajectory. If the ionisation density at this radius is plotted, for each ion, for a range of ion velocities what we obtain is a series of curves such as those shown in figure A4.2, which gives the data for mica at a radius of 1.9 nm. The energy density peaks at a velocity corresponding to approximately 1 MeV/nucleon, with the energy densities getting progressively higher as the ions increase in mass and hence equilibrium charge state. If the experimental data for which ions species and energies produce etchable damage tracks in mica are superimposed on the figure as solid squares (track) and open squares (no track), what we see is that track formation corresponds precisely to those ions and energies which exceed a given threshold ionisation energy density over a diameter of some 4 nm, in this case around 0.1 eV. Other dielectrics fit a similar pattern, although the precise threshold level and critical track diameter vary from material to material.

Thus it is clear that in the case of etchable track formation, the use of this framework for modelling the electronic excitation which occurs in the wake of
Figure A4.2: Comparison of calculated ionisation energy densities at 1.9 nm from the ion trajectory with the observed behaviour of muscovite mica under ion irradiation. Those cases where etchable tracks have been observed are shown as solid squares, whereas tracks are not observed the data are shown as open squares. Note that the criterion for track formation appears to be that of a threshold energy of approximately 0.07 eV at 1.9 nm (the observed radius of the track from TEM observations) (from Kobetich 1968).
A fast heavy ion gives a valuable insight into the physics of the radiation effects which are occurring.

A4.3.2 Response of NaI(Tl) to energetic heavy ions

In a scintillating material, electronic excitation leads to the emission of photons from luminescent species such as thallium in alkali-halide materials like sodium iodide. The radiation-less decay of the electronic excitation limits the distance over which the energy may be transferred to a luminescence centre to some 6 or 7 nm. Thus a given luminescence centre can be imagined as being surrounded by a small sensitive volume, within which the presence of an excitation is likely to lead to the emission of a photon. This is borne out by observations of the way in which the pulse height varies with luminescence centre concentration, which is found to increase linearly until it saturates when the volume per luminescence centre approaches the sensitive volume. The model is of use in predicting the response of scintillators to heavy ions, since the simple assumption that scintillators have a fixed conversion efficiency breaks down as the stopping power of the radiation increases. This is due to the saturation of scintillation centres in the intense excitation around the ion path, which is more usefully described by a model taking into account the spatial distribution of the excitation than by a simple number such as the specific energy loss. Calculation of the spatial distribution curves for ions in NaI have been performed, and by normalising to the observed response to 100 MeV neon ions the critical threshold excitation density was found to be 4 J cm⁻³. Using this value, the expected response to a range of ions and energies were calculated and found to agree well with experimental observations (Kobetich 1968).
A4.4 Application to radiation enhanced adhesion

The above gives two examples of the successful application of the radial energy distribution approach to MeV ion effects. The approach is also valid in the study of radiation enhanced adhesion phenomena. The approach is more logical than attempting to explain the stopping power dependence of the observed effects in terms of a simple power law, as suggested by some workers, since it takes into account the physical extent of the excited region.

For a given velocity of ion, the density of electronic excitation can be calculated as a function of the radial distance from the ion trajectory as shown in figure A4.1, which gives the excitation distribution for ions of velocity 0.04\(c\) in gold. Note that the curve is a universal one for all ions, since the excitation axis can simply be normalised by the factor \(Z^a\), where \(Z\) is the effective charge of the ion. Such curves have been calculated for all the materials used in the present studies, namely gold, silver, tantalum, tantalum pentoxide, silicon and silicon dioxide. To model the radiation enhanced adhesion phenomenon the following procedure was used. For the case of film A on substrate B, the radius of the effected zone exceeding a given interface, the arithmetic mean of the effected zone radii were used, i.e.

\[
r_{\text{eff}} = \frac{(r_A + r_B)}{2}
\]

The resultant radius, \(r_{\text{eff}}\), was used to calculate the effected area per ion

\[
A = \pi r_{\text{eff}}^2
\]

Since any effect would be expected to saturate at a dose where each area of the surface was effected once, on average, the characteristic dose was taken as being numerically equal to \(1/A\), since this is precisely the dose at which unit area would all be effected once (on average). This so called saturation dose was calculated for each ion from
atomic number 1 to 40. The results of calculations for a 1.0 eV threshold and a gold film on silicon dioxide are given in table A4.1, and the resulting curves for threshold energies from 0.1 to 10 eV per atom are given in figure A4.3. At higher energy thresholds the effected zone becomes ever narrower, with the resultant increase in saturation dose. Note that doses above $10^{15}$ ion cm$^{-2}$ imply that less than one atom is effected per ion.

The results of modelling our experimental observations of the radiation enhanced adhesion phenomenon by this approach are discussed in greater detail in the discussion section of this dissertation, but it is apparent that where an effect is observed, the threshold doses required equates to the saturation doses predicted on the basis of a 5 eV threshold excitation energy. This is true of all the systems studied to date, even though the threshold doses vary by an order of magnitude. The physical significance of the 5 eV value is also discussed in chapter 9.
Table A4.1: Results of calculation of effected zone at the interface between gold film and silicon substrate using an energy threshold of 1.0 eV and ions from atomic number 1 to 40. The values for radii and areas are in units of Angstroms and Angstroms squared respectively.

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<th>Effected zone radius GOLD</th>
<th>Effected zone radius SILICON</th>
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Figure A4.3: Result of radial energy distribution model calculations for gold film on a silicon substrate. The expected saturation dose (the dose at which every point of the surface has exceeded the threshold energy density) is plotted against the ion atomic number for energy thresholds from 0.1 to 10 eV per atom.
Bibliography


