UNIVERSITY OF LONDON

SURFACE REACTIONS OF HALOGENS AND HYDROCARBONS ON Si AND GaAs: APPLICATION TO ION-ASSISTED DEVICE PROCESSING

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A dissertation submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of London

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To Wendy
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The current trend in microelectronic processing is towards the reduction of device dimensions, thus allowing a higher density of active components per chip, reduced unit costs, increased performance and reduced power consumption. It is, therefore, necessary to develop processes and materials that conform to these requirements. The transformation of semiconducting material into active devices requires a number of processing steps to be performed. Current methods are based on an empirical approach to change rather than a complete understanding of the chemical or physical nature of the mechanisms. Two prime examples are, firstly, the way in which semiconductor material is etched to delineate a pattern and create the correct device geometry. Secondly, the means by which overlayers are deposited onto the semiconductor for dielectric properties leading to device isolation. The first of these examples often involves the thermal and ion-assisted etching reactions of semiconductor surfaces (e.g. silicon, gallium arsenide) with halogens such as chlorine and bromine. The second may, in the future, require an understanding of the mechanisms of deposition of diamond, diamond-like carbon and silicon carbide films. Mechanistic control in both of these critically rely upon reactions occurring at the surface-gas phase interface; characterisation of this region during such reactions using a variety of surface spectroscopic probes is thus of significant interest.

This thesis examines the underlying surface reactions which occur at a molecular level in these systems using the techniques of Thermal Desorption Spectroscopy (TDS) and other surface sensitive probes e.g. AES, LEED and considers the
future direction of aspects of semiconductor processing in the light of the results obtained. The initial surveys the use of surface science techniques as important tools in obtaining *in situ* information on both deposition onto, and etching of semiconductors. A description of experimental methods employed is then presented, with particular emphasis on the technique of Thermal Desorption Spectroscopy. The interaction of energetic particle beams with surfaces and adsorbate covered regions, which is fundamental to many processing steps, is also discussed at this stage. Then follows a detailed study of the reaction of bromine with silicon (100) surfaces. A mechanism for thermal etching is put forward and the interaction of energetic particle beams with adsorbed states on the semiconductor surface is discussed. A study of the etching reactions of halogens with gallium arsenide, a compound semiconductor is then presented. The mechanism for thermal and ion-assisted etching reactions are evaluated and implications for GaAs etching are discussed. The final results section considers the surface growth processes of silicon carbide, and the novel hard diamond-like carbon (DLC) and diamond film materials. Results are presented for adsorption of ethene and methane on silicon. Activation of the hydrocarbon molecules by a hot tungsten filament are also studied. Perturbation of the surface states by energetic hydrogen and argon neutral beams are also considered. Implications for the growth of device quality diamond, or DLC, layers are then discussed.
CHAPTER 1

INTRODUCTION: THE SURFACE SCIENCE OF ION-ASSISTED ETCHING AND DEPOSITION PROCESSES ON SEMICONDUCTORS

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1.1 Introduction

The use of surface science methods for the analysis of semiconductors, and processes on semiconductors, has become increasingly essential. Until ten years ago the main use of surface structural and spectroscopic techniques for monitoring surface chemical changes was limited to the study of model systems related to heterogeneous catalysis [1.1]. Indeed, the majority of modern surface science research in the UK still addresses the outstanding issues in this area. The field of electronic engineering, however, has demanded an increasingly greater share on the use of surface analytical probes to characterise device features. This has been used to particular effect for compositional analysis of deposited thin films. The drive to accommodate greater numbers of integrated circuit (IC) features onto a single chip has also had a significant influence on the use of surface science techniques. The reduction in device feature size requires more stringent controls on current processing technology and the development of totally new techniques to fully utilise the available wafer surface. Within this context surface science can play two roles. Firstly, standard analysis of the surface region during, or after, device fabrication can aid process reliability and enable higher yields to be achieved. Secondly surface probes can be deployed to investigate the underlying mechanisms of potential high resolution device fabrication techniques to enable future technologies to be developed. The latter is the style of surface analysis carried out during this study where in-situ surface spectroscopies have been deployed during chemical and physical modification of semiconductor surfaces. The microscopic picture which evolves from such an approach then enables the viability or otherwise of a particular reaction route to be assessed.

There is a strong need for advanced semiconductor processing chemistry and physics. This has arisen from both the need to reduce feature sizes and from the rapid diversification in the nature of semiconductor materials used for device fabrication. The first IC structures were created from germanium single crystals, but the most popular and commercially advanced structures for the past twenty five years have been fabricated from silicon (Si). This material, however, has several disadvantages for certain high performance applications. It is an indirect band gap semiconductor and it possesses a
relatively low electron mobility. The former property makes it unsuitable for opto-electronic applications, and the latter limits the speed of operation of an electronic device. A class of materials that do not suffer from these drawbacks are the III-V compounds. In particular, gallium arsenide (GaAs) has been used for some years for applications requiring either high operating speed or opto-electronic properties. A major obstacle to the advancement of GaAs processing has been the relative instability of the material in comparison to silicon due to the high vapour pressure of arsenic at elevated temperatures. In addition, the electronic properties of the material may be degraded by the action of energetic particle beams such as photons, electrons or ions during processing steps. Furthermore GaAs does not possess an insulating 'native' oxide and thus device isolation must be achieved by the deposition of an insulating thin film of a different material (such as SiO₂ or Si₃N₄) on to the surface. A candidate for this role is diamond which in addition to being an electrical insulator is also a good thermal conductor and thus may be used to dissipate the large amounts of heat produced in devices with small feature dimensions. Diamond itself may be used as a semiconductor and has the advantage of being 'radiation hard'. Other materials that are closely related to diamond are the diamond-like carbons. These materials may also be used in microelectronics for either their semiconducting or physical properties; silicon carbide (SiC) may also be included in this group of materials. They may also be used under radiation hard conditions and therefore have specific applications that may not be fulfilled by either Si or GaAs. Clearly, this diversity of materials for semiconductor devices requires a strong knowledge base on which commercial development of fabrication procedures can proceed. If this is coupled with the need for sub-micron size device features it is clear that a complete understanding of the surface properties and reactions which can be driven for material processing is necessary in order to optimise feature quality.

This thesis investigates a series of surface reaction systems which are applicable to the etching of semiconductor materials and deposition of thin films. Both of these are primary processing steps for the realisation of a given device structure. Etching is required to form the given device geometry on
the semiconductor wafer. As such it should be a process which imparts little damage and contamination whilst removing surface layers in a controllable manner with high spatial resolution. Geometric confinement is traditionally achieved with photolithographic masking methods. However, as will be seen later in this thesis, the promotion of etching reactions with focused or patterned beams opens up the possibility of maskless etching and considerable reduction in process sequence complexity. The formation of thin films of dielectrics and metals is required to build the active interfaces that are at the heart of all electronic devices. Thus, such films should not only be of high purity and electrical quality but should be deposited with a minimum of perturbation to the underlying semiconductor material. Hence both etching and deposition critically rely on specifically surface reactions for their realisation. The surface reactions studied here are those of bromine on Si(001), chlorine on GaAs(001) and ethene on Si(001). The modifying effects of energetic argon ions and neutrals are investigated.

To fully understand the microscopic nature of the above reactions it is necessary to employ a range of surface sensitive spectroscopic probes. Those used in this study are Thermal Desorption Spectroscopy (TDS), Auger Electron Spectroscopy (AES) and Low Energy Electron Diffraction (LEED). Each of these techniques gives complementary information on the system under investigation. The full scope of surface probes is discussed in section 1.2 in order to show the range of valuable information that can be obtained using these techniques. TDS is the primary tool employed in this study and as it is a powerful method for elucidating reaction mechanisms. A detailed review is presented within this section.

The next topic to be considered is the range of etching processes that may be applied to removal of semiconductor material. Particular emphasis is paid to the ion-assisted dry etching techniques such as reactive ion etching (RIE), reactive ion beam etching (RIBE) and chemically assisted ion beam etching (CAIBE). The surface chemistry of these processes is not well understood and this thesis addresses some of the outstanding unresolved questions. In addition to the real etching processes considered in this section, some considerable attention is paid to the nature of ion beam interactions with the surface region. A whole menagerie of processes may occur when an ion
impinges on a solid e.g. scattering, sputtering, electronic transitions, implantation, channelling, intermixing, amorphisation etc. Furthermore, the adsorption of gases on to the surface may alter the nature of the surface such as to promote one type of ion-solid interaction at the expense of another.

The experimental approach adopted during the course of this investigation is described in chapter 2. This section includes information on the three chamber ultra-high vacuum (UHV) system used in this study, including an outline of the principles underlying the tools clustered around the sample. The methods of sample preparation, heating and manipulation are also described. The following chapters are divided into the three specific systems under study. The thermal and ion-assisted etching reactions of silicon with halogens is the subject under investigation in chapter 3. The reactions of molecular bromine on Si(100) are investigated in some detail. The following chapter considers the reactions of halogens with GaAs and in particular the thermal and ion assisted etching reactions of molecular chlorine with GaAs. The next chapter considers the surface reactions of hydrocarbons on silicon with particular regard to their suitability for deposition of silicon carbide (SiC), diamond and diamond-like thin films. The nature of the ethene covered silicon surface is considered and then the perturbation of this layer with energetic argon and hydrogen neutral beams is investigated. The application of these techniques to study of other processes such as hot filament growth of diamond is presented.

At the start of each results chapter a brief review of background literature specific to that chapter is presented. A separate section then introduces the results obtained during the investigation, whilst the following section covers the analysis of the results and a discussion within the context of other work in the field. Finally, each chapter is concluded with a section on the implications of this study for application to real processes and also towards the next steps for investigation and development.
1.2 The Use of Surface Probes to Study Ion-Assisted Etching and Deposition of Semiconductor Materials

1.2.1 Introduction

The nature of any etching or deposition event must always be considered as a process which occurs at an interface. These processes most usually occur at solid-gas interfaces, notable exceptions are processes such as liquid phase epitaxy and wet etching which take place at solid-liquid interfaces. The vapour-solid interface is generally amenable to analysis via some form of in-situ surface technique (usually under UHV conditions). Some excellent texts are available for in-depth reviews of surface science techniques [1.2]. The methods of surface analysis which may be applied to the etching and deposition processes considered in this thesis can be classified into the following groups;

(i) Electron Spectroscopies
   e.g. Auger Electron Spectroscopy (AES)
        X-ray Photoelectron Spectroscopy (XPS)
        Ultraviolet Photoelectron Spectroscopy (UPS)

(ii) Surface Crystallography
   e.g. Low Energy Electron Diffraction (LEED)
        Reflection High Energy Electron Diffraction (RHEED)

(iii) Desorption Spectroscopies
   e.g. Thermal Desorption Spectroscopy (TDS)

(iv) Ion Scattering
   e.g. Low Energy Ion Spectroscopy (LEIS)

(v) Vibrational Spectroscopies
   e.g. High Resolution Electron Energy Loss Spectroscopy (EELS)

(vi) Molecular Beam Scattering

(vii) Other Techniques
   e.g. Second Harmonic Generation (SHG)
        Scanning Tunneling Microscopy (STM)
It is generally not possible either in terms of cost or compatibility to employ more than two or three of these techniques in any one in-situ study of reaction system. This brief review intends to highlight the specific surface techniques that have been used in this study, with further brief statements on methods employed by other researchers in order to investigate these surface reactions.

A question often posed by catalysis chemists is 'What can surface science tell us about real catalysis processes?' A variation of this question can also be applied to microelectronic engineering problems. Most surface science techniques require ultra-high vacuum (UHV) conditions i.e. $P<10^{-9}$torr. This is necessary for several reasons. Firstly, the rate of impact of particles upon a surface ($F$) is governed by the kinetic theory of gases such that the Hertz-Knudsen equation dictates the rate of impact

$$F = P \sqrt{\frac{1}{2\pi m k_B T}}$$  \hspace{1cm} [1.1]

where $P$ is the pressure in the system, $m$ is the mass of the impinging molecules and $k_B$ is the Boltzmann constant. Under UHV conditions the rate of impact is such that if one assumes a sticking coefficient of unity, a monolayer of atom will take at least 30 minutes to form. This then allows sufficient time for the surface to be analysed. The use of UHV conditions also allows the sample surface to be studied to be cleaned at an atomic level. The concept of an atomically clean surface is one that is not often appreciated by a device designer or processing engineer. Thin film deposition or etching is usually performed on a quite heavily oxidised substrate at high gas pressures and thus the chemistry involved may be quite different to the pure surface. A clean surface may be achieved in several ways, including thermal cleaning and ion sputtering methods. A further advantage of working under good vacuum conditions is the large mean free paths of molecules and other particles (e.g. electrons) in the gas phase which allow line of sight experiments to be performed. Clearly, UHV and real process pressures can differ by many orders of magnitude. This is known as the
pressure gap between the surface analysis and the real process (i.e. etching and deposition) conditions.

**1.2.2 Surface Probes and their application to In-situ Processing**

*In-situ* processing can be considered as a possible alternative to the conventional step-by-step processing by using one piece of equipment for the complete fabrication of a microelectronic device structure on a single semiconductor wafer. Many processes for III-V deposition are carried out under UHV conditions (such as molecular beam epitaxy, MBE, or chemical beam epitaxy, CBE) and etching, metallisation and oxide deposition can be performed under these circumstances. The principal advantage of this type of processing is the complete control that may be maintained upon the interfaces of the different layers of the device. This is a potential source of improvement in device technology. The initial large cost of MBE deposition would not require significantly greater input to convert to a complete in-situ processing set-up.

A particular advantage of this type of processing equipment is the ability to cluster analytical tools at some central point in order to control and monitor the surface and chemical properties before and after each process stage. Contamination from oxygen, particulates and organic compounds may be controlled.

The surface spectroscopic techniques employed in this study could be expected to be used to elucidate reaction mechanisms, surface structure and impurity levels. The use of the mass spectrometer and ion gauges has also provided an accurate control over the amount and nature of reactive chemical species introduced into the UHV system.

A number of useful surface probes for the elucidation of semiconductor surface reactions are now briefly discussed.
1.2.3 Electron Spectroscopies

A number of powerful techniques such as Auger Electron Spectroscopy (AES), X-Ray Photoelectron spectroscopy and Ultraviolet Photoelectron Spectroscopy (UPS) fall into this category. AES relies on the measurement of electrons from a characteristic three body process within the solid and is discussed in greater detail below. Both XPS and UPS use photon sources to induce emission of photoelectrons from the solid. XPS (often known as ESCA) may give detail about chemical bonding within a solid whilst UPS gives detail about the valence band structure of the surface region. A more detailed review of these techniques may be found elsewhere [1.3,1.4]

In this section the surface diagnostic probes utilizing electron-solid interactions are outlined. The surface sensitivity of electron spectroscopies are determined by the escape depth parameter ($\lambda$). Figure 1.1 shows a graph of experimental measurements obtained by Seah and Dench [1.3] and reveals that $\lambda$ values are lowest at electron energies of 50-100eV. At these values the surface sensitivity is approximately two monolayers. By detection of these electrons following scattering or emission from the surface considerable information on the surface may be obtained since no signals are derived from the bulk region. If the processes that occur when an electron impinges on a surface are considered this leads to a number of possible processes. Figure 1.2 shows a schematic of an incident and scattered electron with the relevant associated electron energy distributions. The schematic shows an incident beam of a single primary energy which upon scattering changes occur to the energy distribution. The proportion of elastically scattered particles is reduced, whilst the major distribution consists of a range of electron energies which may be collectively termed as 'inelastic' scattering processes. The central region of the spectra consists of peaks which derive from characteristic loss peaks from the primary electron energy, and other peaks such as Auger transitions which are independent of the electron energy. It is these latter transitions that are of interest for AES.

Auger electron spectroscopy is able to identify impurities on surfaces to levels
of approximately 1%. The process by which Auger electrons are produced is shown schematically in Figure 1.3. When the primary electron beam impinges on the surface it may cause emission of a core electron. The vacant position left by the departing electron may be filled by one of two emission processes. The first is the three-body process where the core hole is filled by an electron from a higher level followed by emission of a further electron which is ejected from the solid via a radiationless process. These electrons were first detected by Pierre Auger in 1925 [1.6] and have since been named after him. The second process consists of a one electron process from a higher electron energy level which results in the emission of a quanta of radiation which is usually in the X-ray region. Analysis of these radiative processes is the cornerstone of the X-ray fluorescence (XRF) technique.

Analysis by AES is one of the surface sensitive probes utilised in this thesis. the implementation of this technique is described in section 2.4.2

1.2.3 Surface Crystallography

These methods generally involve diffraction of electrons from the surface allowing study of the surface structure. The two principal techniques utilised in semiconductor processing are Low Energy Electron Diffraction (LEED) and Reflection High Energy Electron Diffraction (RHEED). These methods rely on the collection of elastically backscattered electrons on a cathodoluminescent phosphor screen. The former technique is used in this study to determine the precise structure of the semiconductor surface and also the ordering of the adsorbate overlayers. RHEED is a glancing angle technique which is primarily used as monitor of semiconductor growth processes i.e. molecular beam epitaxy (MBE), pulsed laser deposition (PLD).

For a diffraction technique to be applicable to the determination of the structure of a semiconductor it should fulfil two criteria. Firstly, the electron wavelength, \( \lambda \), should be of a similar dimension to the two-dimensional surface grating. The wavelength of the primary electrons may be related to the
kinetic energy by the de Broglie equation;

$$\lambda = \frac{h}{p} = \left(\frac{150}{V}\right)^{1/2} \text{ (in Å)} \quad [1.2]$$

where $h$ is Planck's constant, $p$ is the electron momentum of energy $E$ (in eV) and $V$ is the acceleration voltage of the primary electron. If we consider an example bond length of 1.5Å, this equates to an acceleration voltage of 67eV.

The second requirement for a surface sensitive structural probe is that the electrons should not penetrate too deeply into the bulk structure. Bauer [1.7] estimated that for typical LEED energies of 10-500eV the penetration into the bulk was in the region of 3-10Å. Thus as the escape depth of the electron is dependent upon the degree of inelastic scattering, the first few atomic layers only are probed. This technique, therefore, is essentially a surface structural probe.

LEED was developed as an important structural tool by Farnsworth [1.8] who also was first to observe surface reconstructions. A comprehensive review of many surface structure has been collated by Ohtani et al [1.9].

The technique may be used to obtain information such as

(i) type of surface reconstruction (i.e. periodic superlattice with a different structure to the bulk lattice)
(ii) ordering of adsorbed species on a surface
(iii) monitoring of surface cleaning

A notation for the description of the superlattice overlayer was proposed by Wood [1.10] and is now universal in its application. Thus when describing a Si(100) (2x1) surface the description of the reconstruction (2x1) refers to rows of overlayer atoms on top, or between, the substrate atoms where the distance between the rows is twice that between the substrate atoms.
Chapter 1: Surface Probes

The implementation of this technique within the context of this thesis is described in the experimental methods section.

1.2.4 Desorption Spectroscopies

The technique of temperature programmed desorption (TPD) or thermal desorption spectroscopy (TDS) was first described by Apker by using a filament heated at a fast rate [1.11], although Urbach [1.12] previously measured gas evolution from metal surfaces at changing temperature. Thermal desorption spectroscopy is a particularly useful technique for the determination of thermodynamic information of adsorbed phases on surfaces. It also gives information on the stoichiometry of desorbed phases and thus inferences as to the nature of reactions on clean surfaces. The method has been used extensively for studies of gases on metal surfaces [1.13] leading to elucidation of reaction mechanisms in catalytic processes. During this time the surface processes of adsorbates on semiconductors has attracted less attention. This section reviews the fundamental aspects of TDS whereas the experimental details are covered in section 2.4.1.

The technique is conceptually simple, although implementation and interpretation is usually more complicated. An atomically clean surface is exposed to the adsorbate species so that uptake may occur, this is followed by an increase in the surface temperature. This may induce desorption of species from the surface. This may be desorption of the adsorbed gas, or in some cases a variety of compounds may be desorbed, depending upon whether the binding energy at the surface has been lowered. The process of desorption of a surface bound species into the gas phase may be analysed by monitoring a particular mass unit using a quadrupole mass spectrometer (QMS). The experiment may be performed in one of two ways. Firstly, the sample may undergo a rapid temperature rise, which is termed "flash desorption". The complete heating cycle is performed in less than half a second resulting in
the desorption rate being much greater than the pumping speed of the vacuum system. The second method uses an increase in temperature over a timescale of tens of seconds to several minutes. This regime of heating results in a peak in the pressure-temperature curve rather than the plateau observed in flash desorption experiments. This effect is due to the gas evolution being more closely matched to the pumping speed of the system. It is this latter technique which is referred to as thermal desorption spectroscopy which is utilized in the work covered in this thesis.

The heating cycle used should be linear with respect to time, and conforms to:

\[ T = T_0 + \beta t \]  \hspace{1cm} [1.3]

where \( T \) is a chosen temperature at time, \( t \); \( T_0 \) is the initial temperature and \( \beta \) is the heating rate in K s\(^{-1}\).

If this is applied to the adsorbent surface and the resulting trace is recorded, a desorption spectrum is obtained. The adsorbate-surface system may exhibit several desorption peaks upon heating and for cases where multiple binding sites occur may be described as \( \gamma<\alpha<\beta \) in order of increasing bond strength. This convention is followed in this work. Important features of desorption peaks to be considered are their positions in relation to surface coverage and their peak shapes. the former relationship may give good information on the order of the desorption process. Figure 1.4 shows the ideal desorption traces proposed by Redhead [1.14] for the different reaction orders, \( x_i \), described in Polanyi-Wigner equation (eqn 1.5). For a zero order desorption trace (Fig.1.4(a)) the peak rises exponentially to the maximum value, thereafter the rate falls instantaneously to zero. The peak temperature, \( T_{\text{max}} \), increases with coverage although the leading edge is identical. The first order desorption peak (Fig.1.4(b)) gives exhibits an asymmetric peak shape with the position of \( T_{\text{max}} \) constant at differing coverages. The second order desorption peak (Fig 1.4(c)) shows a symmetrical peak structure with a decreasing \( T_{\text{max}} \) upon increased surface coverage.
Chapter 1: Surface Probes

The pressure versus time plots shown in Figure 1.4 are applicable for cases where the heating rate occurs over a period of several seconds and the pumping rate of the system is fast. The resultant desorption curve obtained under these conditions allows certain properties to be obtained. The rate of desorption per unit area of surface may be calculated from;

\[
\frac{dN}{dt} = \left( \frac{V}{AkT} \right) \left[ \frac{dP}{dt} + \left( \frac{S}{V} \right)^p \right]
\]  

[1.4]

where \( N \) is surface coverage in molecules cm\(^{-2} \), \( P \) is pressure increase, \( V \) is the volume of the desorption chamber, \( A \) is the surface area, \( T_g \) is the gas phase temperature and \( S \) is the pumping speed of the system. The desorption rate is proportional to the pressure increase if \( S/V \) is large and \( \beta \) is low.

The recorded thermal desorption trace obtained may contain several peaks or shoulder features. These may be interpreted as representing different 'binding states' of the adsorbate to the surface. An analysis that may be used to obtain information on these binding states is the Polanyi-Wigner model, which describes the rate of desorption as thus;

\[
-N_i \frac{dN_i}{dt} = \nu_i N_i^{x_i} \exp \left( \frac{-E_i}{RT} \right)
\]  

[1.5]

where \( N_i \) is the population in molecules cm\(^{-2} \), \( \nu \) is a frequency factor, \( x_i \) is the reaction order for the desorption process, \( E_i \) is the desorption activation energy and \( R \) is the gas constant.

The approach proposed by Redhead [1.14] is applicable when the conditions described by equation 1.4 are such that the desorption rate is proportional to the pressure. For a first order desorption process the position of the desorption peak is directly related to the activation energy for desorption by the relation.

\[
E_i = RTP_i \left[ \ln \left( \frac{\nu_i T_{pi}}{\beta} \right) - 3.46 \right]
\]  

[1.6]
The accuracy of this technique for obtaining thermodynamic data relies on a reliable estimation of the frequency factor. This value is usually estimated to be $10^{13}$ s$^{-1}$ and can be defended from either one of two viewpoints. Firstly, vibrational frequencies are approximately $10^{13}$ per second and vibration of the adsorbate-surface bond is probably the initial step of a first order desorption process. The second argument uses transition state theory for which a value of $6 \times 10^{12}$ s$^{-1}$ is obtained at room temperature for $kT/h$.

Miller et al [1.15] have compared TDS methods and their use in determining kinetic parameters such as reaction order, activation energy and pre-exponential factor. They have divided these analytical procedures into two groups. Firstly, the integral approach which looks at the peak characteristics such as half widths and temperatures at peak maxima. These methods are only applicable in circumstance where parameters are not coverage dependent. the second approach for coverage dependent systems looks at differential analyses, where Arrhenius plots may be used to obtain $E_i$ and $n_i$ from the slope and intercept.

The experimental arrangement of the TDS method as used in this study is described in chapter 2.

1.2.5 Incident Ion Scattering Techniques

The techniques most commonly used for obtaining information on semiconductor surfaces are low energy ion scattering (LEIS), otherwise known as ion scattering spectroscopy (ISS)[1.16], and medium energy ion scattering (MEIS). The essential features of this type of experiment are the control of mass, energy and direction of the impinging beams. The technique provides information on the outermost layers of the solid. This surface specificity arises as a result of elastic and inelastic scattering processes which lead to the elimination of scattered ion emission from below the surface. At a fixed angle of scattering, the energy of the impinging ion is
dependent upon the target ion. For ions scattered at 90° the energy of a scattered particle, $E_0$, is represented by

$$\frac{E_i}{E_0} = \frac{(M_s - M_0)}{(M_s + M_0)}$$

where $M_0$ is the mass of the impinging ion, $M_s$ is the mass of the surface atom and $E_0$ is the energy of the incident ion.

The sensitivity to surface atoms by this technique can detect up to a few thousandth of a monolayer. Thus this technique has been used to analyse the surface structure of Si [1.17] and GaAs [1.18], and also to monitor surface stoichiometry changes after reactive ion processes [1.19]. Figure 1.5 shows a schematic of particle ejection processes during ion bombardment and the energy distributions. Ejected species at low energies consist of sputtered material following cascade processes. Peaks at higher energies represent species which are ejected as binary recoils or are scattered.

1.2.6 Vibrational Spectroscopies

The use of vibrational spectroscopies [1.2] can give significant information on the nature of adsorbates and adsorbate-solid vibrational modes. These surface vibrations can be studied using techniques such as Infrared Reflection-Absorption Spectroscopy (IRAS/or RAIRS), Raman Spectroscopy or High Resolution Electron Energy Loss Spectroscopy (HREELS). These techniques are not used in our experimental work, but important complementary bonding information is presented throughout this thesis and thus information on these techniques is introduced at those times.

1.2.7 Molecular Beam Scattering

Modulated molecular beam reaction mass spectrometry has been proven to be a useful technique for studying reactions of halogens with semiconductors.
This halogen beam impinges upon the surface, some of which scatters whilst the remainder chemisorbs. If the molecular beam and the substrate are reactive, a volatile reaction product may reappear. Analysis of phase lag of the reflected signal may give information on the kinetics of the chemical reaction if the timescale of the reaction is comparable to the modulation of the incident beam. The effect of ion beams on a reactive system of this type may be studied by electronically modulating the ion beam. This technique may provide information about the reaction kinetics [1.20]. The applicability of this method is high dependent upon a high reaction probability.

1.2.8 Other Techniques

The previous sections describe a range of surface sensitive analysis techniques. In addition, there are many more variations which have been omitted. These are described in many excellent surface texts [1.1,1.2-4]. Brief mention should be made to two burgeoning techniques. Firstly, Scanning Tunneling Microscopy (STM) and its variants [1.21] are particularly powerful methods of structural analysis of clean and adsorbate covered surfaces. The second example is Second Harmonic Generation in Laser Beams (SHG)[1.22] which may allow analysis of the gas-solid interface without the need for UHV pressures.
Figure 1.1 Inelastic scattering electron mean free paths as a function of energy

after M.P.Seah and W.A.Dench
Surface and Interface Analysis 1 2 (1979)
Figure 1.2 Emitted Electron Distributions from Solid Surfaces
$E_{\text{Auger}} = E_K - E_M - E_L$

Figure 1.3 Auger Electron Emission Process
Figure 1.4 Ideal Thermal Desorption Spectroscopy (TDS) Curves for (a) zero order (b) 1st order and (c) 2nd order desorption processes as a function of surface coverage

Figure 1.5 Particle ejection processes during ion bombardment and the corresponding energy distribution

after D.G. Armour
Methods of Surface Analysis-Techniques and Applications
Ch 8
ed. J.M. Walls
CUP 1989
1.3 Beam Processing for Semiconductor Etching

1.3.1 Introduction

The driving forces behind the development of dry etching techniques have been expounded in the introduction (section 1.1). This review will describe some of the most used etching techniques and lay the fundamental basis for the direction of the in-situ surface engineering aspects of this thesis.

The most common variants for dry etching of Si and GaAs device features are

(i) Plasma Etching
(ii) Reactive Ion Etching
(iii) Ion Beam Etching
   (a) inert gas ion etching
   (b) reactive ion beam etching (RIBE)
   (c) chemically assisted ion beam etching (CAIBE)
(iv) Laser Assisted Etching

The section will concentrate on the Ion Beam Etching (IBE) techniques, which allow greater control over etch parameters such as ion energy, direction and arrival rate of the etch species. Furthermore, greater flexibility with the background pressure is achievable.

1.3.2 Plasma/Reactive Ion Etching

These two techniques are perhaps the most common dry etching methods in use at the present time. Plasma etching is essentially the use of a glow discharge to activate a molecular gas to form excited ions or radicals. These
reactive species can then be transported to the surface either by diffusion or by a field assisted mechanism. A variety of different reaction pathways can now occur leading to volatile etch products which can leave the surface either by a thermal desorption process or by an ion-assisted mechanism.

Plasma etching was first used by Irving [1.23] as a photoresist stripping method. The first application to semiconductor etching was by Abe [1.24] using CF$_4$ to etch Si, SiO$_2$ and Si$_3$N$_4$. The major advantage of this technique in relation to wet etching is that it can produce etch profiles of a highly anisotropic nature due to the directed characteristics of the reactive species [1.25]. It has several disadvantages in that it requires physical masking to prevent non-discriminatory etching. The diversity of the molecular gases used often leads to a complex and poorly understood etch chemistry which is detrimental to good process control. In addition to these problems, the electrical characteristics of the fabricated device are often limited by bombardment effects [1.26]. Several detailed reviews of plasma etching are currently available; an example of which is by Lehmann [1.27].

Reactive ion etching (RIE) is essentially similar to plasma etching except that the r.f. power is applied to the substrate platform rather than the top electrode (as is the case in parallel plate etching). This ensures that the substrate is bombarded by ions with an energy that is equal to the r.f. induced d.c. bias. RIE is generally used for defining highly anisotropic features of sub-micron dimensions and due to its more pronounced physical nature it is not as selective as plasma etching. Furthermore, significant damage may be caused by the highly energetic ions impinging on the substrate surface.

A variety of Cl$_2$ based discharges have been used for RIE etching of III-V compounds such as Cl$_2$ [1.28,1.29], CCl$_2$F$_2$ [1.30-1.32], CCl$_4$ [1.33,1.34], SiCl$_4$ [1.35,1.36], COCl$_2$ [1.37] and BC$_3$ [1.38]. Pearton et al [1.39] found that chlorine residues were typically present in the surface region to a depth of $\leq$20Å, although etching with SiCl$_4$ left cleaner surfaces than Cl$_2$. Wet chemical etching is routinely used to remove the damaged surface subsequent to the RIE process.
1.3.3 Ion Beam Etching

It is essential to differentiate between IBE, RIBE and CAIBE methods. This can be done by briefly describing each technique. In addition, these processes are illustrated in Figure 1.6. IBE is essentially etching of the semiconductor by a physical sputtering process resulting from momentum exchange between the impinging ions and the semiconductor material (Fig.1.6(a)). The RIBE technique (Fig.1.6(b)) relies on a chemical reaction between the incident ion and the etch surface. The sputtering process is therefore enhanced by a reactive etching contribution. CAIBE (Fig 1.6(c)) is perhaps the most versatile technique for semiconductor etching due to the fact that the incident ions and the reactive gases are introduced separately and therefore a chemical reaction is enhanced by a physical sputtering process. The energies generally employed for these etching techniques are less than 3keV. Si and GaAs bonds may be broken by energies of the order of 10eV [1.40,1.41] and hence the processes at their current stage of development (using ion beams of 50eV-5keV) tend to be physical processes with an additional chemical enhancement factor.

The use of RIBE can give good control over device parameters such as etch selectivity. Mayer [1.42] found that for etching of SiO$_2$/Si device structures the use of CF$_4$ in the beam source resulted in an etch selectivity of 0.2 in favour of Si whereas using Cl$_2$ as the etchant gas resulted in a 3:1 ratio. The corresponding IBE etch selectivity using argon ions is 1:1. In addition to good selectivity, the aspect ratio of a device structure may be improved by use of ion beam techniques. For example, CAIBE has been used to obtain aspect ratios of 40:1 for GaAs etched by Cl$_2$/Ar$^+$ [1.43].

The use of CAIBE to reduce substrate damage was also recognised by Geis et al [1.43] and attributed to the adsorbed layer forming a protective barrier against the effects of ion impact. This subject is discussed in greater detail within this thesis.
1.3.4 Laser Etching

The use of laser etching in semiconductor device fabrication has been comprehensively reviewed elsewhere [1.44,1.45]. The advantages of laser assisted etching over reactive ion and plasma techniques are many. They include the ability for wide area maskless etching through the use of projection patterned light, low damage steps through the lack of physical bombardment and also potentially high etch rates. The main applications may be in in-situ environments for specialised circuit repair and processing of high value devices. The principal disadvantage of laser etching remains the unreliability of current industrial excimer lasers. These problems are only slowly being surmounted [1.46]. Etching reactions using photochemical enhancement may also be driven by high intensity lamps which may operate over a broad range of wavelengths.

For etching of III-V compounds the greatest concern with laser etching is the large temperature gradients which may induce strain, and hence lead to lattice defect formation [1.47]. Point defects in Si may be generated at less than the melting threshold \((1.7 \times 10^8 \text{ W/cm}^2)\) when exposed to frequency doubled Nd:YAG (532nm) radiation [1.48]. Surface defect densities of \(10^{14}/\text{cm}^2\) were induced by irradiation at this power density.

Low power laser etching may be performed with liquid etchants, but these can produce surface effects such as ripples [1.49]. Of course this type of etching is incompatible with in-situ processing requirements. A laser modification to a conventional GaAs/CCl\(_4\)/H\(_2\) RIE process was found to increase etch rates by an order of magnitude [1.50].
Figure 1.6 Comparison of typical (a) RIE, (b) RIBE, and (c) CAIBE Etching Processes
1.4 Ion and Neutral Beam Interactions with Semiconductor Surfaces

1.4.1 Introduction

Having assessed the types of ion-assisted etch processes that may be used to fabricate sub-micron features on semiconductor surfaces it is necessary to understand the fundamental basis of how ion/neutral beams provoke chemistry and physics at the surface of a semiconductor. Furthermore, this is essential for determining the potential damage processes that may occur as a result of ion bombardment. The role of adsorbate molecules on the surface may then be discussed with regard to their influence on ion induced processes such as chemical sputtering, implantation and reduction of damage (both structural and electronic). This has particular implications for CAIBE-type etch processes.

Before discussing the possible perturbing influences that an ion beam can have on a semiconductor surface, it is important to summarise the important physical processes that occur when an ion impinges upon a surface.

1.4.2 Ion - Surface Interactions

A fundamental aspect of all ion-surface interactions is the nature of the mechanism by which the ion comes to rest following impact with the solid surface. The 'stopping' of an ion as it impinges on a solid has been addressed by the LSS range theory as proposed by Lindhard, Scharff and Schiott [1.51]. The main modes of energy loss occur by:

(i) collisions between the ion and screened nucleus
(ii) electronic interaction between the coulomb field of the target ion and impinging ion
(iii) charge exchange between ion and atoms in the solid
The energy loss can thus be defined as

\[
\left( \frac{dE}{dx} \right)_{\text{loss}} = \left( \frac{dE}{dx} \right)_{\text{nuclear}} + \left( \frac{dE}{dx} \right)_{\text{electronic}} + \left( \frac{dE}{dx} \right)_{\text{exchange}} \quad [1.8]
\]

Nuclear energy loss processes are related to the energy and mass of the impinging ion, the mass of the target atom and the effect of electronic screening by the surrounding electrons. Electronic stopping is dependent upon the energy of the incoming projectile, because a highly energetic particle is less affected by a coulombic field. Exchange loss processes are addressed later in this section.

The collision process can, however, be treated classically as a scattering event between two ions. Momentum transfer occurs upon an elastic collision between an impinging hard sphere ion and a resting hard sphere (in the solid). The maximum energy loss, \( T_{\text{max}} \), for a collision perpendicular to the surface is

\[
T_{\text{max}} = 0.5 \, M_2 \, V_2^2 = \frac{4M_1M_2}{(M_1+M_2)^2} \, E_0 \quad [1.9]
\]

where \( E_0 \) is the energy of the impinging beam of mass \( M_1 \) with the target material having mass \( M_2 \). Clearly, the most energy is lost if \( M_1 \) and \( M_2 \) are of similar mass, but if their masses differ greatly and a small angle collision occurs, the \( E_0 \) and \( T_{\text{max}} \) may differ by several orders of magnitude.

\( V_2 \) = velocity

1.4.3 Physical Sputtering

Physical sputtering is a process that occurs when an ion beam incident on the material induces a collision cascade in the surface region. The energy of the primary beam is transferred to the atoms in the target material. A surface atom is sputtered if the transferred energy is greater than the surface binding energy. Sigmund [1.52] described three different regimes of physical sputtering.
(i) single knock-on regime
(ii) linear cascade regime
(iii) spike regime

If the energy of the incoming ion is high compared to the lattice bond energy then bond breaking may occur creating a free host species which carries momentum transferred from the impinging ion. An impinging ion, upon penetrating the solid, loses energy to atoms in the solid by way of exchange through binary collision processes. Fast recoils are created which propagate into the solid until the atoms become less energetic. This sequence of events is known as a "collision cascade". A collision cascade is linear if only a small number of the target atoms within the cascade volume are set in motion. Most cascades in metals and semiconductors are close to linear. The actual penetration depth of the ion will depend upon the initial energy of the impinging particle and the atomic density of the solid. This cascade process occurs over a timescale of approximately $10^{-13}$ s and results in a surface region where species possess energies of less than 10eV i.e. the energy threshold for displacement processes. There follows a relaxation period of around $10^{-11}$ s, during which the kinetic energy of the remaining recoils is dissipated through phonon-assisted processes: the so-called "thermal spike". This results from vibrational excitation of neighbouring lattice atoms. The processes described above are represented in Figure 1.7(a). This schematic shows the possible processes which may stop the impinging ion and dissipate the energy of the impact.

The observed trends in experimental data obtained from atomic ions on elemental targets, for absolute sputtering yields as a function of energy and mass have been described by Sigmund [1.52]. The backward sputtering yield for normally incident ions may be described by

$$Y(E_i) = C_{pt} S_n \left( \frac{E_i}{E_{pt}} \right)$$

[1.10]
where \( Y(E_t) \) is the sputtering yield at a defined energy in atoms ion\(^{-1}\). The terms \( C_{pt} \) and \( E_{pt} \) are represented by

\[
C_{pt} = \frac{(Z_p Z_t)^{5/6}}{3U_0} \tag{1.11}
\]

\[
E_{pt} = \left(1 + \frac{M_p}{M_t}\right) Z_p Z_t \left(Z_p^{2/3} + Z_t^{2/3}\right)^{1/2} \left(\frac{1}{32.5}\right) \quad \text{(in keV)} \tag{1.12}
\]

\( S_n \) is the reduced stopping cross section as approximated by

\[
S_n = \frac{1}{2} \ln(1 + \varepsilon) \left\{ \varepsilon + \left(\frac{\varepsilon}{385}\right)^{3/8} \right\} \tag{1.13}
\]

where \( \varepsilon \) is the nuclear stopping cross-section.

This theoretical approach agrees closely with experimental data as is shown in Table 1.1 which presents sputter yield data for silicon after bombardment at normal incidence with \( \text{Ne}^+, \text{Ar}^+, \text{Kr}^+ \) and \( \text{Xe}^+ \) ions.

Thompson [1.53] described the energy distribution of ejected target atoms from the surface normal as

\[
\phi(E) = \frac{E}{(E + U_0)^3} \tag{1.14}
\]

where \( U_0 \) is the surface escape barrier energy which is conveniently taken as the sublimation energy of the target element. Although this quantity describes binding energies in the bulk structure there is close agreement with experimental data.
Table 1.1  Etch Yields of Silicon (Si atoms/ion) [1.62]

<table>
<thead>
<tr>
<th>Ion</th>
<th>Sputter Yield (600eV)</th>
<th>Sputter Yield (1000eV)</th>
<th>Etch Yield with XeF₂</th>
<th>Etch Yield with Cl₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar⁺</td>
<td>0.53</td>
<td>0.9</td>
<td>28</td>
<td>4.5</td>
</tr>
<tr>
<td>Ne⁺</td>
<td>0.54</td>
<td>0.62</td>
<td>20.9</td>
<td>2.68</td>
</tr>
<tr>
<td>He⁺</td>
<td>0.15</td>
<td>0.07</td>
<td>11.7</td>
<td>0.95</td>
</tr>
<tr>
<td>Ar⁺/Ar⁺</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Ne⁺/Ar⁺</td>
<td>1.02</td>
<td>0.69</td>
<td>0.75</td>
<td>0.60</td>
</tr>
<tr>
<td>He⁺/Ar⁺</td>
<td>0.28</td>
<td>0.077</td>
<td>0.42</td>
<td>0.21</td>
</tr>
</tbody>
</table>

A number of simulations describing the collision cascade process have been developed. Models which conserve energy and momentum, but not particle number, include Boltzmann type transport equations [1.54] and Monte Carlo simulations of the TRIM (TRansport of Ions in Matter) type [1.55]. This type of simulation allows parameters such as elastic scattering, surface and interfacial structure to be included in the simulation although at the expense of extended computation times. A binary collision code which considers conservation of particle number is the MARLOWE type [1.56]. Simulations of this type are unable to consider cascades where collisions between moving atoms are frequent events. A detailed description of this area of ion interactions with solids is not appropriate in this context, although it should be remembered that the qualitative description in this section has severe limitations.
Ion bombardment does not only give simple 'billiard ball' type processes. Electronic excitation and ionisation may be induced by an impinging charged particle. Electronic sputtering caused by interaction of the ion and surface atom fields occurs, particularly for ion bombardment of alkali halides [1.57]. Stoneham [1.58] has discussed energy transfer processes between electrons and ions in collisional cascades in solids. A list of assumptions were presented

(a) electrons produced in collisional cascades do not produce recoil atoms
(b) atomic binding energies are negligible in collision cascades
(c) energy transfer to electrons are small (but many)
(d) electronic and nuclear collision contributions to energy loss can be separated.

Several possible electronic processes that may be induced by ion impact, such as exciton generation, exciton self-trapping, non-radiative transitions from excited states to neutral vacancies and interstitial pairs were also discussed. Furthermore, separation of vacancy-interstitial pairs occurs.

In contrast to the theoretical investigations of processes occurring in the cascade, a number of studies of practical etch systems have been performed. This is exemplified by Dieleman et al [1.59] has suggested that for Ar ion bombardment of a Si surface with simultaneous Cl\textsubscript{2} exposure, approximately 20% of the energy of the impacting ion may be lost via electronic and vibrational excitation. This implies that sputtering is not a purely physical process and may contain chemical aspects. This type of sputtering process is now considered.

1.4.4 Chemical Sputtering

The phenomenon of yield enhancement for sputtering of a surface by an ion beam with simultaneous exposure to a reactive gas has been extensively
studied over the last decade. The initial investigations were performed by Coburn and Winters [1.60] on the etching of Si bombardment by Ar\(^+\) ions in the presence of XeF\(_2\) gas. The reduction of the sputtering yield of many metals when oxygen is introduced as a contaminant gas has been known for many years [1.61]. An type of chemical sputtering is often referred to as chemically assisted ion beam etching (CAIBE) or ion beam assisted etching (IBAE). Coburn and Winters [1.62] suggested three possible competing mechanisms which would be responsible for reduction or enhancement of etch rates; ion activated adsorption, ion enhanced reaction and ion induced desorption. These three mechanisms encompass a multitude of processes which may contribute towards chemical sputtering.

It is clear that adsorption of a chemically active species is necessary for a synergistic process. A number of processes caused by ion impact at the surface such as bond breaking, layer intermixing and sputtering may occur as a result of collisional cascades. These are generally fast processes occurring over a timescale of 10\(^{-12}\) s. Significantly slower processes occur as a result of ion enhanced chemical effects in the perturbed surface region. Furthermore, adsorption of reactant gases during this time period does not significantly contribute to etching reactions. The type of processes generally associated with the slow processes are ion induced reaction, diffusion and desorption. The schematic in Figure 1.7 reveals some of the competing events that may occur upon both physical and chemical sputtering processes.

Chemical sputtering can be controlled by modification of parameters such as beam energy and ion mass, thus giving a prospective etching process significant flexibility. Zalm [1.62] has observed that chemical sputtering yield exhibits a sublinear dependence upon ion energy over an energy range 0.25-2.5KeV. For low damage semiconductor processing it is desirable to use ion/neutral beams at the lower end of this range. Comparison of the binding energies for semiconductors reveal values several orders of magnitude lower than the impinging beam. For example, Si 4eV [1.63] and GaAs 10eV [1.40]. It is clear that in order to drive chemical reactions rather than physical sputtering processes the beam energy for the etching step
should be in this energy regime. CAIBE and IBAE type processes generally use energies in the range prescribed above by Zalm [1.62].

Linear cascade theory predicts a relatively weak mass dependence for physical sputtering processes at energies of around 1kV. Gerlach-Meyer et al [1.64] performed a study of the reaction rate of silicon with XeF₂ and Cl₂ with simultaneous irradiation of the surface with 1kV He⁺, Ne⁺ and Ar⁺ ions. Table 1.1 has shown a list of Si etch yields for both ion beam and synergistic processes with XeF₂ and Cl₂. Two sets of sputter yields are presented with additional data from 600eV ions also presented [1.65,1.66]. From these figures it may be observed that the etch yield for He⁺ compared to Ar⁺ is much greater in the presence of a reactive species than the ion alone. It is clear, therefore, that He⁺ is more effective at enhancing processes that require small energy exchanges rather than the larger energy budget required for sputtering processes. The etch yields of Ne⁺ and Ar⁺ ions are only marginally different but greater than that predicted by linear cascade theory. Davis et al [1.67] have demonstrated that light ions such as H⁺ and Ne⁺ induce less damage in silicon than species of higher mass such as Ar⁺ ions. Furthermore, they observe that irradiation of the surface to H⁺ ions subsequent to Ar⁺ ion exposure reduces the electrical damage caused by the argon ion beam. Irradiation by H⁺ ions alone also cause significant disorder and damage.

This chapter has attempted to establish the principles of surface analysis, beam induced etching and ion-surface interactions in order to introduce a more detailed and strategic investigation of the ion assisted etching and deposition processes of halogens and hydrocarbons on semiconductor surfaces in chapters 3 to 5. The next chapter establishes the experimental methods employed to obtain the results.
Figure 1.7 Schematic representation of Processes occurring (a) in the near surface region of a solid following bombardment by energetic ions or neutrals (b) as for (a) but an adsorbate covered surface.
CHAPTER 2

EXPERIMENTAL METHODS

2.1 Concept and Construction of UHV Chamber

2.2 Sample Mounting and Preparation

2.3 Reactant Preparation and Dosing

2.4 Implementation of Surface Spectroscopic Techniques
   2.4.1 Thermal Desorption Spectroscopy
   2.4.2 Auger Electron Spectroscopy
   2.4.3 Low Energy Electron Diffraction

2.5 Ion and Neutral Energetic Beam Sources
   2.5.1 Hot Filament Argon Ion Gun
   2.5.2 Saddle Field Fast Atom Beam Source
2.1 Concept and construction of UHV chamber

The apparatus described in this section was based around the concept of *in-situ* processing where a series of processes may be performed without removing the sample from a clean vacuum environment. The UHV apparatus constructed for these studies consisted of a three chamber system of two 'reaction' cells clustered around a six way cross (6") based central analysis section. In order to attain ultra high vacuum pressures, the entire system was bakeable and hence a removable tent of aluminised 'Rayon' fibre matting was fixed to the system. The source of heating was supplied via five 1.8kW resistive heaters. This arrangement allowed a maximum bakeout temperature of 160°C.

A schematic of the system is shown in Figure 2.1 with a photograph of the system being shown in Figure 2.2. The system design can be sub-divided into pumping, pressure measurement, sample manipulation, reactant introduction and surface analysis requirements. The principal pump was a 600l s⁻¹ water cooled diffusion pump charged with Santovac 5 pumping fluid. This oil is a polyphenyl ether, originally developed as a lubricant with low vapour pressure for space applications. The ultimate vacuum achievable with this oil is typically 4x10⁻¹⁰ mbar and hence is particularly useful for UHV applications. A liquid nitrogen trap was fitted above the diffusion pump to eliminate back streaming and back migration to the high vacuum side of the pumping system. The diffusion pump was 'backed' by a two stage rotary pump charged with a conventional mineral oil, with an immediate foreline trap/solenoid valve combination to prevent back migration of rotary pump oil into higher vacuum regions.

Subsidiary pumping to the chamber was provided by turbomolecular /rotary/sorption combinations. These were attached to each reaction chamber to allow operation at higher pressures than the UHV analysis chamber. This pumping was introduced in order that real etching processes could be performed within the system. In order to achieve this it was necessary to site a
gate valve between each adjacent chamber and provide a long travel sample manipulator to each reaction chamber in order to allow movement of the sample into the analysis chamber. Each reaction chamber was fitted with a quadrupole mass spectrometer (QMS), and thus reactant and product species could be accurately measured. These were also used for residual gas analysis and leak detection within the apparatus.

A number of sorption pumps were also used within the system to allow corrosive gases such as bromine or chlorine to be removed safely from the system without degradation of the mechanical pumps.

Pressure measurement was obtained by using a combination of pirani gauges (atm-$10^{-3}$ mbar), ionisation gauges ($10^{-4}$-$10^{-11}$ mbar) and cold cathode gauges ($10^{-2}$-$10^{-9}$mbar).

The arrangement of each chamber is depicted in Figure 2.3. The side profile of the chamber for analysis of etch reactions is shown in Figure 2.3(a). The sample may be held centrally and rotated so as to be directed at reactant dosing source, QMS or ion/neutral beam source. The cell also possessed a subsidiary turbomolecular pump so as to expose the chamber to high pressures without damaging the central analysis chamber. Figure 2.3(b) shows a plan view of the analysis chamber. A retarding field analyser is positioned on the six-way cross such that the manipulator from either side chamber may be allowed access. The side profile of the cell for the study of the hydrocarbon reactions on silicon is presented in Figure 2.3(c). The pumping arrangement is similar to chamber 1, and also the sample is surrounded by a dosing source, QMS and beam source. The dosing source is also fitted with a tungsten cracking cell (described later) for the study of hot filament assisted reactions.
Figure 2.1 Schematic of 3-Chamber UHV System for Studies of Etching and Deposition Surface Reactions
Figure 2.2 Photograph of UHV System for Studies of Etching and Deposition Surface Reactions
Figure 2.3(a) Side Profile of Chamber 1
(Study of Etch reactions)
Retarding field Analyser with electron gun

Chamber 3

Viewport

Chamber 1

Figure 2.3(b) Plan View of Chamber 2
(Analysis Chamber)
Figure 2.3(c) Side Profile of Chamber 3
(Study of Hydrocarbon reactions on silicon)
2.2 Sample Mounting and Preparation

The two semiconductors employed in this study are silicon (Si) and gallium arsenide (GaAs). Both of these materials were supplied in the form of well characterised single crystal wafers with (100) orientation. The wafers were cleaned prior to insertion to remove greasy contaminants. This was followed by a thorough in-situ cleaning process to remove the native oxide and residual contamination from the surface. This oxide removal is then followed by suitable processing to leave a stable and reproducible reconstructed surface. The physical and electronic properties of the two semiconductors are quite different and require different mounting and cleaning methods.

2.2.1 Silicon

The mounting of a silicon sample for this series of experiments required that the sample may be firmly held in place with adequate provision for movement in the x, y and z directions. This enabled movement of the sample between dosing source, mass spectrometer, ion source and electron spectroscopic probes such that the angles and distances are accurately known. In addition, the sample must be heated to high temperatures (1200K) in order to provide sufficient surface preparation prior to experimentation and to allow a linear heating ramp for thermal desorption experiments. Furthermore, the sample temperature must be accurately recorded for correct analysis of thermal desorption data.

The Si(100) wafer (p-type, 10 Ω.cm) was cut to dimensions of 14mm x 7mm and mounted to two tantalum support clips, which were previously spot-welded to 3-ply Ta wire spirals attached to stainless steel support rods. This mounting is shown in Figure 2.4(a). The Si(100) was kept in position by correct tensioning of the clips around the silicon, which also enabled good thermal contact. The thermocouple junction was of the chromel-alumel type and was spot-welded to a third Ta foil positioned centrally on the wafer. This
sample arrangement allowed a resistive current to be applied to the single crystal. The nature of Si requires that two interswitchable power supplies (Farnell 100V,1A; Farnell 12V,12A) are necessary to provide an adequately linear heating rate.

The arrangement of the silicon crystal was such that all heated metal surfaces were out of line-of-sight contact with the front surface of the crystal such that contributions from the metal-halogen chemistry were limited.

The sample preparation of silicon after insertion of the crystal into the vacuum system consisted of a 12 hour bakeout at 160°C, thus achieving UHV pressures. Once the system had cooled and reached 1x10^-9 torr, gradual heating of the wafer was applied in order to desorb the native oxide from the surface. Removal of the oxide prior to bakeout results in the clean silicon surface being contaminated with desorption products from the walls of the system during the bakeout procedure. This occurrence was observed by Chang et al [2.1] who reported strong carbon and oxygen Auger signals after a 6Hr bakeout at 200°C, whilst analysis prior to bakeout showed no contamination within the limits of Auger sensitivity.

Kirby and Lichtman [2.2] showed that insertion of a silicon sample without pre-treatment by an HF etch was preferable, as this treatment introduced stubborn carbon contamination which could not be removed by subsequent sputtering. The oxide layer thus protected the silicon until in vacuo cleaning was attempted. They also found that two in-situ methods provided clean Si surfaces to within the sensitivity limits afforded by AES. The first of these methods employed three heating cycles of 3-5 minutes at 1550K followed by slow cooling to room temperature whilst the second method involved bombarding the sample surface with Ar+ ions for approximately 20 minutes, followed by subsequent annealing at 1000-1100K. The former of these two methods involves rapid desorption of oxygen from the sample surface and Dylla et al [2.3] observed that facetting of the silicon surfaces occurs when the silicon was exposed to oxygen partial
pressures of >10^{-7} mbar whilst at 1000K. Thus an extended and less rigorous cleaning procedure for Si wafers was employed.

### 2.2.2 Gallium Arsenide

The sample mounting for the GaAs consisted of a backing plate of thin tantalum foil as shown in Figure 2.4(b) and (c) which held the fragile GaAs wafer in place with small tabs. The GaAs wafer is structurally weaker than Si and therefore would snap if held between two tensioned clips. GaAs is also a poor electrical conductor at room temperature and thus a resistively heated backing plate was necessary to heat the sample. The temperature of the sample was measured using a chromel-alumel thermocouple with the junction spot-welded to a strip of tantalum foil.

The GaAs single crystal was mounted in two distinct fashions. Firstly, for adsorption at room temperature as shown in Figure 2.4(b,c) and secondly for low temperature using liquid nitrogen cooling as depicted in Figure 2.4(d). For room temperature experiments the sample rods were mounted to a machinable glass ceramic block. The backing plate was cut such that the thermocouple-bearing foil wrapped around the wafer with an insulating piece of mica between the foil and the backing plate thus allowing for close agreement between the sample and thermocouple temperatures. Liquid nitrogen cooling was used by tensioning the backing plate onto sapphire block attached to the manipulator cooling block. Sapphire is electrically insulating, whilst at room temperature and above it is thermally insulating. At low temperatures, however, it becomes a good thermal conductor and therefore the liquid nitrogen cools the sample.

The GaAs has a tendency to lose As if heated to greater than 850K and extreme care was taken during TDS experiments and during surface cleaning to ensure that the surface was not irreversibly damaged.
Figure 2.4 Sample mounting for (a) Si, (b) GaAs and (d) liq. N₂ cooling for GaAs
2.3 Reactant Preparation and Dosing

2.3.1 Introduction

The adsorbate molecules employed throughout this study were dosed onto the semiconductor surfaces in the form of low pressure gas or vapour phase species. The gases used in the experiments described in Chapters 3 and 4 were halogens, whilst those used in Chapter 5 were hydrocarbons.

2.3.2 Halogens

The two principal halogens used were molecular bromine and chlorine. There were two possible methods of introduction of these gases into the UHV reactant chamber. Firstly, the halogen may be introduced in the gas phase from a proprietary cylinder (BDH) in the case of chlorine, or via the vapour pressure over liquid in the case of bromine. The liquid bromine (BDH chemicals) was purified by a number of freeze-pump-thaw cycles to remove volatile impurities before exposure to the semiconductor surface. The second method of halogen generation involved the solid state electrolysis of silver halide, thereby producing the halogen in-molecular form. Electrochemical cells of this type were first developed by Wagner [2.4] using an Ag2S electrolyte. Heegeman et al [2.5] utilised this to introduce molecular sulphur into an UHV system, whilst Spencer et al [2.6] adapted the design to produce molecular halogens. The electrochemical cell is of the type

$$\text{Ag} / \text{Ag X} / \text{Pt},X$$  \hspace{1cm} \text{where X is a halogen}

The passage of an electric current through the silver halide causes electrolysis to silver and the molecular form of the halogen. The electric field induces movement of $\text{Ag}^+$ ions via defects in the AgX lattice. The mobility of
Ag⁺ ions in the AgX may be enhanced by addition of a suitable dopant, such as cadmium halide, to increase the defect concentration of the lattice. The electrical resistance of the cell is lowered by doping the lattice, whilst modest heating of the cell to approximately 420K allows an extended lifetime of molecular halogen production at modest operating currents.

The electrolytic cell as depicted in Figure 2.5 was manufactured by fusing the AgX into a cylindrical pellet of approximately 20mm length and 7mm diameter using the supporting pyrex tube as a mould. A spiral of silver wire was embedded at the cathodic end during the moulding process, whilst a platinum gauze was fused to the other end and thus acting as the anode. Tantalum wires were then spot-welded to the electrodes. A CF70 flanged UHV feedthrough with six separate connections was used for construction of the cell. Two diametrically opposed connections were used as support/heating rods by spot-welding two stainless steel rods to the feedthroughs. A multi-stranded spiral of tantalum wire was used between the two support rods to hold the quartz tube enclosing the electrolytic cell, and thus allowed resistive heating to be applied to the cell. Temperature measurement was afforded by a chromel-alumel thermocouple spot-welded to the platinum gauze.

The operation of the dosing cell was enhanced by mounting the arrangement within a UHV compatible linear transfer mechanism which allowed the source to be positioned at precise distances from the sample, whilst allowing withdrawal of the pellet to allow clear passage of the sample and manipulator rod to the central analysis chamber. During dosing, the halogen cell was positioned approximately 10mm from the semiconductor surface. A known current was passed through the cell for a measured time, thus allowing calculation of the emitted flux of halogen from Faraday's law [2.7] where the charge required to liberate a mass, m, is given by

\[ Q = \frac{F m z}{M} \]  

[2.1]
Thus the amount of halogen produced was proportional to the total current passed. A constant current source was thus used to allow control of the electrolysis current in the range 1-200mA.

A cosine distribution function was found to describe the spatial distribution of the halogen beam emanating from the electrolytic source [2.8]. Thus the chlorine flux impinging on the surface may be calculated from

\[ F = \frac{c}{\pi(r^2 + d^2)} \]  \[2.2\]

where

- \( F \) = flux per unit cell
- \( c \) = total flux from source
- \( d \) = surface-anode distance
- \( r \) = pellet radius

The emanating beam of chlorine was tested for high concentrations of atomic chlorine; by comparison with pure \( \text{Cl}_2 \) gas and was found to be identical, thus showing that chlorine produced from the electrolytic cell is released in molecular form [2.9]. This was also verified for electrolytic cells of bromine using mass spectrometric methods.

A dosing arrangement of gaseous (and high vapour pressure liquids) was also utilised as shown in Figure 2.3(a). This consisted (for bromine) of a glass reservoir with two high vacuum PTFE valves connected using a Sno-Trik metal-glass connector to a sorption pump array. The bromine was then purified by a series of freeze-pump-thaw cycles and was then introduced to the UHV chamber by allowing the \( \text{Br}_2 \) overpressure through an all metal
precision leak valve. The measurement of the partial pressure of dosed gas was by means of an adjacent ionisation gauge. This method did not give a direct measurement of impinging gas and therefore comparison with the electrolytic cell yields an enhancement factor for the gas doser array.

A combination of the two methods of halogen introduction was used because of the advantages and disadvantages of each technique. The electrolytic cell gives an absolute value for production of molecules and is useful for small adsorbate doses. This method is less effective for large exposures as the behaviour of the source becomes erratic over extended usage. This is due to the development of short currents produced by growth of silver dendrites through the pellet and this is known to limit the lifetime of these electrochemical sources [2.6]. The cell may occasionally be repaired by passage of a very high current through the heated cell. The gaseous introduction of halogen was found to be more reliable and allowed greater exposures and was the preferred method, with calibration by use of the electrochemical cell.

2.2.3 Hydrocarbons/Hydrogen

These gases were introduced via a lecture bottle through pumped stainless steel lines to the leak valve assembly. The local pressures were greater than those measured by the ionisation gauge, thus accurate calibration with a well characterised surface was necessary. Dosing of gases was restricted to pressures of between $1 \times 10^{-9}$ and $1 \times 10^{-6}$ torr thus avoiding degradation of the ultra high vacuum and the pumping system. Figure 2.3(c) also shows the presence of a hot filament placed adjacent to the exit of the dosing nozzle. This facility allows the activation of hydrocarbon or hydrogen/hydrocarbon gases.
Figure 2.5 Schematic of electrolytic Cell for Production of Bromine

(a) circuit diagram
(b) pellet construction
2.4 Implementation of Surface Spectroscopic Techniques

2.4.1 Thermal Desorption Spectroscopy (TDS)

A schematic of the TDS experiment is shown in Figure 2.6. The single crystal substrate was dosed (see Figure 2.3(a)) with a known amount of adsorbate gas and then was resistively heated with a linear rate of temperature increase. For Si, current limiting was necessary during the heating cycle due to the semiconducting nature of the material. During the heating process the single crystal was placed directly opposing a quadrupole mass spectrometer (QMS) at a distance of approximately 20mm. The QMS could be moved towards or away from the sample by means of a linear transfer mechanism. This allowed the collection of the maximum amount of desorbed species into the ion source of the QMS. The mass spectrometer was tuned to the desired mass fragment of interest and the signal output was fed to the Y-terminal of an X-Y recorder. The sample temperature was measured by a chromel-alumel thermocouple which was also fed to the X-Y recorder. The sample was then cleaned in order to return it to its initial state. The purity and structure of the surface was then verified by AES and LEED.

2.4.2 Auger Electron Spectroscopy

The AES system used in this investigation is shown schematically in Figure 2.7. A retarding field analyser (RFA) was used as the basis for measurement of Auger electrons. The RFA can collect Auger electrons and possesses a resolution of approximately 1eV at 100eV. The collector is the RFA screen and is positively biased. A series of transparent grids before the screen can be either negatively biased or earthed. The negative biasing of one of the grids allows a retard voltage to be applied and hence the grid can act as a high pass filter. Electrons of energy below that of the applied potential are retarded. The earthed grids provide a field free region before and after the retarding potential.
The primary beam source consisted of an electron gun which allowed a focused beam (1mm diameter) of electrons, with a beam current of 1-3μA, to impinge on the sample surface. The beam energy of the electrons was variable in Auger mode between 500-3000eV. The detected Auger current, resulting from this emission mechanism, is typically five orders of magnitude less than the primary beam current, and hence electronic differentiation is necessary. This is achieved by using a lock-in amplifier to measure the second harmonic of the signal referenced against the frequency doubled grid modulation signal. The spectra was recorded as dN(E)/dE versus E. Control of the modulation voltage allows compromise between resolution and sensitivity. Typical values used in this study were 10V.

2.4.3 Low Energy Electron Diffraction

The RFA can also be used as the basis for the LEED technique. The schematic of this technique is shown in Figure 2.8. An electron beam of low energy, typically 50-150V is focused at the sample. A number of the electrons are elastically backscattered towards the RFA. The outer grids were earthed in order to provide a field free region, whilst the inner grid was negatively biased at approximately 10V below the primary beam energy. This allowed control of inelastically scattered electrons moving towards the RFA. The screen, which has an applied voltage of +5kV, consists of a P43 type cathodoluminescent phosphor which results in a directly visible representation of the reciprocal space pattern of the surface under study. The incident beam current was 1-3μA with a spot diameter of approximately 1mm.
Figure 2.6 Schematic of Thermal Desorption Spectroscopy Experiment
Figure 2.7 Experimental arrangement for Auger Electron spectroscopy using a retarding field analyser (RFA)
Figure 2.8 Schematic of experimental arrangement used in LEED
2.5 Ion and Neutral Energetic Beam Sources

2.5.1 Hot Filament Argon Ion Gun

The source of argon ions employed in this study were obtained from a hot filament argon ion sputter gun (AS10). Beam currents of up to 10\(\mu\)A were obtained. This beam source operated on a fixed beam energy of 500V, and was augmented by application of a +180V bias on the sample. This allowed a 680eV Ar\(^+\) ion beam to modify the surface region. In addition, this beam source was used to sputter clean the GaAs(001) surface.

2.5.2 Saddle Field Fast Atom Beam (FAB) Source

The FAB source employed in this study is the Ion Tech FAB 114 broad beam saddle field source. This neutral beam array is based on a dc-energised cold cathode source utilising the charged particle oscillator effect produced by an electrostatic saddle potential field [2.10].

The operating principle of the beam gun relies on the effect described by McIlraith [2.10] that electrons can traverse long oscillatory paths in the presence of an electrostatic field. The particular configuration of electrostatic field that allows this phenomenon to occur is shown in Figure 2.9, where two positively charged parallel graphite anode rods symmetrically placed on the axis of a surrounding cathode cylinder. The resulting electrostatic field has a 'Saddle point' midway between the two anodes allowing electrons from the cathode wall to oscillate through the saddle point with extended mean free paths. In the presence of a gas, the positive ions formed from the discharge travel towards the cathode and emerge along straight paths through an aperture. The increased mean free path of electrons allows the ions produced in the discharge to be neutralised and hence the saddle field beam source is a provider of essentially neutral beams. Franks [2.11] suggested that neutralisation may be due to
recombination of ions with slow secondary electrons from the edges of the aperture, whilst Fitch et al [2.12] proposed that the fast atoms are produced by a charge exchange mechanism within the discharge chamber.

The 114 FAB source used in this study may produce energetic neutrals with a kinetic energy of 800eV to 2.5keV. The beam profiles produced from this source are presented in Figure 2.9 and show equivalent flux densities from the source at varying working distances. The working distance used in the series of experiments was 100mm. This distance was used as the FAB 114 source had to be enclosed in a 'custom-built' UHV housing which could be sited no closer than 100mm from the sample surface. The equivalent beam density produced is ten times that produced by the AS10 ion gun and therefore working distance only posed problems in regard to the beam divergence and hence possible sputtering from surfaces other than the sample i.e. support rods.
Figure 2.9 Beam Profile of the Fast Atom Beam Source (Ion Tech FAB114) (data courtesy of Ion Tech Ltd)
3.1 Introduction

3.2 Surface Structure of Silicon (001) and Adsorbed Halogen Phases
  3.2.1 Surface Structure of the Si(001) Surface
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3.3 Ion/Neutral Enhanced Etching Reactions on Silicon
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  3.4.1 LEED and AES Spectra of the Si(001) Surface
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  3.4.4 The Br-Si(001) Surface: Bombardment with argon neutrals
    3.4.4.1 Br Detected Signal
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3.5 Analysis and Discussion
  3.5.1 Adsorption and Thermal Etching of Br₂ on Si(001)
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    3.5.2.1 Ion Beam Induced cross-sections-Ar⁺ ions
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    3.5.2.2 Beam Induced Cross-sections-Ar⁰ neutrals
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3.6 Summary and Implications for Ion/Neutral Assisted Etching of Silicon with Halogens
3.1 Introduction

It has been established that bombardment by inert ions may enhance, or even induce, the rate at which some gas phase species react with semiconductor surfaces [3.1]. Halogens react with silicon to form volatile silicon halide compounds. This type of reaction has been utilised to achieve etching of device features required in the fabrication of microelectronic devices. The term chemically assisted ion beam etching (CAIBE) is often applied when exposure of the silicon to the halogen is accompanied by ion beam irradiation. At least two forms of damage may be introduced at the surface during this process. Firstly, the halogen molecule introduced to the reaction chamber may react at all points of contact on the semiconductor surface and therefore it is ultimately desirable to choose etch precursors with low intrinsic reactivity to control the profile of the etch feature. The second damage inducing process involves the stopping mechanisms when an ion impinges upon a solid surface. This has been discussed in the introductory chapter (section 1.4). The use of low energy focused inert gas ion or neutral beams (e.g. liquid metal ion sources) on to a suitable precursor/surface region may, however, provide a low damage single step patterning capability thus leading to a greater density of active components per unit area. An understanding of the chemistry and physics invoked in these ion induced processes may give insights into how the reaction may be limited to a localised region on the surface. In order to proceed with investigations into a more controllable etch precursor it is essential to study the reactions of the basic halogen molecules with silicon.

This chapter explores the thermal and ion-assisted reactions of halogens, most particularly bromine, with silicon in order to understand the mechanisms of these processes. Bromine is used as an alternative to chlorine due to the less corrosive nature of the reagent at the surface These studies may lead to further improvement and optimisation of real etching methods for VLSI device manufacture and also point the way to developing etchants suitable for future ULSI processing. This chapter also considers the reaction of bromine and silicon as a model etching system of an elemental
Chapter 3: Introduction

semiconductor by an halogen molecule. The etching of more complex semiconductors is also of importance thus the nature of ion-assisted etching of gallium arsenide is addressed in the next chapter.

In order to put the observations recorded in this chapter into context it is essential to consider the current state of knowledge on the fundamentals of halogen-silicon surface interactions. Section 3.2 addresses the phenomena of adsorption of halogens on silicon e.g. the nature of bonds formed at the surface region and the arrangement of the atoms with respect to the reconstructed surface. The current theories of ion-assisted reactions of halogens with silicon are considered in section 3.3 and include a discussion of the existing mechanisms proposed for the enhancement of the silicon-halogen reaction. This section also deals with the studies of ion induced damage on silicon surfaces and the considerable effects that they exert on device performance. Results obtained from thermal desorption experiments on the Br₂/Si(100) system are presented in section 3.4, with detailed investigation of the ion/neutral beam modification of the surface phase leading to ion-assisted etching. A discussion follows in section 3.5 on the mechanisms of thermal and ion etching in the light of observations from the TDS experiments. Implications for in-situ etch processing of VLSI structures are also considered.
3.2 Surface Structure of Silicon (001) and Adsorbed Halogen Phases

3.2.1 Surface Structure of Silicon (001)

To fully characterise any adsorption process, it is first necessary to describe the structure of the adsorbent surface. The most commonly used surface orientation for device processing is the Si(001) plane. In general, MOS devices are fabricated on Si(001) whilst bipolar devices utilise Si(111). The nature of the Si(001) surface, therefore, is of great interest and is used in these TD studies. The structure of other silicon surfaces are also considered at certain junctures in order that adsorption and etching reactions of halogens with other surfaces may be comparatively analysed in later sections. The surface reactivity of different orientations may not be assumed to be constant. The density of atoms in the Si(111) plane is greater than that for the Si(001) plane, therefore some processes occur faster in this plane e.g. Si{111} planes oxidise faster than Si{100}.

The bulk structure of a semiconductor upon termination at the surface is known to reconstruct to an energetically more stable arrangement [3.2]. Reconstruction is the term used for movement of atoms at the surface in a direction parallel to the surface. Such changes in the periodic spacing may be observed by LEED experiments. In addition, the term 'relaxation' is often used to describe movement normal to the surface plane, which may compress or expand the distance between surface layers. Without the process of reconstruction and relaxation the surface would resemble the bulk structure.

The bulk structure of silicon as depicted in Figure 3.1 may be described as a diamond lattice which consists of two interpenetrating face centred cubic lattices consisting of exclusively silicon atoms. Truncation of the lattice results in the formation of dangling bonds which have a tendency to reposition surface atoms to a state of lowest energy. Hence the periodicity of a clean silicon surface will reconstruct to this low energy state. The most common method to study these reconstructions over the past thirty years
has been by use of low energy electron diffraction (LEED). Other methods such as ion channelling [3.3], electron energy loss spectroscopy (EELS) [3.4], photoemission [3.5] and optical absorption [3.6] have been employed as complementary techniques.

Early LEED studies by Schlier and Farnsworth [3.7] showed half-order beams in two orthogonal (100) azimuths, which were interpreted as a (2x1) unit cell on the surface. Furthermore, these researchers proposed a surface structure where silicon atoms were pulled together in pairs, or dimerised rows where alternate rows of atoms move together forming bonds, thereby leaving only one dangling bond per surface atom as is shown in Figure 3.2(a). Lander and Morrison [3.8] proposed a model which added an additional layer of dimers to the top of the simple dimer model to give c(4x2) symmetry as depicted in Figure 3.2(b). Recent studies of the surface by scanning tunnelling microscopy (STM) have resolved many of the questions concerning the Si(001) structure [3.9,3.10]. Up to this time considerable debate over the precise nature of the surface and the orientation of the surface silicon atoms led to uncertainty in adsorbate-surface studies.

Applebaum et al [3.11], however, developed the dimer model using a theoretical pseudopotential analysis of the sub-surface strains induced by surface reconstruction. This approach is a calculation method which originally was used for determination of bulk energy levels. An artificial potential is added to the attractive potential from the ion cores in the lattice. The resultant 'pseudopotential' is substituted for the potential term in the Schroedinger equation which is then solved for the lattice under investigation. A model as depicted in Figure 3.3(a) was introduced that the calculated formation of dimers and showed the strain displacements of silicon atoms up to five layers into the bulk structure. They concluded that the dimers lay flat in the plane of the surface with the sub-surface displacements occurring in order to reduce the overall strain energy. Two surface states were present; dangling bonds normal to the surface and a $\sigma$-bonding state parallel to the surface. The latter force accounts for the reconstruction of the surface which should be metallic in character. Chadi
Chapter 3: Surface Structure of Si(001)

[3.12] suggested that buckling of the dimers out of the plane would result in the experimentally observed semiconductor character of the surface. This structure is shown in Figure 3.3(b). Roberts and Needs [3.13] have recently performed further total energy calculations for dimer reconstructions on the Si(001) surface and suggested that a single missing dimer model may exist in the ground state structure of the surface. Study of the Si(001) surface by STM has resulted in confirmation of the dimer model [3.9-10]. A typical STM topograph is presented in Figure 3.4 [3.9] for the Si(001) surface. The light regions represent surface protrusions whilst the darker regions are depressed areas. The marked region is proposed as a (2x1) unit cell and the protrusions are surface dimers. Both buckled and non-buckled dimers were observed which produced regions of (2x1), c(4x2) and p(2x2) symmetry.

As well as a knowledge of possible surface structures it is essential that a comprehensive understanding of silicon cleaning methods are known in order to obtain a reproducible adsorbent for the TDS experiments. The cleaning procedure for preparation of a Si(001)(2x1) surface is described in the experimental section. A faceted surface is sometimes observed if the thermal cycling procedure is carried out too rapidly. Dylla et al [3.14] observed that silicon may form faceted surfaces when exposed to pressures of approximately 10 mbar of oxygen at surface temperatures of 1000K. Hamers et al [3.10] also observed the formation of (111) microfacets upon high temperature (1450K) annealing of the Si(001) surface which resulted in irreversible roughening of the surface. Similar observations were reported by Gundry et al [3.15] using LEED, and Norton [3.16] using reflection high energy electron diffraction (RHEED). It is thought that initial outgassing of silicon during the thermal cycling cleaning treatment may cause high surface partial pressures of oxygen leading to faceting of the surface. As previously stated in the experimental section careful slow outgassing of the silicon is therefore necessary in order to obtain a smooth clean reconstructed Si(001)(2x1) surface.
3.2.2 Structure of the Halogen-Silicon Surface

Florio and Robertson [3.17] were the first to study the surface reactions of halogens on Si(111). They found an initial sticking probability of 0.15 with adsorbed chlorine occupying two states, one weakly bound and the second more strongly held to the surface. They also observed that 0.04ML of Cl removed the surface reconstruction. Chlorine forms well ordered overlayers on Si(111), with x-ray photoelectron spectroscopy (XPS) studies on Si(111)-(7x7) showing silicon atoms bonding to multiple chlorine atoms upon adsorption [3.18,3.19]. Schrell et al [3.20] have shown SiCl$_2$ and SiCl$_3$ in addition to SiCl on a Si(111)(7x7) surface after adsorption of Cl$_2$ at 300K. Annealing to 673K results in the presence of just SiCl on the surface. Rowe et al [3.21] and Larson et al [3.22] used a combination of photoemission spectroscopy, LEED and local density of states calculations to study a number of Si/Cl systems. The Cl-Si bonds on Si(001) 2x1 were observed to be covalent but tilted with the 2x1 LEED pattern persisting at Cl saturation coverages. Aoto et al [3.23] using LEELS found different adsorption configurations, where Cl atoms sit obliquely on Si atoms on the Si(001) and Si(110) surfaces, whilst Cl adatoms sit atop the Si atom on the Si(111) surface. The saturated Cl concentration for Si(111) was found to be four times that necessary to saturate the Si(001) surface, as determined from AES peak heights. Adsorption of Cl atoms does not cause dimer bond breaking, because adsorption is proposed to occur at steps and sites of missing dimers. This is confirmed by the low saturation concentration of Cl with low Cl$_2$ exposure. This adsorption process leads to tilted bonds with two bonding types. Firstly a $\sigma$-type bonding state from Si($p_z$), to the Cl($p_z$) antibonding state, whilst the second is $\pi$-type from the Cl($p_x,p_y$) state to the Cl($p_z$) antibonding state of the Si-Cl bond. These probably correspond to the $\beta$ state and $\alpha$ state respectively as described by Jackman et al [3.24] for thermal desorption states of chlorine on Si(001). The $\pi$-type bond may act as a precursor adsorption state for corrosion layer formation.
Citrin and Rowe [3.25] used surface extended x-ray absorption fine structure (SEXAFS) to determine the position of chlorine and iodine on the Si(111)-(7x7) surface. SEXAFS is the absorption of synchrotron radiation as monitored with a photon energy considerably above the absorption edge, which may excite a core electron. Information on bond lengths may be obtained from this technique. Adsorbate systems may be studied as the method is suitable for systems with no long range periodicity. Michel et al [3.26] have used x-ray standing wave fields to determine the position of I on Si(111) and Si(110). They observe that the iodine adsorption site is a hollow position along the atomic chains at the bulk-terminated surface. The adsorption of bromine on Si(001)(2x1) surface was studied by Etelaniemi et al [3.27] using x-ray standing wave field analysis. Br atoms are found to saturate the free dangling bonds of the 2x1 surface with the dimerized surface persisting after adsorption. The reconstruction should lift above monolayer coverage although there is no literature evidence for this for the Br$_2$/Si(001) system.

Clearly, most structural problems on the Si(001) surface and the related adsorbate systems have been elucidated. A survey of the outstanding issues with regard to the mechanisms of ion assisted etching of silicon is now presented.
Figure 3.1  Bulk Structure of Silicon (Diamond Structure)
Figure 3.2  Surface Reconstructions of Si(100)

(a) Si(100) (2x1)

(b) Si(100) c(4x2)
Figure 3.3 Schematic of Si(100) surface showing (a) movement of atoms away from ideal dimer positions in the near-surface region (b) asymmetric dimer model

(a) Without Reconstruction

adapted from J. A. Applebaum and D. R. Haneman
Surface Science 74 (1978) 21

Arrows indicate the directions in which atoms move from their ideal dimer position to lower strain energy

Top View

(b) Asymmetric Dimer

adapted from D.J. Chadi J. Vac.Sci.Technol 16 (1979) 1290
Figure 3.4 STM topograph of Si(001) surface

after R.J. Hamers, R.M. Tromp and J.E. Demuth
3.3 Ion/Neutral Enhanced Etching Reactions on Silicon

Ion-assisted processes have been extensively studied as they are widely applicable to improvement on plasma etching methods. Anisotropic etches that avoid undercut have been required in order to reduce the width-to-depth ratio of etch features. A number of other etch processes have also been developed that either use reactive ions or reactive gas adsorption to a surface with subsequent activation by an inert ion. This has resulted in the development of several novel etching methods which utilise either reactive ions (RIE and RIBE) or simultaneous bombardment of surfaces with reactive gaseous molecules and inert ion beams (CAIBE). Thus the precise effects of ion bombardment on the etch surface and near-etch regions is of critical importance. Silicon is also useful to study as a model system as it is a one component system. A comprehensive study of an elemental system may also be of use when analysing more complex etching systems such as halogen etching of III-V compounds.

3.3.1 Ion-Enhanced Gas-Surface Chemistry: Mechanisms

The reactions of fluorine and chlorine with silicon have attracted considerable attention because of their ability to form volatile halide compounds. The extent of enhancement by ions and photons in these reactions has also been addressed for the purpose of practical application to dry etching of silicon. Mechanisms have been proposed for ion enhanced etching reactions and some of these are surveyed in this section.

A number of researchers have studied chemically assisted etching (CAIBE) processes where an inert gas ion and a reactive gas molecule are exposed simultaneously to the surface of a semiconductor. This often enhances the ion beam etching to a level higher than the sum of the spontaneous etch rate or the inert ion etch rate. This is particularly true when halogens are used as the reactive species, although the etch rate may be
reduced if molecules such as oxygen are introduced.

Three models have been proposed to account for these observations. The first mechanism was suggested by Coburn et al [3.28] and Flamm and Donnelly [3.29] claiming that ion bombardment actually enhances the reaction between the halogen molecule and the surface. The second theory by Coburn et al [3.30] and Winters et al [3.31] suggest that thermal processes are activated by collisional cascade processes at the surface which provide the driving force for the reaction. Mauer et al [3.32] proposed that a sputtering based process on an altered surface region is responsible for enhanced etching.

Winters [3.33] proposed a thermal etching sequence consisting of;

(i) non-dissociative adsorption of a reactive gas phase species.
(ii) dissociative chemisorption of the adsorbate on the surface.
(iii) reaction between the adsorbate and the surface.
(iv) desorption of the reaction products into the gas phase.

The products of reaction are volatile and hence etching may be achieved. It is important to determine how ion bombardment may enhance the etch rate of silicon and what steps influence the rate of reaction.

There are a number of factors which may contribute to ion beam enhancement of dissociative chemisorption. Firstly, it is known that dissociative chemisorption may be enhanced at a defect site. Ion bombardment increases the density of defect sites on the surface thereby enhancing the adsorption process. Secondly, an ion beam may transfer some of its energy upon impinging with the surface to cause the intra-molecular bond of the reactive gas molecule to break thus forming the atomic species. Finally, the ion beam may also 'clear' the surface of adsorbed species and reacted volatile molecules. These species usually retard the process of further adsorption, thus enhanced adsorption is observed subsequent to their removal.
To achieve fast etch rates, it is necessary to involve more than the monolayer surface in the reaction. Diffusion of the reactive species to the sub-surface region is one route of achieving this goal. Thermal methods may be used but the effect is more efficiently produced by ion irradiation. An impinging ion, as discussed in section 1.4, may cause significant structural and electronic perturbation upon impact. These bond breaking and intermixing influences allow a greater volume at the surface for reaction product formation. A similar effect may also be produced by increasing the thickness of the adsorbate layer to greater than one monolayer. This may be achieved by producing a corrosion phase of intermixed Si and halogen atoms. There are limitations with this as the nature of adsorption changes from a chemical to a physical process. Therefore, monolayer formation is generally a rapid process, whereas further adsorption occurs as a physisorption process. The sticking coefficient of this process is generally much lower than the initial monolayer coverage.

The influence of ion beams on the desorption of the reaction product is important, with the most decisive influence being contributed by the enhancement of the backward sputtering yield of the weakly bound reaction products by the energetic beam. Electronic interactions with the surface may also cause desorption to occur causing profound electronic transitions to occur in the solid as is the case in the Knotek-Fiebelman model of electron stimulated desorption [3.34].

This discussion deals with ion/neutral enhanced etching of silicon with halogens and this places great emphasis on the chemical reactions induced by the beam, rather than the purely physical sputtering processes. Dieleman et al [3.35] estimated that an Ar+ ion of energy 1keV, upon a silicon surface, loses approximately 80% of it's energy by displacement of host atoms, whilst some 20% is transferred via vibrational and electronic processes. The displacements are proportional to the ion energy and occur at depths several times the calculated projected range of the impinging ion. Further intermixing is caused by ion enhanced diffusion of silicon interstitials into the bulk region, some several times deeper than the cascade damaged layer.
Further processes such as ion induced segregation from bulk to surface and vice versa also contribute greatly to the intermixing process. In addition, Ar$^+$ ions are implanted into the sub-surface region. A consequence of this process is that the amorphised region produced by ion bombardment also expands as a result of the high dose of argon incorporated into the sub-surface region. Dieleman et al [3.35] also suggested that in addition to the reduction of the surface binding energy, ion bombardment resulted in the formation of considerable numbers of molecules of SiCl and SiCl$_2$ originating from voids in the surface region. These molecules possess very low binding energies.

Tu et al [3.36] proposed a process known as "chemical sputtering" in which the incoming particle causes a chemical reaction which results in subsequent desorption of the reaction product. This process differs from physical sputtering because chemistry is being induced rather than the physical cascade phenomena found in ion milling methods. This contrasts strongly with the knowledge that introduction of molecular oxygen into a sputtering chamber considerably reduces the sputtering yield [3.37]. Oxides produced in this manner are relatively involatile whereas the silicon halides have favourable high vapour pressures. Coburn and Winters [3.1,3.38] studied the etch rate of Si bombarded by Ar$^+$ in the presence of XeF$_2$. They proposed competition of three mechanisms to account for enhancement or retardation of sputtering; ion activated adsorption, ion stimulated reaction and ion enhanced desorption. These processes may influence one another, and therefore complicate the etching parameters. Ion activated adsorption of a chemically active species is a necessary prerequisite for surface reaction. The ion stimulated reaction step may be produced by ion damage to the surface. These processes include bond breaking, intermixing and sputtering. They are all caused by "collisional cascade" processes that occur within $10^{-13}$ seconds of ion impact. The ion induced reactions that occur subsequent to the cascade event are diffusion, bond formation and desorption which occur within $10^{-12}$-$10^{-8}$ seconds and therefore at a faster rate than ion assisted adsorption may occur.
Gerlach-Meyer et al [3.39] measured the sputter yield of silicon atoms per impinging ion for bombardment of the surface with a range of inert ions. Significant enhancement of the sputtering yield was observed when the surface was simultaneously exposed to a flux of chlorine molecules. For normal bombardment using 1kV Ar+, Ne+ and He+ with an impinging flux of 3-6x10^{13} ions cm^{-2} s^{-1} the enhancement factors are 5, 4.3 and 13.6 respectively. The chlorine flux used was 6x10^{16} molecules cm^{-2} s^{-1} and therefore the chlorine surface was constantly saturated. It was suggested that ion assisted formation of SiCl₄ was caused by transfer of energy from the ion to the surface via phonon mechanisms. Competing processes such as physical sputtering of silicon chlorides and ion induced desorption of SiCl₄ were also proposed. They did not explain the high enhancement factor of He+ ions although the reduction of intermixing due to the lower impact momentum coupled with the reduction in surface binding energy of the silicon chloride species may explain maximum enhancement. The absolute sputter yields for He+ ions, however, are still lower than those of the large inert ions of neon and argon.

Kolfschoten et al [3.40] performed a study of the argon ion-assisted reaction of silicon with molecular chlorine using a modulated ion beam technique. The neutral products ejected from the surface were detected using a quadrupole mass spectrometer (QMS), and their kinetic energy distributions were measured using a time-of-flight (TOF) technique. A typical kinetic energy distribution plot for SiCl is shown in Figure 3.5 and clearly has contributions from a Maxwell-Boltzmann distribution (kT=0.025eV) which accounts for approximately 10% of the ejected particles. The majority contribution comes from a collisional cascade model distribution where the binding energy U₀=0.3eV and the dissociation energy is 4eV. It was found that SiCl and SiCl₂ particles were ejected and so the thermal evaporation of silicon tetrachloride as a complete description of the etch products was discarded. The proposed mechanism consists of a collisional cascade process in tandem with an evaporative contribution caused by a reduction of the surface binding energy during the sputtering event.
A comparison of studies on the Cl\textsubscript{2}/Si system, and Coburn and Winters [3.38] study on the XeF\textsubscript{2}/Si etching process show that silicon etches spontaneously in a fluorinated atmosphere whereas chlorine reacts only slowly. It is predicted that bromine reacts more slowly still and hence is a suitable precursor for ion-assisted etching reactions. The anisotropic etching of silicon should also be more controlled using a less reactive halogen.

At this stage it is necessary to evaluate the extent to which the impinging ions during the processing procedure damage the substrate material.
Figure 3.5 Kinetic Energy Distributions of SiCl₂ (m/e=98) species emitted from Si(Cl₂, Ar⁺) as obtained from the time-of-flight spectra.

Cl₂ flux  $3 \times 10^{16}$ mol cm⁻² s⁻¹
1keV Ar⁺ $2 \times 10^{14}$ ions cm⁻² s⁻¹

3.3.2 Ion Induced Damage on Silicon Surfaces

It is clear that any interpretation of our surface studies of the ion assisted etching of silicon with molecular bromine must be considered in the light of previous studies of the interaction of ions with the silicon surface. Reactive ion etching has been used for VLSI processing for several years and the impinging plasma (ions/neutrals/electrons) cause device problems such as gate oxide breakdown [3.41]. It would seem that laser processing of these features would compete favourably with ion beam processing. It has been shown, however, that ArF (193nm) excimer radiation causes neutral trap formation in thin gate oxide [3.42]. This occurs by Si-OH bond breaking by absorption in the low energy OH absorption band. The use of low energy neutral beams for etching processes is favoured due to less radiation damage as observed from capacitance-voltage (C-V) measurements of SiO₂/Si interfaces [3.43]. Furthermore, neutral beams were observed to be less damaging than vacuum ultraviolet photons.

It is clear that it is important to appreciate the extent of ion induced damage in Si and how this damage may be minimised in a real etching process. Understanding of this may lead to effective etch techniques where the ion beam may couple with the adsorbate-surface region such that the majority of energy provokes and enhances chemical reaction rather than the physical processes.

Bean et al [3.44], showed that damage increased upon exposure to 0.5 and 1keV argon beams at higher temperatures in the range 423-1073K. Furthermore, the high temperature damage was found to be more stable than that produced at 300K. This was attributed to the high doses irradiated on the surface (1x10¹⁹ cm⁻²). The formation of complex gas-defect complexes occurs at low dosages.

Two recent studies of damage caused by collisional cascade processes have
been those of Al-Bayati et al [3.45] and Konomi et al [3.46]. The first of these investigations used high resolution medium energy ion scattering (MEIS) to study the radiation damage and gas build-up effects caused by low energy (60-510eV) Ar+ ion bombardment of Si(001). They found that for an Ar dose of 5x10^{15} \text{cm}^{-2} the damage at 510eV decreased as a function of bombardment temperature over the range 300-673K. The amorphisation region produced at the surface was 45Å at 300K and 20Å at 673K. Figure 3.6 shows the accumulation and distribution of Ar in Si(001). It clearly shows that a considerable quantity of Ar is implanted at depths of between 10 and 40Å below the silicon surface. Konomi et al [3.46] determined an expression for the damage width from experimental data. For Si(001) exposure of 3x10^{15} \text{Ar}^+ \text{cm}^{-2} (1mA \text{ cm}^{-2}) at 0.5, 1, 2 and 3keV gave a damage width of 5.7E^{2/3} (where E is the argon ion energy expressed in keV). This relationship may be applied to our experiments to give amorphisation depths at 680eV, 1keV and 2.5keV of 44Å, 57Å and 105Å respectively.

Figure 3.7 shows data for damage width plotted as a function of Ar+ ion energy for observed and calculated data. It is noted that use of the LSS theory, described in Chapter 1, to predict the projected range of the Ar+ ions leads to a considerable underestimate. This is consistent with the expression of the amorphisation region due to high doses of Ar+ ions. This is clearly a factor to be considered when analysing TDS data in the subsequent sections. Vitkavage et al [3.47] have shown for high ion doses (2.3x10^{17} \text{ cm}^{-2}) for 1keV ions that the amorphisation depth is 65Å for argon, 80Å for neon and 275Å for hydrogen. Furthermore, using ion channeling techniques they detected crystalline damage to a depth of >475Å.

A model of increased damage with increasing ion dose has been proposed by Linros et al [3.48]. Defects generated at the crystalline-amorphous interface may either annihilate to form recrystallised material or accumulate at this interface. The latter process leads to amorphisation. The Si divacancy is postulated to be the defect that controls the equilibrium between the crystalline and amorphisation processes at the amorphous/crystalline
interface. These processes are dependent upon crystal temperature, ion
dose and bombarding species. As defects are more likely to form at the
vacuum interface rather than the end of the projected range there is a
migration process for defects into the silicon. Taoufik et al [3.49] measured the
ion doses necessary for saturation of both surface and bulk damage for 750eV
Ar\(^+\) bombardment. These were \(8 \times 10^{14}\) and \(3 \times 10^{15}\) cm\(^{-2}\) respectively.
Figure 3.6 Accumulation and Distribution of Ar in Si(001) as a function of dose for 510ev Ar ion bombardment


Figure 3.7 Damage Width of Ar+-irradiated Si(001) as a function of ion energy

observed damage width (0) is fitted by the relation \( \text{EXP}_{1/2} = 5.7 \times E^{2/3} \) (dashed line)

3.4 Results

3.4.1 LEED and AES Spectra of the Si(100) Surface

Using the surface preparation method described in the experimental methods chapter, a reproducible adsorbent surface was obtained. A typical Auger spectrum is shown in Figure 3.8 for a thermally cleaned Si(001) sample. This spectra is in good agreement with previously published spectra [3.50,3.51]. A number of features may be observed from this spectra. The most apparent is the intense peak at 92eV which has been attributed to an $L_{2,3}$VV Auger transition. Other observed peaks in this spectra occur at energies of 36, 44, 57, 74, 83 and 107eV. A complete analysis of the surface structure of thermally cleaned using AES and LEED methods has been performed by Jackman [3.52] and the likely assignments for the observed peaks is presented in Table 3.19.

As discussed previously, it has been shown that semiconductor surfaces do not generally follow their bulk structure but tend to reconstruct to positions of lowest energy. This is generally ascribed to the covalent nature of the bonding for these materials [3.53]. Previous studies on reconstructions of the Si(001) surface have been discussed in section 3.2.1. A typical LEED pattern for a thermally cleaned Si(001) surface is shown in Figure 3.9 and clearly shows the presence of a stable (2x1) reconstruction.

An essential prerequisite of any TDS study of a surface-gas study is the ability to obtain a consistent surface structure throughout the course of a set of experiments. Continuous AES/LEED analysis was, therefore, performed throughout the ensuing experiments to verify a stable Si(001)(2x1) reconstruction.
Figure 3.8 Auger Electron Spectrum of clean Si(100) surface

- Emission Current: 8.2 μA
- Filament Current: 2.6 A
- Beam Energy: 2.5 keV
- Beam Focus (A2): 1.3 keV
- Modulation Voltage: 10 V

Lock-in Amplifier:
- Signal sensitivity: 2.5 μV
- Time constant: 0.3 s
- Phase reference: -10°
- Mode: 2f
- Post filter: 1 s
- Scan rate: 5 mV s⁻¹
- Chart recorder: Y=1V/cm, X=10mV/cm
Table 3.1 AES Peak Assignments for Si(100)

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<th>Assignment</th>
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</tr>
<tr>
<td>44</td>
<td>$L_1L_{2,3}V$ (Coster-Kronig)</td>
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</tr>
<tr>
<td>57</td>
<td>2nd order bulk plasmon loss peak</td>
<td>5</td>
</tr>
<tr>
<td>74</td>
<td>1st order bulk plasmon loss peak</td>
<td>4</td>
</tr>
<tr>
<td>83</td>
<td>$L_{2,3}VV$/Surface plasmon loss peak</td>
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</tr>
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<td>92</td>
<td>$L_{2,3}VV$</td>
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<td>107</td>
<td>$L_{2,3}VV$ from an ionised Si atom</td>
<td>1</td>
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</table>

after R.B.Jackman [3.52]
Figure 3.9 LEED pattern observed for Si(001) clean surface
3.4.2 Thermal Desorption Studies of Adsorbed Bromine on Si(100) at 350K

A clean reconstructed Si(100) surface, as evaluated in the preceding section, was exposed to controlled quantities of gaseous molecular bromine dosed through a stainless steel tube via a UHV compatible leak valve. The enhancement factor was calculated by reference to solid state electrolytic silver bromide source. Thermal desorption spectra were recorded in the temperature range from 350-900K. The linear heating rate employed in these experiments was 40Ks\(^{-1}\). The detected products appeared at masses representing Br and SiBr\(_x\) (where \(x=1-3\)). A 300amu mass spectrometer was used for these experiments. The SiBr\(_4\) molecule could therefore not be measured directly on this apparatus.

The TD spectra for the Br\(^+\) mass fragment (79amu) is shown in Figure 3.10(a). Exposure of the Si(100)(2x1) surface to low doses of Br\(_2\) result in a high temperature desorption peak which appears at approximately 780K; this is labelled the \(\beta\) peak. Further bromine exposure leads to saturation of the \(\beta\) peak and the formation of a peak which appears at a lower temperature. This is labelled the \(\alpha\) peak and appears at approximately 480K. Application of the Redhead equation as described previously \[1.14\],

\[
E_i = RT_p \ln\left(\frac{V_{i \text{TP}}}{\beta}\right) - 3.46
\]

\[\text{[1.6]}\]

yields the desorption activation energies \((E_i)\) for the \(\alpha\) and \(\beta\) states resulting in values of 124 and 205 \text{kJ mol}^{-1} respectively. The peak area of the detected product in the mass spectrometer is directly proportional to the quantity of product desorbed from the surface. This signal may derive, however, from any number of parent molecules such as molecular bromine or a SiBr\(_x\) molecule. A plot of peak area of desorbed product versus the quantity of bromine exposed to the surface, known as an uptake curve, gives useful information about the surface region itself and also the nature of the desorbed species. A typical uptake curve for Br\(^+\) is presented in Figure 3.10(b) extracted from the TDS spectra in Figure 3.11(a). The principal feature of the uptake curve is the behaviour of the curve upon increased exposure to
the dosing gas. The curve for the β peak for the Br⁺ detected product reveals an initially fast uptake followed by drop in the rate of increase of peak area with increasing exposure exposure. This indicates a saturation of the desorption peak. The α peak rises steadily with increasing dosage, but does not saturate at high coverage.

A series of TD spectra are presented in Figure 3.11(a) for the desorption of the SiBr⁺ detected mass fragment (107amu). Similar features are noted in that at low exposures of bromine the only desorption peak is the β signal at 780K. At exposures above 100L the a peak appears. Increased exposure of the surface to bromine results in a strengthening of the α peak whilst the β peak saturates towards large doses. The uptake curve derived from the SiBr⁺ TD spectra is shown in Figure 3.11(b). It is clearly observed that the β state signal saturates at high bromine exposures whilst the a signal continues to increase without saturation occurring.

A similar series of desorption spectra are presented in Figure 3.12(a) for the SiBr₂⁺ detected mass fragments. The α and β states exhibit comparable behaviour to those described previously with the uptake curves in Figure 3.12(b) showing the β state saturating at high exposures whilst the α state intensity increases with bromine exposure. The final silicon halide fragment to be studied showed slightly different behaviour to the previously described mass fragments. The SiBr₃⁺ TD spectra are presented in Figure 3.13(a) and show that the α and β states appearing at similar bromine exposures. The uptake curves in Figure 3.12(b) clearly show the α and β peaks increasing with exposure without saturation. These features are fully examined in the discussion.

The detected product distribution of the surface phases are presented in Table 3.1 and are compared to previously published data for the mass spectrometer cracking patterns of SiBr₄ [3.73]. These are discussed in depth in section 3.5.
Figure 3.10 (a) Thermal Desorption Spectra of Br⁺ (79amu) following bromine adsorption on Si(001) plotted as a function of increasing exposure (in Langmuirs); (b) Uptake curve for the adsorption states derived from data in Figure 3.10(a).
Figure 3.11 (a) Thermal Desorption Spectra of SiBr⁺ (107amu) following bromine adsorption on Si(001) plotted as a function of increasing exposure (in Langmuirs); (b) Uptake curve for the adsorption states derived from data in Figure 3.11(a).
Figure 3.12 (a) Thermal Desorption Spectra of SiBr$_2^+$ (188amu) following bromine adsorption on Si(001) plotted as a function of increasing exposure (in Langmuirs); (b) Uptake curve for the adsorption states derived from data in Figure 3.12(a).
Figure 3.13 (a) Thermal Desorption Spectra of SiBr$_3^+$ (267amu) following bromine adsorption on Si(001) plotted as a function of increasing exposure (in Langmuirs); (b) Uptake curve for the adsorption states derived from data in Figure 3.13(a).
Table 3.2 Comparison of Cracking Patterns for the Thermal Desorption Study of Bromine on Si(001)

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<td>0</td>
<td>70</td>
</tr>
<tr>
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<td>0</td>
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</tr>
</tbody>
</table>
To assess the changes which ion bombardment induced in the chemisorbed states of the silicon-bromine system, a surface exposed to 5L (7.4 x 10^{18} molecules m^{-2}) of bromine was irradiated by a flux of Ar$^+$ ions (680eV, 5.8x 10^{13} Ar$^+$ cm^{-2} s^{-1}) for varying times, prior to analysis by thermal desorption methods.

A typical series of TD spectra are presented in Figure 3.14(a) showing the effect of ion bombardment on the SiBr detected mass signal. The uppermost curve represents the TD spectrum obtained if no ion irradiation is performed. The spectra below represent increasing Ar$^+$ ion exposures. There is no significant change to the shape or position of the detected peaks. The $\alpha$ state, however, rapidly diminishes in size upon ion irradiation but remains non-zero at all coverages which still display a $\beta$ state peak. The $\beta$ state peak, intriguingly, drops in intensity at a lesser rate than the $\alpha$ state. At prolonged irradiation times both the $\alpha$ and $\beta$ states are completely removed. It is also observed that at high irradiation times the $\alpha$ to $\beta$ peak ratio is one that cannot be formed by spontaneous adsorption of molecular bromine at low exposure ie. $\alpha$ state formation preceded by $\beta$ state. The peak areas of the states in Figure 3.14(a) represent the relative amount of material adsorbed in that state. The semi-logarithmic plot shown in Figure 3.14(b) for the peak area versus ion exposure portrays the behaviour of the adsorbed state upon ion exposure. The erosion curves are fitted with a linear curve which may allow calculation of a value for the desorption cross section. The $\alpha$ state reveals two distinct slopes whilst only one curve fits the $\beta$ state. This slope is then used to calculate the cross section for removal of the adsorbed phase from the surface. The calculation and use of cross sections for desorption towards evaluation of a mechanism for the ion-assisted etching of silicon is dealt with fully in the discussion section.

Figures 3.15(a) and 3.16(a) present results for the ion induced changes observed for the SiBr$_2^+$ and SiBr$_3^+$ detected signals. The TD spectra for SiBr
show that the $\alpha$ and $\beta$ states are eroded at similar cross sections of desorption. The $\alpha$ state does not show the initial rapid erosion process observed in the $a$-SiBr detected signal. Measurement of the SiBr$_3$ detected mass fragment in Figure 3.16 reveals that at high beam exposures of greater than $10^{16}$ Ar$^+$ ions cm$^{-2}$ there appears to be little perturbation of the adsorbate region with respect to the desorption product. The semi-log plots for the loss of the signal intensity for SiBr$_2$ and SiBr$_3$ are presented in Figures 3.15(b) and 3.16(b). The SiBr$_2$ data reveals a linear erosion of the signal from the $\alpha$ and $\beta$ state with increasing ion exposure, whereas the SiBr$_3$ signal shows little difference from the desorption peaks prior to ion irradiation.
3.4.4 The Br-Si(100) Surface - Bombardment with Ar Neutrals (1keV, 2.5keV)

This section presents results obtained upon irradiation of a bromine-silicon surface by energetic argon neutrals (Ar°) produced by an Ion Tech fast atom beam (FAB) source. This beam source was run under two regimes for this series of experiments. The source was operated at two beam energies, 1kV and 2.5kV. The discharge currents used at these two beam energies were 3mA and 28mA respectively, with the 'equivalent ion' flux obtained being $6.4 \times 10^{13}$ and $4.3 \times 10^{14}$ neutrals cm$^{-2}$ s$^{-1}$ respectively. Some comparative results for the source run at discharge currents of 28mA for beam energies of 1kV and 2.5kV are also presented.

The results of the thermal desorption experiments for the neutral beam induced changes at the surface are presented for each detected mass fragment. The mass fragments studied were Br$^+$ (79amu), SiBr$^+$ (107amu), SiBr$_2^+$ (188amu) and SiBr$_3^+$ (267amu).

3.4.4.1 Br Detected Mass Signal

Figure 3.17(a) shows a series of TD spectra obtained for the bombardment of a Si(100)-(2x1) surface exposed to 750L ($1.1 \times 10^{21}$ molecules m$^{-2}$) of molecular bromine. The uppermost curve in the series of TD spectra represents the desorbed products from the adsorbate covered Si surface prior to exposure of the surface to argon neutrals. The $\alpha$ and $\beta$ adsorption states previously described are clearly observed. The three intermediate TD spectra of the series were obtained after exposure to a 1kV Ar$^0$ beam with increasing ion dose. The bottom TD spectra represents desorption from a surface exposed to the 2.5kV beam for the same time period as the TD curve immediately above; although at significantly higher ion dose due to the FAB source operating conditions. It is immediately apparent that the position of the desorption peaks appear not to change significantly after exposure of the surface to the energetic beam. The most noticeable feature from the thermal desorption spectra, however, is the
immediate broadening of the $\alpha$ peak that occurs upon neutral beam bombardment. Desorption of the $\alpha$ state extends over a temperature range of 350-600K. Furthermore, the total peak area of the $\alpha$ state also increases. Prolonged exposure of the surface to the beam, however, does not result in complete erosion. This observation is discussed fully in section 3.5. The $\beta$ state is also resilient to complete erosion, even at doses as high as $5 \times 10^{17}$ Ar cm$^{-2}$. This is due to continue intermixing into the sub-surface region by the impinging neutral beam. A broad high temperature feature ($\beta^1$) is also observed in the tail of the $\beta$ state desorption peak and may be due to desorption from the sub-surface region. The logarithmic plots for the loss of the Br signal from the adsorbed phase are shown in Figure 3.17(b), and reveals an immediate gain in $\alpha$ state intensity upon neutral beam exposure. This rapid signal enhancement slows significantly after an exposure of $5 \times 10^{15}$ Ar$^0$ cm$^{-2}$. The $\beta$ state signal undergoes steady erosion and appears to decay exponentially upon exposure of the 1kV argon fast atom beam.

A note of caution about these experiments is necessary. The mass spectrometer detected a gas phase Br signal prior to the TD experiment, thus it is necessary to allow the background to equilibrate prior to performing the TD experiment. This signal originates from beam bombardment of the surface, and it is possible that some readsorption to the surface occurs. This is unlikely, however, due to the partial pressures involved being less than $10^{-11}$ torr such that readsorption over the equilibration time would be minimal.
3.4.4.2 SiBr Detected Mass Signal

The TD spectra obtained for the SiBr detected signal upon bombardment of the chemisorbed states by argon neutrals at beam energies of 1kV and 2.5kV are now considered. The main features of the TD spectra are those that have been described previously for the Br mass signals. The series of thermal desorption spectra for the loss of SiBr upon irradiation by the 1kV beam (6.4 x 10^{13} neutrals cm^{-2} s^{-1}) is shown in Figure 3.18(a). The uppermost curve shows the desorption of SiBr signal from the surface prior to bombardment. Subsequent curves show increasing neutral beam irradiation of the surface. The main features of this series of curves is that the α state erodes rapidly at initial beam exposure. In addition, the β state increases slightly in intensity upon immediate neutral beam perturbation. This immediate neutral dose is approximately 2 x 10^{14} Ar^0 cm^{-2}. The β state then erodes rapidly for a similar period to the α state. Prolonged exposure of the surface to the neutral beam results in both states being eroded at similar rates, until complete loss of the adsorbed phase occurs. It is again noticed that the α to β peak ratio is one that cannot be formed by spontaneous adsorption at low bromine exposures. The α state also broadens slightly upon neutral beam exposure although not to the extent observed for the Br α state. Furthermore, prolonged exposure of the surface to the neutral beam results in a broad peak at desorption temperatures greater than the β peak. This is believed to result from desorption from the sub-surface region. The effect of impact of energetic argon neutrals will be to recoil implant bromine atoms some distance into the subsurface. These atoms will react with silicon in this region. The implications of this process are attended to in the discussion of these results. The semi-log plot of the peak area versus neutral beam dose is shown in Figure 3.18(b). This plot appears to be complex with three cross sections for loss/gain of the reaction product. Both α and β phases clearly have two cross sections for loss of the SiBr detected signal. In addition to this there appears to be a cross section for uptake/ or increase of the signal. This appears upon initial bombardment of approximately 2 x 10^{14} Ar^0 cm^{-2} for the β state, whilst the α state signal increases between 5 x 10^{14} and 5 x 10^{15} Ar^0 cm^{-2} exposure. These cross sections are discussed more fully in section 3.5.
Chapter 3: Results

The 750L exposed Br/Si(100) surface was also exposed to a 2.5kV (4.3 x 10^{14} \text{ Ar}^0 \text{ cm}^{-2} \text{ s}^{-1}) beam of argon neutrals and the TD spectra for the SiBr^+ signal recorded. The series of TD spectra are shown in Figure 3.19(a). The spectra show a rapid loss of the detected signal and both peaks appear to broaden. A significant background peak appears at high temperatures and this merges with the \beta desorption peak at high neutral doses. This is due to the still greater recoil implantation of bromine into the sub-surface region. The semi-log plot of peak area versus neutral beam exposure is presented in Figure 3.19(b) and shows the loss of adsorbed phase for SiBr to have two cross sections. The first is a rapid loss of signal followed by a slower process upon increased beam exposure. No increase in detected signal was measured and this may be due to the experimental problem of operating the beam source in this exposure regime. The FAB source would need to sustain a discharge of less than one second to obtain data in this regime. Manipulation of the sample at exposures this low is not possible, and even neutral exposures under ten seconds are susceptible to increased error.

A further series of experiments was performed on the neutral bombardment of a surface previously dosed with molecular bromine such that the surface only possessed a \beta state. The TD spectra for the erosion of the SiBr detected signal by 1kV and 2.5kV beams are presented in Figure 3.20(a) and show a loss of intensity as the beam energy increases. The erosion curve for the loss of signal versus neutral exposure is shown in Figure 3.20(b). The calculated cross section for loss is for the 1kV beam than the 2.5kV dose although the ion dose in the latter case is approximately five times greater.
Chapter 3: Results

### 3.4.4.3 SiBr$_2^+$ Detected Mass Signal

The changes induced by bombardment of energetic argon neutrals on a 750L bromine dosed surface was studied for the SiBr$_2^+$ detected mass fragment. The TD spectra of the 1keV bombarded surface are shown in Figure 3.21(a). The uppermost curve shows the TD spectrum prior to neutral beam bombardment. The $\alpha$ and $\beta$ states are shown, with profound changes occurring upon initial argon neutral beam irradiation. The $\alpha$ state erodes steadily upon exposure, whereas the $\beta$ state is is actually enhanced considerably. The semi-log plot for these TD spectra are presented in Figure 3.21(b) showing the nature of the changes to the adsorbed phase. The region of $\beta$ state signal enhancement again occurs at less than $5 \times 10^{14}$ Ar$^0$ cm$^{-2}$ exposure in a similar manner to the changes observed for the SiBr$^+$ mass fragment. Increasing the sensitivity of the measurement at high neutral beam doses showed that prolonged bombardment does not completely remove either phase upon prolonged beam exposure. The bombardment of a similar surface to the above by 2.5kV argon neutrals is shown in Figure 3.22(a) and reveals erosion of the adsorbed states to complete loss at high neutral doses. It is again noticed that $\beta$ state enhancement cannot be observed for this series of experiments as previously discussed for the $\beta$-SiBr$^+$ detected signal. The control of the neutral beam source at these fluxes present considerable problems. The erosion curves are presented in Figure 3.22(b) and reveals two distinct cross sections for loss of the adsorbed phases from the surface. The cross section data is discussed more fully in section 3.5.

A comparative study of the effect of beam energy on the SiBr$_2^+$ detected mass signal was made by bombardment of the surface with 1kV and 2.5kV beams generated with the same 'equivalent ion' flux ($4.3 \times 10^{14}$ Ar$^0$ cm$^{-2}$ s$^{-1}$). Figure 3.23 shows the erosion of the 750L bromine dosed silicon surface by the 1keV beam, revealing almost complete loss of the adsorbed layer upon prolonged exposure to the neutral beam. Figure 3.24 shows a similar curve for bombardment of the surface with 2.5keV neutrals. The background signal induced by the impinging beam at high neutral energy is slightly greater than is the case for the low energy irradiation.
3.4.3.4 SiBr$_3$ Detected Mass Signal

The effect of a 1kV argon neutral beam on the detected SiBr$_3$ signal obtained from a Si surface exposed to 750L of molecular bromine is shown in Figure 3.25. The top TD spectrum shows the surface prior to neutral beam irradiation. Onset of beam exposure produces rapid erosion of the $\alpha$ state. It is not clear from these spectra whether the $\alpha$ or $\beta$ states are lost sequentially or simultaneously. The former case would be consistent with previous observations. The $\beta$ state peak is, however, lost upon prolonged exposure but is eroded slowly. The erosion curve for loss of this signal is presented in Figure 3.26.

It is clear that some interesting effects are produced by irradiation of the Br$_2$/Si(100) surface. The nature of these processes are examined in detail within the discussion section.
Figure 3.14(a) Thermal Desorption Spectra for SiBr$^+$ (107amu) desorption following exposure to $7.5 \times 10^{18}$ molecules m$^{-2}$ for Br$_2$ plotted as a function of ion beam irradiation for 680eV Ar$^+$ ions ($5.8 \times 10^{13}$ Ar$^+$ cm$^{-2}$ s$^{-1}$)
Figure 3.14(b) Semi-logarithmic plot of SiBr+ (107amu) peak intensities plotted as a function of argon ion dose for Si(001) dosed with 5L of bromine
Figure 3.15(a) Thermal Desorption Spectra for SiBr$_2^{+}$ (188amu) desorption following exposure to $7.5 \times 10^{18}$ molecules m$^{-2}$ for Br$_2$ plotted as a function of ion beam irradiation for 680eV Ar$^+$ ions ($5.8 \times 10^{13}$ Ar$^+$ cm$^{-2}$ s$^{-1}$)
Figure 3.15(b) Semi-logarithmic Plot of SiBr2+ (188amu) peak intensities plotted as a function of argon ion dose for Si(001) dosed with 5L of bromine
Figure 3.16(a) Thermal Desorption Spectra of $^{7}\text{SiBr}_3^+$ (267amu) following exposure to 5L of bromine plotted as a function of argon ion dose (680eV)
Figure 3.17(a) Thermal desorption Spectra for Br⁺ (79amu) desorption following exposure to 750L of Br₂ plotted as a function of irradiation of 1keV Ar⁰ neutrals (6.4 x 10¹³ cm⁻² s⁻¹) (b) semi-logarithmic plot of peak intensities as function of neutral dose from data in (a)
Figure 3.18(a) Thermal desorption Spectra for SiBr$^+$ (107amu) desorption following exposure to 750L of Br$_2$ plotted as a function of irradiation of 1keV Ar$^0$ neutrals ($6.4 \times 10^{13}$ cm$^{-2}$ s$^{-1}$) (b) semi-logarithmic plot of peak intensities as function of neutral dose from data in (a)
Figure 3.20(a) Thermal Desorption Spectra for SiB$_5^+$ (107 amu) desorption following exposure to 0.5 Langmuirs of Br$_2$ plotted as a function of irradiation of 1 keV and 2.5 keV Ar$^0$ neutrals at differing Discharge Currents

(28 mA = $4.32 \times 10^{14}$ Ar$^0$ cm$^{-2}$ s$^{-1}$)

(3 mA = $6.4 \times 10^{13}$ Ar$^0$ cm$^{-2}$ s$^{-1}$)

Figure 3.19(a) Thermal Desorption Spectra for SiBr$^+$ (107 amu) desorption following exposure to 750 Langmuirs of Br$_2$ plotted as a function of irradiation of 2.5 keV Ar$^0$ neutrals

($4.32 \times 10^{14}$ Ar$^0$ cm$^{-2}$ s$^{-1}$)
Figure 3.19(b) Semi-logarithmic plot of SiBr+ (107amu) peak intensities as a function of 2.5keV argon neutral dose for Si(001) dosed with 750L of bromine.
Figure 3.20(b) Semi-logarithmic plot of SiBr⁺ (107amu) peak intensities as a function of argon neutral dose at 1keV and 2.5keV energies for a low coverage (0.5L) bromine/Si(001) surface.
Figure 3.21(a) Thermal desorption spectra for 
SIBr$_2^+$ (188amu) desorption following exposure to 
750L of Br$_2$ plotted as a function of irradiation of 
1keV Ar$_2$ neutrals (6.4 x 10$^{13}$ cm$^{-2}$ s$^{-1}$). (b) semi-
logarithmic plot of peak intensities as function of 
neutral dose from data in (a).
Figure 3.22(a) Thermal desorption Spectra for SiBr$_2^+$ (188 amu) desorption following exposure to 750L of Br$_2$ plotted as a function of irradiation of 2.5keV Ar$^0$ neutrals (4.32 x 10$^{14}$ cm$^{-2}$ s$^{-1}$) (b) semi-logarithmic plot of peak intensities as function of neutral dose from data in (a)
Figure 3.23 Thermal Desorption Spectra for SiBr$_2^+$ (188amu) desorption following exposure to 750 Langmuirs of Br$_2$ plotted as a function of irradiation of 1 keV Ar$^0$ neutrals using a discharge current of 28mA
\[ 4.32 \times 10^{14} \text{ Ar}^0 \text{ cm}^{-2} \text{s}^{-1} \]

Figure 3.24 Thermal Desorption Spectra for SiBr$_2^+$ (188amu) desorption following exposure to 750 Langmuirs of Br$_2$ plotted as a function of irradiation of 2.5 keV Ar$^0$ neutrals using a discharge current of 28mA
\[ 4.32 \times 10^{14} \text{ Ar}^0 \text{ cm}^{-2} \text{s}^{-1} \]
Figure 3.25  Thermal Desorption Spectra for SiBr$_3^+$ (267amu) desorption following exposure to 750 Langmuirs of Br$_2$ plotted as a function of irradiation of 1 keV Ar$^0$ neutrals
($6.4 \times 10^{13}$ Ar$^0$ cm$^{-2}$ s$^{-1}$)
Figure 3.26 Semi-logarithmic plot of peak intensities for SiBr$_3^+$ (267amu) derived from Figure 3.25 as a function of argon neutral irradiation
3.5 Analysis and Discussion

This discussion considers the Si(100)/Br$_2$/Ar$^+$(Ar$^0$) system from several viewpoints. Firstly, the fundamental aspects of semiconductor surface etching by halogens is assessed whilst secondly the ion/neutral beam assisted etching of silicon is discussed with particular emphasis on the role of the adsorbed state in the etching process.

3.5.1 Adsorption of Br$_2$ on Si(100)

A schematic of possible processes that may occur upon bromine impinging on a silicon surface is shown in Figure 3.27(a). The initial decision upon a bromine molecule is whether it sticks to the surface or scatters back into the gas phase. If a halogen molecule impinges upon a clean silicon surface it encounters a reconstructed surface that presents 'dangling bonds'. Some early surface studies by Florio and Robertson considered the adsorption of molecular chlorine on Si(111) and calculated the initial sticking coefficient to be approximately 0.15 at 300K with the value decreasing by two orders of magnitude upon saturation of the surface as shown in Figure 3.28 [3.17]. The sticking coefficient also decreases with increasing sample temperature. They also reported a reduction in the LEED intensities to a diffuse background which implies a disordered chlorine overlayer. Madix and Schwarz [3.55] using modulated molecular beam studies at Cl beam pressures of between $10^{-5}$-$10^{-6}$ torr that the only observed product was SiCl$_2$ at 770-1500K. This followed in close agreement on the formation of $\beta$SiCl$_2$ surface species on surface defects as proposed by Florio and Robertson [3.17]. Data obtained for Br$_2$/Si(100) shows an analogy in that the $\beta$ state SiBr$_2$ is a preferred surface phase at submonolayer coverage, but some SiBr$_3$ species may remain after thermal removal of the corrosion layer. The adsorption processes of Br$_2$ on Si(100) may be better visualised by use of a one-dimensional potential energy diagram as depicted in Figure 3.27(b). This shows the gaseous bromine molecule as Br$_2$(g) with the dissociative state 2Br$_{ads}$ which represents the adatoms at the surface. In addition, there may be two further
potential wells which are described as precursor states. The first of these, \( \text{Br}_2^{\text{(ads)}} \), can be described as the intrinsic precursor state, whilst the other, \( \text{Br}_2^{\text{(ads)}} \), is designated the extrinsic precursor state. The bromine molecule lies over an empty adsorption site in the former case whilst the extrinsic precursor describes \( \text{Br}_2 \) lying over a filled adsorption site. Application of this model to the adsorption kinetics of \( \text{F}_2 \) on Si(100) has been considered by Engstrom et al [3.55]. They also observe that the initial probability of adsorption is independent of both the substrate temperature (between 120-600K) and also the incident translational energy of the fluorine molecule (at \( E_t \) between 1.5 and 19 kcal mol\(^{-1}\)).

Once the halogen molecule has adsorbed on the Si(001) surface, the nature of the bonding must be considered. Chemisorption of the halogen on the silicon surface usually results in the dissociation of the molecular bond at the surface. If the TDS results presented in section 3.4.2 are now considered the nature of the adsorption process may be evaluated for the Si(100)/Br\(_2\) system. Furthermore, considerable insight into the thermal etching process may be obtained. This information is essential if a complete understanding of the ion-assisted processes is to be acquired.

The silicon halide desorption products formed at the surface may compete such that a combination of SiBr\(_x\) species of varying stoichiometry may desorb into the gas phase. A mechanism by which these processes occur may be proposed by analysis of the TDS spectra for the Si/Br\(_2\) system.

There are two distinct desorption states for the reaction products of molecular bromine on Si(100) as can be clearly observed from the TDS spectra presented in Figures 3.10-13(a). These have been identified as the \( \alpha \) and \( \beta \) states, the \( \alpha \) state is a low temperature/high coverage phase whilst the \( \beta \) peak is a high temperature/low coverage state. Observation of the adsorption system shows initial population of the \( \beta \) state at low bromine coverage. The \( \beta \) phase populates rapidly, but saturates at relatively low exposures of molecular bromine. Formation of the \( \alpha \) state occurs after the \( \beta \) state, but continues to populate without saturation. The \( \beta \) state is attributed to the presence of a
Chapter 3: Analysis and Discussion

strongly bound chemisorbed overlayer, whilst the α state is believed to represent a more weakly bound silicon halide corrosion phase. Similar descriptions have previously been applied to adsorption systems of halogens upon metals [3.57-61]. A particular example is the interaction of halogens (Cl₂ and Br₂) with vanadium and chromium (100) surfaces [3.57,3.58]. The stoichiometry and growth rate of the corrosion phase are strongly dependent upon the rate of interdiffusion through the growing layer and the residence lifetime of the weakly bound X₂ precursor via which the corrosion process occurs. At high exposures of halogen, corrosion of the metal substrate occurs resulting in the formation of metal dihalides by an island growth (Volmer-Weber) mechanism. The Pd(111)-Cl₂ system [3.59], however, exhibits two halide growth regimes. Initial growth of the corrosion phase obeys Mott-Cabrera kinetics [3.62]. This mechanism proceeds via ion transport normal to the surface and is assisted by the electric field arising from the potential difference between the corrosion layer and the metal substrate. This growth may be rapid for initial growth of thin films due to the large field presence. The growth of the corrosion phase by Mott-Cabrera kinetics follows the equation

\[ \frac{1}{X} = -A \ln E + B \]  \hspace{1cm} [3.2]

where

\( X = \text{film/layer thickness} \)
\( E = \text{exposure of halogen} \)
\( -A,B = \text{constants} \)

A plot of 1/X versus lnE may be used to test for this growth behaviour. If this model is applied to the Br₂-Si(100) system for formation of the α state, or corrosion phase. The peak area of the α state may be substituted for X, the layer thickness. This results in a plot of 1/peak area versus lnE. These Mott-Cabrera curves for the α states of the Br⁺ and SiBr⁺ detected signals are plotted in Figures 3.29(a) and (b) respectively. At the initial appearance of the α state, the data does not conform to the model, but as the corrosion phase is established the curve exhibits linearity. The growth of the α phase therefore
appears to show agreement with the Mott-Cabrera theory after the initial dissociative chemisorption process has occurred. Studies of Cl\textsubscript{2} exposure to Ag(111) show that chlorine may penetrate to 20nm below the surface [3.60]. This penetration of halogen into the sub-surface region is even more pronounced in copper. Molecular chlorine may diffuse 1mm into the bulk structure [3.61]; the diffusion depth was also found to increase non-linearly as a function of increasing pressure. The corrosion phase growth is therefore comparable to a conventional silicon oxidation processes, except that in the case of the bromine-silicon system the reaction products have high vapour pressures and low surface binding energies compared to oxides. An important question to resolve is the degree of diffusion of bromine into a silicon (100) crystal. It is apparent that by following Mott-Cabrera oxidation theory the potential difference between the corrosion phase and a semiconductor will be less than the corresponding corrosion phase-metal field. In general, the growth rate of the halide phase on silicon will, therefore, be less than the corrosion layer growth on a metal surface. Quantitative evaluation of this corrosion layer have not been reported in the literature. Estimation of this depth may be performed.

A knowledge of the depth of the corrosion surface is necessary to accurately discuss ion-assisted processes on the adsorbed layer. The implantation depth of impinging ions on a silicon surface have previously been discussed. The presence of an adsorbate layer will influence this depth and also may protect the sub-surface region from the damaging implications of impacting ions. Sesselman et al [3.63] have studied the reaction of Cl\textsubscript{2} with Si(100) for exposures of between 10 and 1000s for pressures of 0.7 to 66 mbar. they have shown that the chlorine is confined to the first atomic layer of silicon using angle-resolved XPS. This reacted layer is described as SiCl\textsubscript{x} with an average stoichiometry x less than unity. Jackman et al [3.64] used AES to determine a Si(100)/Br region of approximately 3 layers. This was calculated on the basis of an escape depth for Br(55eV) Auger electrons of 6Å [3.65] and a Br atomic radius of 1.95Å [3.66]. Sesselman et al [3.60] also found that the SiCl\textsubscript{x} acted as a passivating layer which allows negligible sub-surface penetration of molecular chlorine. This is because dissociation of Cl\textsubscript{2} on the SiCl monolayer
is a slower process than initial uptake. When atomic chlorine is formed a high degree of surface chlorination is achieved. This model does not account for diffusion of molecular chlorine through the surface layer in an analogous way to the oxidation of silicon as verified by the corrosion phase formation observed in the TDS spectra. Estimations of the thickness of the adsorbed layer for Br\textsubscript{2} on Si(100) for exposures of 750L (1.1×10\textsuperscript{21} molecules m\textsuperscript{-2}) at a sticking coefficient of approximately 0.01 produced an adsorbed layer thickness of 15Å prior to ion/neutral beam exposure [3.69]. Jackman et al [3.64] also revealed that for Si(100)/Br\textsubscript{2}, exposure of the halogen at low temperatures (100K) revealed a new surface state at approximately 200K. This was named the γ peak and was detected exclusively for Br\textsuperscript{+} and Br\textsubscript{2}\textsuperscript{+}, therefore implying that simple growth of a physisorbed condensed phase occurs at low temperatures. The desorption energy obtained for this peak is close to the sublimation energy for Br\textsubscript{2} (31 kJ mol\textsuperscript{-1}). A similar condensed phase was also detected for adsorption of I\textsubscript{2} at low temperatures. In order to assess ion beam assisted etching processes for the silicon/bromine system, it is necessary to understand the mechanism for thermal etching of Si(100) with halogens. The preceding discussion has described the nature of the adsorbate-surface region following adsorption of molecular bromine at 350K. The thermal etching processes from this region may now be considered. This may be achieved by analysis of the thermal desorption data presented in section 3.4.2. Previous studies by Jackman et al [3.24,3.64] have shown that the nature of the desorbing Si species perceptibly changes using differing halogens. The thermal desorption products observed from states formed by halogen adsorption on Si(100) are shown in Table 3.2. It is clear that the degree of halogenation of the reaction product decreases with increasing halogen adatom size. The steric effects of bromine at the silicon surface caused by the larger atomic radius of bromine compared to chlorine [3.68] should inhibit the formation of volatile silicon bromides at low temperature. It is noticed in these studies that a β state SiBr\textsubscript{3}\textsuperscript{+} detected mass signal was observed at high exposures of molecular bromine on the silicon surface. This contradicts results obtained by Jackman et al [3.64] which detect only α state SiBr\textsubscript{3}. A likely explanation for this observation is that high exposures in this
study were obtained by dosing at $5 \times 10^{-7}$ torr. Thus the increased exposure at relatively high pressure may assist formation of a small percentage of the SiBr$_3$ bonded at the SiBr$_x$/Si interface. Jackman et al [3.64] also noticed that spontaneous etching of the surface occurs at room temperature. A relaxation process involving emission of neutral species as a possible de-excitation mechanism was proposed on the basis that similar processes involving emission of photons, ions and electrons have been detected upon halogenation of some metal surfaces, such as yttrium, titanium and zirconium [3.68]. The precise mechanism for spontaneous etching has not yet been elucidated. Early studies by Sullivan and Kolb [3.69] demonstrated that molecular bromine did not etch silicon at temperatures less than 400°C. These observations were also verified by Sveshnikova et al [3.70]. Further investigation by the same researchers [3.71] of Br$_2$ etching of Si(001) at temperatures between 490 and 550°C found that the etch rate reached a limit at 5-15torr pressure. The conclusion reached is that the reversible adsorption of the molecule on the surface saturates at these pressures. More recent studies by Walker and Ogryzlo [3.72] suggest that bromine atoms may form in the gas phase at high gas pressures and contribute to the level of adsorbed bromine at the surface. Their results, however, do not take into consideration the complex nature of the surface region and do not specify likely product distributions. The formation of atomic bromine is likely to increase etch rates at low substrate temperatures. Beterov et al [3.73] demonstrated this by dissociation of molecular bromine in the gas phase using a high power argon ion laser (30Wcm$^{-2}$).

The thermal etching process is shown as a schematic in Figure 3.30 and reveals the two stage nature of the phenomenon. The low coverage case exhibits rapid adsorption followed by slow desorption whereas the high coverage regime shows slow adsorption followed by rapid low temperature desorption. Clearly, enhanced etching by energetic beams may occur if a regime of rapid adsorption followed by rapid low temperature desorption is induced. This problem is considered in the next section.
Figure 3.27(a)
Processes that may occur upon adsorption of molecular Bromine on a Si(100)(2x1) Surface
Figure 3.27(b) Potential Energy Diagram showing the Dissociative Chemisorption Process of Bromine on Si(100)
Figure 3.28  Sticking Probability as a function of chlorine surface concentration for various substrate temperatures

Figure 3.29(a) Mott-Cabrera Plot of Br alpha state with increasing exposure to bromine
Figure 3.29(b) Mott-Cabrera Plot of SiBr alpha states with increasing exposure to bromine
Figure 3.30 Schematic showing the thermal etching behaviour of the bromine/Si(001) system
Table 3.3 Thermal Desorption Products observed from the $\alpha$ and $\beta$ states formed by Halogen desorption on Si(100)

<table>
<thead>
<tr>
<th>Chlorine [3.63]</th>
<th>Bromine</th>
<th>Iodine [3.63]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>$\beta$</td>
<td>$\alpha$</td>
</tr>
<tr>
<td>Cl</td>
<td>Cl</td>
<td>Br$_2$</td>
</tr>
<tr>
<td>SiCl$_x$</td>
<td>SiCl$_x$</td>
<td>Br</td>
</tr>
<tr>
<td>x=1-4</td>
<td>x=1-4</td>
<td>x=1-&gt;3</td>
</tr>
<tr>
<td>SiBr$_x$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>x=1-&gt;3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$x = l \to 4$
3.5.2 Ion/Neutral Beam Assisted Etching of Silicon with Halogens

It is of great interest to use the results obtained in section 3.4 and apply them to real etching processes. In order to achieve this the conditions under which these experiments take place must be directly related to commercial applications. The use of surface science techniques to study these processes invariably leads to what is generally known as a 'pressure gap'. This is most commonly encountered in surface studies of catalytic processes, where real catalysis occurs at super-atmospheric pressures. The pressure gap between our thermal desorption studies and dry etching methods is approximately 4-7 orders of magnitude. Coburn [3.74] has viewed etching processes using another qualitative approach. This is shown schematically in Figure 3.31 where the ratio of the reactive neutral flux to the ion 'Flux x energy' product is plotted. Thus at zero halogen presence, processes such as sputter etching and ion milling are grouped together. RIBE and CAIBE processes are perceived to be sub-monolayer coverages whilst the RIE method may cover a range of halogen coverages from sub-monolayer to multilayer coverages. Thus the amount of undercut for a particular etch feature may be controlled. Finally, plasma etching is described as a multilayer coverage technique which inevitably precludes anisotropic control. The TDS experiments described previously may be placed in this multilayer region. The real etching application is more applicable to CAIBE processes and thus a more rigorous qualification of this scheme is required.

The first parameters to be discussed are the ion beam induced cross sections for desorption. From this data we may be able to describe the chemical changes induced by the ion/neutral beams. The description of Coburn does not consider the chemical versus physical process balance between the various dry etching processes.

3.5.2.1 Ion beam Induced cross sections - Ar+ ions

Clearly if simple erosion of, already present, surface phases was occurring, a straightforward drop in the $\alpha$ state intensity, followed by loss of $\beta$ state
intensity would be expected. That this is not the case indicates additional processes are being induced by the incoming beam. The data presented in Figures 3.14-3.16 show that whilst the ion beam leads to eventual removal of all bound forms on the surface under prolonged exposure (and hence etching), shorter exposures to the beam give rise to a change in the nature of the chemisorbed phases present. This effect is witnessed by the shift in the distribution of thermally desorbed products detected. An example of this are the relative intensities of the thermal desorption products for the $\alpha$ and $\beta$ states of the SiBr and SiBr$_2$ mass fragments which are presented in Table 3.4. The ratio of these fragments expected from the cracking pattern of SiBr$_4$ is also included [3.54]. The ratio of SiBr$^+$ to SiBr$_2^+$ $\alpha$ state increases dramatically upon Ar$^+$ irradiation of the surface. The $\beta$ state ratios also follow this trend although prolonged irradiation of the surface later reduces the $\alpha$ state ratios.

In addition the rate of apparent loss of the detected species differs with the fragment studied. Since the surface concentration ($X$) of the detected phases can be expressed as

$$X = X_0 \exp (-\sigma n t) \quad [3.3]$$

where $n$ is the ion flux leading to the removal of material and $s$ is the cross section for desorption (or loss) of the phase. The logarithmic plots of peak area versus ion dose shown in Figures 3.14(b)-3.16(b) show the cross sections for these loss processes. The numerical values are displayed in Table 3.5.

The initial loss of SiBr ($\alpha$) intensity through ion bombardment is fast as indicated by $\sigma_1$; $\sigma_2$, however, shows the same value as $\sigma_5$ (SiBr$_2$ $\beta$ loss) indicating the process involved at this point may have a similar origin. the apparent cross section for SiBr$_2$ loss from the $\alpha$ state ($\sigma_4$) is higher; thus the effective loss of intensity here has an additional component. The cross section for the loss of SiBr intensity from the $\beta$ state ($\sigma_3$) is comparable to this value. All values other than $\sigma_1$ are lower than those found by Knabbe et al [3.75] during SIMS studies of the removal of fluorine from a silicon surface by
1KeV argon ions at very high fluorine coverages (100Å²) and value that may be anticipated for purely physical sputtering (10Å²).

### 3.5.2.1.1 α State Induced Changes

The rapid process indicated by σ₁ (SiBr) is not mirrored by the SiBr₂ response for this state. Whilst this could be due to preferential loss of SiBr from the adsorbed layer, the SiBr signal shows little decrease over this period, prior to establishing σ₄. This suggests the reaction:

\[
\text{SiBr} \rightarrow \text{SiBr}_2
\]

is being driven by the beam. The SiBr signal then decreases at a steady rate coincident with the SiBr₂ β state processes and must therefore be no longer present as a species (being detected only as a fragment of higher parent halides). α state SiBr could be formed by conversion of β phase species, but the results indicate that this would be slow compared to this ion beam chemical conversion (σ₁). The SiBr₂ signal, initially enhanced by the reaction above, is then seen to decline, indicating the further reaction:

\[
\text{SiBr}_2 \rightarrow \text{SiBr}_x \quad (x>2)
\]

The size of σ₄ (SiBr₂ loss) presumably reflects its role in this reaction sequence. Comparison of the data presented in Table 3.4(a) with the limited cracking pattern data available suggests that even when remaining surface concentrations are low the SiBr₂ signal remains significantly higher than expected for pure SiBr₄ desorption. It therefore seems likely that the ion beam does not lead to total conversion but gives rise to the formation of SiBr₂, SiBr₃ and SiBr₄. The coincidence of (σ₂+σ₃) with (σ₄+σ₅), along with the persistence of the SiBr signal to high ion beam exposures clearly indicates β to α conversion is occurring, and that it is only the desorption of α state species which leads to etching. Thus, ultimately β to α conversion plays a rate determining role in the removal of all surface phases.
A plot of SiBr/SiBr$_2$ ratios for the $\alpha$ and $\beta$ states as a function of ion dose is presented in Figure 3.32. This represents the data in Table 3.4 and clearly shows for the $\alpha$ state a rapid increase in the amount of SiBr$_2$ in the system at initial ion exposure. Prolonged exposure of argon ions returns the signal to close to the original values. At this stage, however, the majority of the phase has sputtered from the surface.

3.5.2.1.2 $\beta$ State Induced Changes

As discussed above $\beta$ to $\alpha$ state conversion occurs upon irradiation by the ion beam. However, most intriguingly, the stoichiometry of the thermally desorbed products from the $\beta$ state following increasing ion beam irradiation is also seen to change as revealed in Table 3.4(b). As opposed to the case of the $\alpha$ state, the SiBr$_2$ to SiBr signal ratio is seen to rise steadily with increasing beam irradiation. This is demonstrated in Figure 3.32 where the SiBr/SiBr$_2$ ratio upon prolonged exposure becomes close to unity.

The cross section for SiBr$_2$ removal ($\sigma_3$) from this state is also lower than for the $\alpha$ phase. These observations suggest that prolonged exposures do not lead to further reaction to yield silicon halides with higher coordination. Since the favoured desorption products from this state, without ion beam irradiation, are thought to be SiBr$_2$, SiBr and Br, the reaction being induced here is:

\[
\text{Br$_{ads}$} \rightarrow \text{SiBr$_2$}
\]

The fact that this chemical change occurs simultaneously to the $\beta$ to $\alpha$ state conversion indicates such conversion is not simply related to the degree of halogenation of each Si atom. It would therefore seem likely that beam induced breaking of the silicon (in the silicon halide) from it's neighbours is occurring. This then allows it to occupy a less strongly bound ($\alpha$) site on the surface.
The SiBr$_3$ phase shown in Figure 3.16(b) appears to show little change at exposures of $<3 \times 10^{16}$ cm$^{-2}$. Although ion irradiation removes both $\alpha$ and $\beta$ states simultaneously at low cross sections. A possible explanation for this behaviour may be due to intermixing of the surface region. The formation of the SiBr$_4$ species appears therefore to be a minority reaction.

3.5.2.2 Beam induced Process Cross sections - Ar Neutrals

It is clear from the previous discussion that an energetic particle beam has a profound effect on chemisorbed Br-Si surfaces, and may promote chemical change as well as physical sputtering processes. The effect of increasing the beam energy is now studied by use of fast atom beam source which provides energetic neutrals within the range 800eV to 2.5keV. The effect of the thickness of the chemisorbed surface phase upon detected desorption product formation and their desorption cross sections are also discussed.

The cross sections for desorption are calculated via the method in equation 3.3 and are presented in Table 3.6. This data is representative of neutral beam irradiation by 1kV and 2.5kV Ar$^0$ on a silicon surface, previously exposed to 750L of gaseous molecular bromine. This exposure results in a highly brominated surface region. The nature of this surface has been comprehensively discussed in section 3.5.1 and it is the perturbations of this layer by a beam source that is fundamental to potential etching applications.

It is immediately apparent that the initial desorption cross sections for irradiation of these surfaces are generally greater than those calculated for 680eV bombardment of a less heavily dosed silicon surface. This is easily explained by the increase in the intensity of the $\alpha$ state signal i.e. the quantity of corrosion phase present on the surface. The surface binding energy is low for this phase and the sputtered proportion of this phase will be large compared to a thinner corrosion layer. It is also clear that sequential erosion
of desorption peaks does not occur and therefore a degree of intermixing is likely resulting in chemical rather than physical processes occurring. An interesting difference to the 680eV Ar$^+$ ion bombardment experiments showed that some desorption cross sections are negative, thus showing an increase of detected signal. This increase in signal for certain phases implies a complex series of processes occurring within the surface region. Jackman et al [3.24] have shown interesting augmentation effects of the $\alpha$ state following irradiation of a Si/Cl$_2$ surface by an UV source. On no occasion, however, was the $\beta$ state enhanced.

Before fully discussing the nature of possible induced processes on this surface it is necessary to understand the nature of the chemical changes inferred by analysis of the cross sections of loss/gain from the surface

Initial bombardment of the Br-Si(100) surface at high coverages results in high desorption cross sections at ion doses of less than $5 \times 10^{14}$ Ar$^0$ cm$^{-2}$. This is experimentally verified for exposure to 1kV argon neutrals, but is not possible for 2.5 kV neutrals due to the operating conditions of the beam source. Knabbe et al [3.75] in a SIMS study of ion-assisted etching mechanisms of adsorbed layers of fluorine on silicon suggested that large desorption cross sections (100Å$^2$) may be found at high surface coverages. They measured the initial transient cross section ($\sigma$) as described by

$$\sigma = \frac{1}{\alpha v^+} \frac{d(SiX)}{dt}$$  \hspace{1cm} [3.4]

This is essentially the same treatment as applied to cross section calculations presented here. These TDS experiments measure desorption loss cross sections at prolonged exposure to an ion dose and hence the results may be susceptible to the effects described by Taglauer et al [3.76] where recoil implantation and mixing of the adsorbed halogen into the sub-surface region by energetic particle bombardment are likely to occur. Loss cross sections of around 10Å$^2$ have been observed by Winters [3.77] for sputtering of adsorbed gases with 1kV argon ions. It is also appropriate to mention the depth of the
amorphisation region at this point. An estimation of this is possible by recourse to previous experimental and theoretical calculations by other researchers. It has been previously mentioned in section 3.3 that the estimated amorphisation depth by the LSS theory is less than those estimates obtained from experimental data. For the case of 680eV, 1keV and 2.5keV argon beams the LSS calculations are 35Å, 45Å and 70Å respectively whereas calculation from Konomi's empirically derived expression [3.46] gives values of 44Å, 57Å and 105Å respectively. The presence of the corrosion phase is likely to absorb some of the energy of the impinging ion and, therefore, Konomi's estimates may be taken as maximum limiting values for the depth of the amorphous layer. The initial stages of ion sputtering of the corrosion layer, however, usually results in an increased volume at the surface. This can be assumed because of the implantation of the impinging argon ions and also the assumption that some of the bromine atoms in the corrosion layer are recoil implanted. A complex series of events are, therefore, likely with formation of voids in the sub-surface region allowing formation of volatile silicon halide species. This ion induced gasification process occurs as a result of collisional cascades within the near surface region and is currently a popular description of the ion assisted etching mechanism. Dieleman et al [3.35] have suggested that an important role of ion bombardment is the mixing of the adsorbed halogen species into the silicon surface region. Processes such as recoil implantation, ion enhanced diffusion, atomic relocations and creation of strings of connected vacancies which allow absorption of the the reactive gas into the top 10-30Å of the surface may occur. A reduction of the surface binding energy within the surface region thus increases the sputtering yield. Mayer and co-workers [3.78,3.79] have provided experimental evidence to support this case. TDS studies presented here also supply indirect evidence for these assertions. In order to assess specific chemical changes in the nature of the surface the induced changes of the surface phases are evaluated.
3.5.2.2.1 Induced Changes - α State

The α state signal loss cross sections for 1keV neutral irradiation are shown in Table 3.6. The processes $\sigma_{15}$ (SiBr), $\sigma_{21}$ (SiBr$_2$) and $\sigma_{27}$ (SiBr$_3$) show comparable orders of magnitude. Slightly faster loss of SiBr is observed than SiBr$_2$ or SiBr$_3$ values. Furthermore, increase of the initial Br cross-section ($\sigma_{10}$) implies conversion from more highly halogenated species to less coordinated species. Preferential sputtering of SiBr from the adsorbed layer is also likely but also suggests an induced reaction of SiBr to SiBr$_2$ as observed in the case of low energy ion bombardment. Further analysis of the α desorption cross sections reveals that $\sigma_{16}$ (SiBr) increases whilst $\sigma_{22}$ (SiBr$_2$) shows loss of the same magnitude. Furthermore detected signals for $\sigma_{10}$ (Br) and $\sigma_{11}$ (Br) show an increase upon initial neutral exposure followed by a low cross section of desorption. These observations suggest that at initial high beam energies on thick adsorbed phases a high degree of chemical sputtering occurs caused from a reduced surface binding energy. Intermixing of bromine and silicon follows, thus forming a less halogenated overlayer. Prolonged beam exposure merely results in further intermixing as opposed to chemical sputtering which occurs on the heavily halogenated overlayers.

A plot of the intensity ratios for the α state signals as a function of neutral beam dose augments the cross section data presented above. Figure 3.34 presents intensity ratios for α state signals following 1keV bombardment. The immediate observation from this graph is the rapid decrease of the SiBr$_3$ peak after prolonged exposure of the surface to argon neutrals. The SiBr/SiBr$_3$ ratio remains approximately constant with perhaps a slight trend towards increasing under high dose conditions.

The cross sections for loss caused by exposure to 2.5kV argon neutrals appear to be an order of magnitude less than the 1kV beams. There are two possible explanations for this observation. Firstly, the initial transient cross section is measured over an increased dose of the neutral beam. This is due to the restrictions in the operating conditions of the FAB source. Secondly, the
increased energies impinging on the adsorbed phase surface should lead to an increased amount of intermixing. Comparison of $\sigma_{23} (\text{SiBr}_2)$ and $\sigma_{40} (\text{SiBr}_2)$ $\alpha$ state cross sections for equivalent ion dose at beam energies of 1kV and 2.5kV show remarkable similarity. Furthermore, the $\beta$ state comparison of $\sigma_{26} (\text{SiBr}_2)$ and $\sigma_{43} (\text{SiBr}_2)$ also agree closely. This implies that the use of the initial transient cross sections is not totally applicable to determination of the initial processes occurring upon impact of the energetic particle beam upon the adsorbate covered surface.

The intensity ratio data is presented in Figure 3.35 and shows a rapid increase in the signal of the desorbed products following the trend $\text{Br}>\text{SiBr}>\text{SiBr}_2$. Prolonged exposure to the argon neutrals results in an increase of the SiBr$_2$ signal to SiBr. Under this regime the Br signal is approximately constant. The implications of these data are that the after initial bombardment of the surface, the surface region contains predominantly Br species caused by intermixing of the adlayer by the highly energetic impinging particles. The broadening of the $\alpha$ state signal for Br adds further weight to the intermixing argument, but also implies that $\beta$ to $\alpha$ state conversion may also occur as shown in the low energy beam studies. As irradiation continues SiBr$_2$ appears to form at the expense of SiBr species.

It is important that these processes are not interpreted in isolation, and thus the induced changes for the $\beta$ state within the ion bombarded phases are now assessed.

3.5.2.2.2 Induced Changes - $\beta$ state

The possibility of $\beta$ to $\alpha$ state conversion is witnessed by measurement of the desorption cross section for Br ($\sigma_{13}$) which shows a value of 0.24Å$^2$. Comparable initial values for $\sigma_{18} (\text{SiBr})$ and $\sigma_{24} (\text{SiBr}_2)$ show a rise in the $\beta$ state signal. The $\alpha$ state SiBr$_3$ cross section ($\sigma_{28}$) reveals a massive loss of the surface phase, thereby inferring that a competing reaction is occurring. Ion beam induced intermixing causes rapid loss of the already low levels of SiBr$_3$
\( \beta \) state to enhance the reaction of adsorbed bromine to silicon dihalide.

Thus a reaction scheme such that

\[
\text{Br}_{\text{ads}} \quad \rightarrow \quad \text{SiBr} \quad \leftarrow \quad \text{SiBr}_3
\]

occurs with \( \text{SiBr}_2 \) formation being the reaction product for 1keV induced changes. The reaction scheme for irradiation by 2.5keV argon neutrals is such that all cross sections are in close agreement. This resultant intermixing effectively leads to a \( \beta \) to \( \alpha \) conversion, with the stoichiometry of the adsorbed phase remaining the same as before exposure to the neutral beam. This scenario appears to be intuitively wrong until the full effect of Si/Br intermixing of a thick adsorbate covered surface region is considered. The proportion of recoil implantation to backward sputtering yield should be significantly greater for a 2.5keV beam as opposed to a 1keV neutral beam.

The intensity ratios for the 1keV and 2.5keV \( \beta \) state signals are presented in Figure 3.36 and 3.37 respectively. For the 1keV experiments, the most significant trend is the rapid reduction in the SiBr/SiBr\(_2\) ratio which indicates the formation of SiBr\(_2\) as previously indicated. It is clear that after beam bombardment the formation of highly halogenated \( \beta \) state species at the surface is much reduced, but the SiBr\(_2\) surface state appears to be favoured. The intensity ratios for the 2.5keV bombardment suggests very little change in the SiBr/SiBr\(_2\) ratios, whilst the Br/SiBr and Br/SiBr\(_2\) ratios increase rapidly upon bombardment followed by a stable ratio after 10s exposure.

From the observations of the \( \beta \) state intensity ratios it is clear that the 2.5keV beam thoroughly intermixes the adsorbed layer within the amorphisation region at the surface. The processes therefore appear to be of a more physical nature, whereas the 1keV beam induces chemistry to a more highly halogenated form. The high beam energy results in significant bond breaking, thus leaving Br species in the surface region. Furthermore, The SiBr/SiBr\(_2\)
ratio remains approximately constant and therefore Br is lost equally from either SiBr or SiBr$_2$ surface species. In addition, a $\beta$ to $\alpha$ conversion also occurs. This is more prevalent for the higher beam energies.

3.5.3 Comparison with Modulated Beam Experiments

A large body of study has used modulated beam experiments in order to elucidate mechanisms for ion-assisted etching processes. This is particularly true of the Cl$_2$-Ar-Si system [3.40,3.74].

Kolfschoten [3.40] measured mass spectra of emitted products of simultaneous Cl$_2$ exposure and ion beam irradiation. Figure 3.5 shows a typical kinetic energy distribution for the ejected SiCl$_2$ species It should be noted that the ratio of Cl$_2$/Ar in these experiments is 150:1 and thus the surface may be considered to be in the multilayer region. Thus the measured surface regime is similar to the TDS experiments performed in this study. The nature of the measurements, however, differ greatly. It is clear that in order to measure kinetic energy distributions the temporal measurement is very short (ie.milliseconds). It must be emphasised that the TD experiments measure the surface in an equilibrium state after the ion irradiation process has ceased. It is clear, therefore, that the modulated beam studies give good information upon the nature of the chemical sputtering process. Thermal desorption experiments give supplementary information on the nature of the surface region and the surface chemistry induced rather than the physical ejected species upon initial ion irradiation.
Figure 3.31 Dry Etching Methods in terms of the ratio of reactive neutral flux to the ion "flux x energy" products and the resulting halogen coverage

- Multilayer
- Monolayer
- Sub-monolayer
- No undercut (anisotropic)
- Slow discharge etching
- Sputter etching
- Ion milling
- RIE
- CAIBE
- Plasma
- High pressure
- Low pressure
- Intensified discharge
- Controlled undercut

Reactive Neutral Flux Ion "Flux x Energy" Product

Figure 3.32 Relative Intensities of TDS Products from Br2/Si following argon ion beam irradiation (680eV)
Figure 3.33 The Effect of Adsorbate Thickness and Amorphisation Depth on Thermally Desorbed Silicon Halide Products
Figure 3.34 Relative Intensities of alpha state TDS Products from Br₂/Si Surface Following neutral beam irradiation (1kV)
Figure 3.35 Relative Intensities of alpha state TDS Products from Br2/Si following argon neutral beam irradiation (2.5kV)
Neutral Exposure (s)

Figure 3.36 Relative Intensities of beta state TDS products from Br2/Si Surface following argon neutral beam irradiation (1kV)
Figure 3.37 Relative Intensities of beta state TDS Products from Br2/Si Surface following argon neutral exposure (2.5kV)
Table 3.4 Relative Intensities (normalised) of Thermal Desorption Products from the Br$_2$/Si(100) System following Ar$^+$ ion beam irradiation (ions cm$^{-2}$)

<table>
<thead>
<tr>
<th>Fragment</th>
<th>Ar$^+$ ion irradiation (x10$^{15}$ cm$^{-2}$)</th>
<th>SiBr$_4$[3.73]</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiBr$^+$ α</td>
<td>100 100 100 100 100</td>
<td>100</td>
</tr>
<tr>
<td>SiBr$_2^+$ α</td>
<td>19 42 154 62 24</td>
<td></td>
</tr>
<tr>
<td>SiBr$^+$ β</td>
<td>100 100 100 100 100</td>
<td></td>
</tr>
<tr>
<td>SiBr$_2^+$ β</td>
<td>13 18 24 83 24</td>
<td></td>
</tr>
</tbody>
</table>
Table 3.5 Cross Sections for Desorption of Phase for 680eV Ar⁺

<table>
<thead>
<tr>
<th></th>
<th>desorption peak</th>
<th>Å²</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiBr</td>
<td>σ₁</td>
<td>α₁</td>
</tr>
<tr>
<td></td>
<td>σ₂</td>
<td>α₂</td>
</tr>
<tr>
<td></td>
<td>σ₃</td>
<td>β</td>
</tr>
<tr>
<td>SiBr₂</td>
<td>σ₄</td>
<td>α</td>
</tr>
<tr>
<td></td>
<td>σ₅</td>
<td>β</td>
</tr>
</tbody>
</table>
Table 3.6 Cross sections for Desorption of Phases by 1kV and 2.5kV Neutral Ar° Irradiation

<table>
<thead>
<tr>
<th></th>
<th>1kV</th>
<th>2.5kV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Br</td>
<td>SiBr</td>
</tr>
<tr>
<td>α</td>
<td>σ₁₀ +9</td>
<td>σ₁₅ 47</td>
</tr>
<tr>
<td></td>
<td>σ₁₁ 1</td>
<td>σ₁₆ +7</td>
</tr>
<tr>
<td></td>
<td>σ₁₂ 0.1</td>
<td>σ₁₇ 0.4</td>
</tr>
<tr>
<td>β</td>
<td>σ₁₃ 0.24</td>
<td>σ₁₈ +20</td>
</tr>
<tr>
<td></td>
<td>σ₁₄ 0.03</td>
<td>σ₁₉ 31</td>
</tr>
<tr>
<td></td>
<td>σ₂₀ 0.34</td>
<td>σ₂₆ 8.1</td>
</tr>
<tr>
<td></td>
<td>(28mA)</td>
<td>(28mA)</td>
</tr>
</tbody>
</table>
3.6 Summary and Implications for Beam Etching of Silicon with Halogens

The results obtained in this study of the Br₂/Si(001) system can now be summarised;

- fast initial formation of a strongly bound monolayer (β state) which desorbs at high temperature and yields silicon halides of low coordination.

- slow subsequent population of a thick corrosion layer (α state) which desorbs at lower temperatures and gives more highly coordinated silicon halides.

- some spontaneous silicon halide formation at room temperature is observed.

- ion beam irradiation of these observed surface phases leads to the formation of silicon halides of increased halogen:silicon coordination ratios. Thermal removal of the phases formed indicate SiBr₂ and SiBr₄ to be the favoured products from the α state whilst the SiBr₂ is the enriched phase from the β state.

- simultaneous inter-conversion of β state type adsorbates into more weakly held α state species occurs. These are then desorbed by further bombardment, leading to removal of all surface phases and etching.

- whilst vibration or electronic excitation of the surface region, by the incoming beam, may give rise to chemical changes in the adsorbed phases, a collisional cascade type process is favoured for this β to α conversion. It is this step that, in this static system gives rise to etching of the silicon.

A list of essential features for any etching process applicable to VLSI/ULSI devices are likely to include attributes such as good etch rates, materials selectivity and high anisotropy. In addition, minimal damage to the device structures is of overriding importance. It is clear that a number of possible
etching processes may be utilised. If we first consider CAIBE processes as a prime technology for those applications one may envisage the ideal extension of this technique; an ideal precursor for this process would spontaneously adsorb to the surface giving rise to a region of several atomic layers which passivates the surface. Irradiation of this surface region by an energetic beam would then promote a reaction between an active part of the precursor and the surface. Removal of the inactive precursor components as a stable by-product would be achieved by sputtering. A critical aspect of this scenario is the prevention of beam induced intermixing effects. Another factor for consideration in this study is the effect of the charge component of the impinging ion. The positive charge of the Ar+ ion exerts an attractive potential for electrons in the surface region. This is a critical point to consider for the etching of semiconductor materials, which are carefully doped to obtain the desired device characteristics. The use of a FAB source to obtain energetic neutrals is an important processing tool to avoid the deleterious effects of ion bombardment. In addition, the use of energetic neutrals prevents surface charge build up on insulating surfaces.

It is clear that the results in this chapter do not describe the actions of an ideal precursor. These results, however, may act as an initial step in understanding the chemistry of halogenated precursors on semiconductor surfaces. A clear extension to this strategy is the study in the following chapter which cover the reactions of halogens on a compound semiconductor surface, namely GaAs.
CHAPTER 4

SURFACE CHEMISTRY OF HALOGENS ON GALLIUM ARSENIDE: APPLICATION TO ION-ASSISTED ETCHING PROCESSES

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4.2 Ion Beam Etching: Applications to Device Processing
   4.2.1 Metal-Semiconductor Field Effect Transistors (MESFET's)
   4.2.2 High Electron Mobility Transistors (HEMT's)
   4.2.3 Heterojunction Bipolar Transistors (HJBT's)
   4.2.4 Optoelectronic and Optical Devices
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4.3 Structure of Gallium Arsenide
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      4.5.4.1 Adsorption of Chlorine on GaAs at 300K-Gallium containing desorption products
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4.5.5.1 Bombardment with Ar\(^+\) ions- Gallium desorption products
4.5.5.2 Bombardment with Ar\(^0\) neutrals- Gallium desorption products
4.5.5.3 Bombardment with Ar\(^0\) ions- Arsenic desorption products

4.6 Discussion

4.6.1 Chlorine Adsorption on the GaAs(001) Surface
4.6.1.1 Analysis of Desorption Products
4.6.1.2 Mechanism for Thermal Etching

4.6.2 Beam Assisted Reactions of GaAs with Halogens
4.6.2.1 Ion/Neutral Beam Induced Cross-Sections for desorption
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4.6.3 Summary and Implications of GaAs CAIBE Processes
4.1 Introduction

Gallium arsenide (GaAs) has become an important material for electronic and optoelectronic integration over the past decade. A significant use of this material is for high frequency devices. Similar magnitudes of device integration are required to those currently available in silicon based device structures. This necessary reduction of device feature size below three microns has resulted in a trend towards dry etching processes in preference to wet etching techniques. Dry etching enables the production of well delineated patterns with greater process control than wet etching methods. Many device structures require sub-micron feature size capability despite the associated difficulty in achieving adequate etch profile and depth control specifications.

The chemical and physical nature of GaAs presents additional problems for optimizing dry etching processes. This material chemically dissociates at temperatures greater than 900K via loss of the arsenic component. This change in the stoichiometry is due to the high vapour pressure of arsenic at elevated temperatures in high vacuum. Most current GaAs dry etching methods use either plasma or reactive ion etching. The use of energetic ions or neutrals is likely to induce structural damage more readily than for etching of silicon. The potential use of low temperature/low ion energy processing is of significant interest for the further development of GaAs digital integrated circuit technology. The necessity for selective area etching with a high aspect ratio is also desirable. Techniques such as reactive ion beam etching (RIBE) and chemically assisted ion beam etching (CAIBE) are in direct competition with laser assisted etching processes.

As the application of ion-assisted etching techniques to commercial III-V microelectronics become more commonplace it is desirable to understand, at an atomic level the processes occurring at the etch interface and within the immediate near surface region. This understanding is crucial for the development of reliable and reproducible etch technologies. This is particularly true of the burgeoning RIBE and CAIBE processes where the
chemical and physical information of the surface is likely to result in improved etch strategies. Furthermore, the manipulation of precursors on the GaAs surface may be used for improving etch selectivity, control of equirate processes, passivation of etch walls and for reduction of damage caused by ion impact.

This chapter studies the fundamental interactions between molecular chlorine and the surface of GaAs with particular emphasis on real etching applications to device processing. The techniques of TDS, AES and LEED are employed to provide specific information on the nature of both the adsorption process and the desorption products. The next section (4.2) surveys the current state of development of GaAs devices and their specific etch requirements, thus setting the agenda for the remainder of the chapter. The structure of GaAs is described in section 4.3 with particular attention being paid to the (100) surface reconstructions. The structure and stoichiometry of the surface when exposed to halogen is also examined. Damage processes caused by ion assisted etching processes are discussed in section 4.4.

The results of thermal desorption studies of molecular chlorine on a GaAs(100)(4x1) surface are presented in section 4.5, and the effect of ion and neutral beam irradiation on these surfaces is also explored. The nature of desorption products gives an indication of the thermal and ion-assisted etching mechanisms under a variety of etch conditions. Discussion of these results with particular regard to their implications for GaAs processing is covered in section 4.6.
Chapter 4: Ion Beam Etching of GaAs

4.2 Ion Beam Etching: Applications to Device Processing

A number of GaAs electronic and electro-optical applications require stringent etch controls. Etch parameters such as high anisotropy, etch uniformity, selectivity and equirate etching are essential for the fabrication of many III-V device structures. The scale of removal of material can be used to classify the type of etch. There are three main usages

(i) etching of surface features (sections 4.2.1-4)
(ii) holes and vias (sections 4.2.5)
(iii) pre-deposition cleaning

The first of these categories is discussed in detail in regard to the main device structures that require low damage ion-assisted etch processing. The examples discussed include metal-semiconductor FET's, high electron mobility transistors and the heterojunction bipolar transistors.

4.2.1 Metal Semiconductor Field Effect Transistors (MESFETs)

GaAs MESFETs have found considerable application due to their high electron mobility and saturation velocity for microwave devices [4.1]. The two most common types are the planar depletion-mode MESFET and the enhancement mode MESFET. The latter has greater potential for VLSI due to its low power dissipation. The fabrication is, however, more complex due to the introduction of recessed gate technology.

A typical enhancement MESFET structure is shown in Figure 4.1. An active n-GaAs region, which is formed by ion implantation of dopant upon a semi-insulating GaAs substrate, is required. The source and drain are ohmic contacts, whilst the control electrode (gate) is a Schottky barrier i.e. a potential barrier against electron injection from the metal into the semiconductor conduction band. The MESFET acts as a voltage controlled resistor with the
gate electrode modulating the flow of carriers through a channel between the source and drain electrodes. MESFET design takes many forms, but one of particular interest is the use of recessed gate technology. Gate recessing offers several advantages:

(i) the effects of surface depletion are reduced, so that the voltage control of the gate is dominant. The gate recess should be approximately 0.1mm for the channel current to be dominated by the gate rather than surface depletion.

(ii) a smooth ramped etch side gives a high gate-drain breakdown.

(iii) a low resistance structure is formed.

(iv) recess etch may remove an n+ contact layer.

MESFET recessed gate devices are particularly vulnerable to damage to the source-drain channel below the recessed gate caused by ion-induced introduction of deep level trap carriers during etching. These traps reduce the free electron population and hence reduce device conduction. It can be postulated that a reduction of damage may be facilitated by the use of low energy ion species of high mass, and use of an adsorbed layer on the etch surface as a protective layer [4.2]

4.2.2 High Electron Mobility Transistor (HEMT)

The enhancement of electron mobility in modulation-doped GaAs-Al_{x}Ga_{1-x}As superlattices was first reported in MBE grown structures [4.3]. This effect was transcribed to the fabrication of a FET with high speed microwave capabilities by Mimura et al [4.4] and coined as the high electron mobility transistor (HEMT). This type of device as depicted in Figure 4.2 is also known as a modulation doped FET (MODFET), selectively doped heterojunction transistor (SDHT) and two-dimensional electron gas FET (TEGFET). The main advantage of the HEMT is the fast 'turn-on' which is due to the low (200mV)
gate logic voltage swings needed to obtain full transconductance. This occurs because the mobility of electrons in the channel are higher than in a MESFET structure due to the absence of scattering of carriers by dopant ions. Large scale integration (LSI) of HEMT structures has led to the incorporation of these devices in communications systems and superfast computers [4.5].

The fabrication of HEMT structures poses several problems for acceptable device performance. An additional layer of n-GaAs of 60nm thickness is necessary to allow good ohmic contact between the source/drain and the metallisation. A recessed gate is therefore necessary for the enhancement mode operation Schottky gate contact. The HEMT logic gate structure therefore requires the use of a selective dry etch which etches n-GaAs but stops at the N-Al$_x$Ga$_{1-x}$As ($x=0.3$) layer [4.6]. Hikosaka et al [4.6] reported a selectivity ratio of greater than 200:1 for GaAs/AlGaAs etching for a CCl$_2$F$_2$/He reactive ion etch (RIE) process, with near vertical etch profile. Although the physical etch process is satisfactory, significant perturbation of the AlGaAs region can occur resulting in device degradation. These damaging effects are discussed more fully in section 4.4.

4.2.3 Heterojunction Bipolar Transistors (HJBTs)

The MESFET and HEMT structures described previously have low logic voltage swings with highly non-linear properties, with a uniform threshold of operation. Overetching of these structures may significantly alter the operating threshold. These structures are also susceptible to damage by ion beam processing techniques as outlined. Bipolar transistors, however, have high threshold uniformities in comparison to FET's as the threshold voltage is determined by the band gap of the GaAs and AlGaAs. This is more easily controlled than the channel doping and layer thickness within the HJBT device structure. It has been estimated that a HJBT device may operate in the 100-200 GHz region, with gate delays of less than ten picoseconds [4.7].
Chapter 4: Ion Beam Etching of GaAs

typical HJBT device is depicted in Figure 4.3, with the pre-grown heterostructure to illustrate the complexity of fabrication for this device.

A number of key features for low damage etching are necessary. The development of etch stop technology to complement the anisotropy of ion-assisted etching is desirable for uniform device characteristics. Control over etch selectivity is desirable between GaAs and AlGaAs in both directions, and also low damage equirate etching.

4.2.4 Optoelectronic and Optical Devices

A number of optoelectronic and optical components may be fabricated from GaAs; for example, semiconductor lasers, light emitting diodes, waveguides, lenses and optical gratings.

Somekh and Casey [4.8] studied the use of ion assisted techniques on the development of integrated optical devices. Distributed-feedback lasers were fabricated with periodic corrugations using ion beam milling techniques. The use of methane-hydrogen RIE has resulted in high quality GaAs and InP DFB laser structures [4.9]. Physical damage by ion bombardment at, or in the vicinity of, active layers in laser structures as detected by photoluminescence or Schottky evaluation has been shown to be dependent upon ion dose [4.10]. The use of CAIBE has been employed to fabricate large (10-100mm) optical structures such as spherical microlenses, with low damage etches at energies of less than 100eV resulting in reduced scattering losses and aberration effects [4.11].

4.2.5 Vias and Holes

The ion-assisted etching of via connections for GaAs monolithic microwave integrated circuits (MMIC) has been extensively [4.12,4.13] studied in order to improve device gain performance. This is achieved by providing low
inductance grounding. Specific etch requirements for these large (>100mm) device features are high GaAs/mask selectivity, good dimensional control, control of smoothness and slope of the sidewall, good selectivity with respect to the metallisation on the wafer, and high etch rate. Hipwood and Wood [4.13] used a Freon 12 RIE and identified polymer formation on the sidewalls. The hole profile was found to change by controlling the amount of polymer produced.
Figure 4.1 Enhancement Mode FET
Figure 4.2 Schematic of High Electron Mobility Transistor (Fujitsu HEMT)
Figure 4.3 Schematic of a GaAs/AlGaAs Heterojunction Bipolar Transistor (HJBT) showing layered as-grown structure and final processed device structure.
4.3 Structure of Gallium Arsenide

To fully discuss the nature of thermal and ion-assisted reactions of halogens with gallium arsenide it is necessary to understand the structure of the surface region. The bulk structure is considered first followed by an analysis of the reconstructions observed at the surface.

4.3.1 Bulk Structure of GaAs

The bulk structure of GaAs can be described by the zinc blende structure as shown in Figure 4.4 which consists of two interpenetrating face centred cubic (f.c.c.) lattices; one comprising Ga atoms whilst the other consists of As atoms. These sub-lattices are separated by 2.45Å along the body diagonal of the unit cell and are displaced by coordinates of (1/4, -1/4, 1/4). Most electronic and electro-optical devices are fabricated on the (100) plane of GaAs offset 2° away from the [100] axis towards the [110] axis. This allows an optimum terraced surface for growth of epitaxial layers of III-V compounds on the wafer.

Terminations of the bulk structure, however, leads to the formation of new localised atomic states at surfaces and may influence the properties of any junction that is subsequently formed. It is, therefore, of importance to understand the arrangement of atoms in the immediate surface region.

4.3.2 Surface Structure: Reconstructions of Low Index GaAs Surfaces

The GaAs surface relaxes at the interface with the vacuum, taking a reconstruction of lowest energy. This reconstruction is highly dependent upon the stoichiometry of the surface region. The structure of the surface is determined by the orientation of the single crystal wafer and is discussed in more detail below with particular emphasis on the GaAs(001) surface.
The GaAs(001) surface has been extensively studied due to its usefulness in microelectronic applications. The preparation of the surface by molecular beam epitaxy (MBE) is most popularly used for surface structural studies as this technique allows deposition of layers with differing stoichiometry. While the Si(100) surface has found to reconstruct to several structures, a significantly larger number of surface reconstructions for GaAs(001) have been found over an expansive range of surface stoichiometries.

The first LEED patterns of the GaAs(001) surface were shown by Jona [4.14] in which he identified the (1x6) and c(8x2) reconstructions. Further studies by Cho [4.15] isolated a c(2x8) pattern which was attributed to an As-stabilized surface. The GaAs(001)c(8x2)surface was found to be Ga-stabilized, whilst the (1x6) surface observed by Jona was ascribed to a transition between the Ga and As stabilized structures. Van Bommel et al [4.16] found that ion bombardment and subsequent annealing to 773K showed a GaAs(001)(1x6) pattern, whilst further annealing to 873K revealed a transition to the GaAs(001)c(8x2) reconstruction.

It has been noted [4.17-19] that III-V semiconductor surfaces prepared by ion sputtering and annealing are usually deficient in the anion component, which in this case is arsenic. Singer et al [4.17] attributed this to preferential sputtering of As. Wang and Holloway [4.20] found, using angle resolved x-ray photoelectron spectroscopy (ARXPS) data, that As was enriched on the surface by bombardment of 5keV Ar⁺ ions. Similar experiments with 1keV Ar⁺ ions revealed depletion of As at the surface. Arthur [4.21] and Joyce and Neave [4.22] have suggested that an As out-diffusion process exists from the bulk to the surface region.

Mendez et al [4.23] recently characterised GaAs(100) surfaces prepared by simultaneous ion bombardment and annealing (SIBA) cycles inside the vacuum chamber and showed that SIBA treatment prevents the formation of As-rich structures. The c(8x2) reconstruction prepared at 800K was shown to have a composition of 0.5 Ga ML and 0.75 As ML whilst SIBA at 850-870K
causes loss of arsenic to reveal 0.5 Ga ML and 0.5 As ML. These measurements have been verified by STM experiments [4.24]. Ion bombardment and thermal anneal processes are found, in this study, to produce a GaAs (001)(4x1) reconstructed surface. A model for this reconstruction is presented in Figure 4.5.

Low energy ion spectroscopy (LEIS) has been used to considerable advantage due to the surface specificity of the technique. A typical LEIS spectrum as obtained by Orrman-Rossiter et al [4.25] is shown in Figure 4.6. Two types of peak are observed. Firstly, binary scattering peaks are due to binary collisions between Ne⁺ ions and the surface. Binary recoil processes are observed when surface atoms are sputtered as a result of binary collisions between the probe ion and the surface. They found that ion bombardment with 5keV Ar⁺ ions produced As enriched surfaces at ion doses greater than 5x10¹⁵ ions cm⁻². This was attributed to a type of defect related diffusion process.

Frankel et al [4.26] showed using high resolution electron energy loss spectroscopy (HREELS) data that no As-dimers exist on the surface of the Ga-rich c(8x2) structure, and proposed a model of three Ga dimers and one vacancy existing within an individual unit cell as shown in Figure 4.7. The vacancy exposes four As atoms in the second layer. They also suggested that the (4x1) structure has the basic unit cell as the c(8x2) structure with three Ga dimers and one dimer vacancy but that there is imperfect long range order between individual unit cells along the [110] direction.

Bachrach et al [4.27] have used angle integrated photoemission to obtain detail on the surface stoichiometry of GaAs(100) and AlAs(100) and detected an As coverage of 0.52 for the c(8x2) reconstruction. Figure 4.8 shows the ratio of Ga 3d and As 3d core level peak areas as a function of As coverage on GaAs(100). The figure shows the surface stoichiometry for various atomic reconstructions at the surface and thus an As coverage of 0.52 was obtained for the c(8x2) reconstruction. Drathan et al [4.28] using Auger peak-to-peak ratios produced a value of 0.22 and thus is at variance with these results. These surfaces were not thermally annealed but produced by
deposition of Ga and as thus possibly not resulting in an equilibrium surface phase. They conclude that more Ga-rich surface structures are not produced due to out-diffusion of arsenic from the bulk.

DeLouise [4.29] noted that surface preparation of the GaAs(110) surface with 3keV Ar$^+$ ions and subsequent annealing at 550 °C yielded a (1x1) reconstructed surface with a Ga rich structure. XPS studies showed a As/Ga ratio of 0.87.
Figure 4.4 Bulk structure of GaAs showing Crystallographic Information
Figure 4.5 (4x1) reconstruction of the GaAs (001) structure
Figure 4.6
(a) Schematic of the Ion Scattering Geometries for the GaAs (001) Surface
(b) The Energy Spectrum from a LEIS study on GaAs (001) at Ts 523K for Ne⁺ ion doses of (i) $2 \times 10^{14}$ ions cm⁻² (ii) $10^{15}$ cm⁻²

Figure 4.7 Planar View of the c(8x2) Structure showing three Ga dimers and one dimer vacancy per unit cell

[D.J.Frankel, C.Yu, J.P.Harbison and H.H.Farrell
Figure 4.8 Ga 3d/As 3d Core Level Peak Area ratios versus As Coverage

[R.Z.Bachrach, R.S.Bauer, P.Chiaradia and G.V.Hanson
4.4 Damage to GaAs from Ion-Assisted Etching Processes

A variety of ion-assisted etching processes, for example plasma etching, RIE, RIBE, IBM and CAIBE may be employed for etching of GaAs device structures. The question of what happens when an ion beam impinges on the surface of a semiconductor has been examined in the first chapter. The specific application of these interactions on GaAs surfaces and their implications for dry device etching processes are discussed. Particular emphasis on the structural damage to the surface and sub-surface region is considered and how the electrical and optical properties of the material are perturbed. Ions in the energy range from several tens of electron volts to 5keV are discussed, whilst energies relevant to ion implantation processes are beyond the scope of the discussion. Ejection of species from the GaAs surface can occur from transfer of momentum of the impinging particle to the surface when the ion energy exceeds 10eV [4.8].

4.4.1 Structural Damage

The impact of ions on the surface of GaAs may create lattice vacancies and other surface defects and may even disrupt the crystalline structure of the lattice. This may cause complete amorphisation of the near-surface region. Medium Energy Ion Scattering (MEIS) is particularly sensitive with regard to energy and depth resolution and is often used to characterise surfaces. Konomi et al [4.30] studied 1-3keV Ar+ irradiation of the GaAs(001) surface using MEIS, and determined an expression for the damage width (in nm) as 4.0E^{0.5} where E is the argon ion energy in keV. These values are approximately twice those calculated using LSS theory for projected ranges for Ar+-GaAs. Ivey and Piercy [4.31] irradiated GaAs(001) with 3-6keV argon ions at an angle of 75° to the surface normal and studied the damage using scanning transmission electron microscopy (STEM). Amorphisation layers of 30Å and 35Å were found for 3 and 6keV respectively. Calculation to convert to normal incidence gave amorphised
depths of 116Å and 135Å for the respective ion energies.

Germann et al [4.32] measured the optical emission of a GaAs/AlGaAs single quantum well at low temperature. This acted as a local probe of ion damage which showed that even at ion energies as low as 250eV a SQW device is damaged to a depth of 400Å; approximately four times the calculated projected range value (110Å) as calculated using the TRIM Monte Carlo simulation [4.33]. This excessive projected range value was attributed to ion channeling. Weaver et al [4.34] used atom scattering to detect changes to the GaAs(110) surface after exposure to 600eV Ar ions. This technique is sensitive to the effects of low ion fluences, and shows that one ion impingement per hundred surface atoms may cause a significant decrease in atom scattering amplitude. An average impact at 300K was found to cause 2-5 defects which move around the surface before coming to rest. An increase of adatom jumps is caused by bombardment at 500K although the defect creation rate is similar to the lower temperature. At 600K the target adatoms remain mobile until recombination with surface vacancies occur, whilst at 700K the surface effectively thermally anneals. Kang et al [4.35] using AES and RHEED analytical probes detected preferential sputtering from the surface. Bombardment with 2keV argon ions causes a gallium rich surface region to form at 300K caused by preferred sputtering of arsenic since the surface binding energy of gallium is much higher than that of arsenic [4.36].

4.4.2 Electrical Damage

Electrical damage induced by ion beam etching of GaAs has been assessed by several researchers. A common method of assessment of damage is the use of capacitance-voltage (C-V) and current-voltage (I-V) measurements on Schottky barrier structures. Damage may be reduced by use of lower ion energies or an increase in the atomic number of the ion projectile [4.37]. Deterioration of electrical properties may exist to a depth of 100nm in GaAs [4.38] which is up to ten times greater depth than the structural
disruption as measured by TEM and AES [4.39]. The presence of chlorine gas in the chemically assisted process leads to a reduction in damage [4.40] which is attributed to the adsorption of molecular chlorine as a passivating adsorbate. Adsorption of NO₂ also reduces electrical degradation, but also reduces the etch rate by an order of magnitude due to the non-volatility of the reaction products [4.40]. Pearton et al [4.41] have shown that damage caused by low energy ions (<200eV) may be reduced by annealing at 773K, whilst damage caused by energies of 500eV are more thermally stable, requiring annealing to 1073K to partially restore the surface region. Similar damage processes have been reported for ion beam etching of InP structures [4.42]; these problems exist throughout III-V processing. Yuba et al [4.43] used deep level transient spectroscopy (DLTS) to study the defects induced by ion beam etching. They resolved five different defect centres at levels far below the ion range and with differing depth distributions.

4.4.3 Optical Damage

Ion assisted etching may also cause degradation to optical properties; Watt et al [4.44] used Raman scattering techniques to investigate the nature of damage to quantum dot structures. Damage was found to be restricted to the first few hundred angstroms. Quantum well structures have been used as in situ probes to measure damage caused by reactive ion etching [4.45]. Comparison of cathodoluminescent (CL) spectra provided a highly sensitive probe for assessment of device quality.
4.5.3 Surface Structure of GaAs(001): LEED Studies

The GaAs(001) sample was cleaned using the sequential IBA technique with the anneal temperature at 800K. The resultant surface exhibited a (4x1) reconstruction pattern. A diagrammatic representation of this pattern is shown in Figure 4.10. Dosing of 5L of Cl₂ on to the (4x1) reconstructed surface resulted in a (1x1) structure which gradually reconverted to a (4x1) pattern upon heating to 650K. The diffraction pattern appeared diffuse at all chlorine coverages greater than 5L.

4.5.4 Thermal Desorption Studies of Chlorine on GaAs(001)(4x1)

Thermal desorption studies were performed by adsorption of molecular chlorine upon an atomically clean GaAs(001)(4x1) reconstructed surface. The experimental details have been previously outlined in Chapter 2. The GaAs sample was maintained at two temperatures, 100K and 300K whilst Cl₂ dosing was performed.

4.5.4.1 Adsorption of Chlorine on GaAs at 300K: Gallium containing Desorption Products

The characteristics of the Ga-containing thermal desorption products are considered in this section. The mass fragments studied were Ga (69amu), GaCl (104amu), GaCl₂ (139amu) and GaCl₃ (174amu). These were the major products detected although both gallium and chlorine have two isotopes present in significant proportions [4.47]. Gallium has isotopes of mass 69 amu and 71 amu with natural abundance of 60.1% and 39.9% respectively. Chlorine has an isotope of 35 amu with an abundance of 75.8%, whilst the other major isotope (24.2%) has mass of 37 amu.

A series of desorption curves for Ga⁺ (69amu) are shown in Figure 4.11.
recording the intensity of the spectrometer signal at this mass versus crystal
temperature with increasing exposures of molecular chlorine upon the
GaAs(001)(4x1) surface. The heating rate employed for these TDS spectra was
2 K s\(^{-1}\). There are two main desorption peaks discernible which appear at two
distinct temperatures. The first to develop as a result of increasing Cl\(_2\)
exposure is at a peak maximum of 680-700K; this is assigned as the \(\beta\) peak.
Further exposure of chlorine does not appear to greatly increase the
magnitude of this peak. A second desorption peak, however, appears at a
lower temperature and with a significantly reduced signal intensity than the \(\beta\)
peak. This broad low temperature desorption peak has a maximum intensity
at approximately 450K. The activation energies for desorption for these states
may be calculated using the Redhead equation [4.48] (Equation 1.6). The
energies of desorption are 119 and 187-200 kJ mol\(^{-1}\) for the \(\alpha\) and \(\beta\) states
respectively. The pre-exponential factor is assumed to be \(10^{13}\) s\(^{-1}\). Uptake
curves for the desorption of this Ga\(^+\) (69amu) mass fragment are presented
in Figure 4.12. They show the TDS peak area of each Ga\(^+\) detected mass
fragment plotted versus increasing exposure of Cl\(_2\) (in Langmuirs). The curve
for the \(\beta\) peak increases sharply at low exposures with higher exposure
yielding a plateau where no further increase in signal is observed. This
behaviour is indicative of a state saturating at monolayer coverage.
Saturation occurs at approximately 5-10L exposure, which corresponds to a
dose of 1.1-2.2 \(\times 10^{15}\) Cl\(_2\) molecules cm\(^{-2}\) on the GaAs surface. The \(\alpha\) peak
does not appear until approximately 5L of chlorine has been dosed upon the
surface. This peak increases slightly upon further exposure to chlorine. The
uptake curve does not show saturation behaviour for this adsorption state,
but indicates that uptake into this state is slow.

The TD spectra for the GaCl\(^+\) detected mass fragment are presented in Figure
4.13 and show the intensity of the 104 amu mass spectrometer signal versus
the crystal temperature for increasing exposures of Cl\(_2\) to the GaAs surface. It
is clearly observed that the only peak present appears at 700K and saturates at
coverages of greater than 5L. This corresponds to the \(\beta\) state peak identified
for Ga (69amu) in Figure 4.11. The initial appearance of this state is at a
maximum of 670K and shifts to a higher temperature after exposures greater
than 0.5L of molecular chlorine. This behaviour is not noted in Figure 4.11 for Ga (69amu) desorption, although the peak shape at low coverages also differs slightly between these two states. The uptake curve for GaCl (104amu) is shown in Figure 4.14 and agrees closely with the behaviour of the Ga β state uptake curve shown in Figure 4.12. The β state signal appears to populate rapidly between 0-10L followed by saturation of the signal at higher chlorine exposures.

TD spectra for the GaCl₂⁺ mass fraction (139amu) are presented in Figure 4.15 and show one broad desorption peak appearing at approximately 500K. This corresponds to the α state isolated in Figure 4.11. The uptake curve for GaCl₂ α state is presented in Figure 4.16 and appears to build up with increasing exposure of molecular chlorine. This α state appears to develop slowly, but continuously, indicating that the sticking coefficient of molecular chlorine to the surface region has decreased markedly at this stage. The intensity of the GaCl₂⁺ peak is measured at a partial pressure of 10⁻¹³ torr in the mass spectrometer. This is an order of magnitude less intense than the Ga⁺ or GaCl⁺ signal.

The GaCl₃⁺ detected mass fragment exhibits similar behaviour to the observed GaCl₂⁺ signal. Only one desorption peak is apparent and corresponds to the α state detected for Ga (69amu) and GaCl₂⁺ (139amu). The α state signal is approximately one twentieth of the intensity of the GaCl₂ signal. The uptake curve for the GaCl₃ desorption products are presented in Figure 4.17 and show similar characteristics to the GaCl₂ fragment. Uptake appears slow, but continuous, upon prolonged exposure to chlorine.

Figure 4.18 shows a comparative analysis of TDS spectra for the Ga-containing mass fragments described previously. The spectra were recorded following an exposure of 15L of chlorine upon the clean GaAs surface. The figure clearly shows the two desorption states and their relative intensities for each mass fragment. An analysis of the relative intensities of all the GaClₓ (x=0-3) allow the low temperature peak to be assigned as
originating from the desorbing GaCl$_3$ species (with Ga and GaCl$_2$ intensity arising through parent ion fragmentation in the mass spectrometer). The $\beta$ state signal, however, appears to derive from a strongly bound gallium monochloride species. High temperature background levels for GaCl$_2$ and GaCl$_3$ do not contribute to the GaCl signal and hence the $\alpha$ and $\beta$ states derive from two distinct surface phases. The nature of the adsorbate-surface region, the desorption products and their implications for thermal etching of GaAs are fully discussed in section 4.6.
Figure 4.9 Auger Electron Spectrum of an atomically clean GaAs(100)(4x1) reconstructed Surface

- Ga 55eV
- As 32eV

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Figure 4.10  LEED pattern observed for GaAs(001) clean surface
Figure 4.11 Thermal Desorption Spectra of Ga+ (69amu) mass fragment at increasing exposures of Cl$_2$.

Figure 4.12 Uptake Curve for TDS Spectra of Ga showing Peak Area plotted as a function of Chlorine Exposure (derived from spectra in Figure 4.11)
Figure 4.13 Thermal Desorption Spectra of GaCl⁺ (104amu) mass fragment at increasing exposures of Cl₂.

Figure 4.14 Uptake Curve for TDS Spectra of GaCl showing Peak Area plotted as a function of Chlorine Exposure (derived from spectra in Figure 4.13).
Figure 4.15 Thermal Desorption Spectra of GaCl$_2^+$ (104amu) mass fragment at increasing exposures of Cl$_2$.

Figure 4.16 Uptake Curve for TDS Spectra of GaCl$_2$ showing Peak Area plotted as a function of Chlorine Exposure (derived from spectra in Figure 4.15).
Figure 4.17 Uptake Curve for TDS Spectra of GaCl₃ showing Peak Area plotted as a function of Chlorine Exposure

Figure 4.18 Thermal Desorption Spectra for the Gallium containing mass fragments of 15L exposure of Cl₂ on GaAs(100)
4.5.4.2 Adsorption of Cl₂ on GaAs at 300K: Arsenic containing Desorption Products

Thermal desorption spectra of arsenic containing desorption products are now presented to complement the data on the Ga-desorption products presented in the previous section. The mass fragments studied were As⁺ (75amu), AsCl⁺ (110amu), AsCl₂⁺ (145amu), AsCl₃⁺ (180amu) and As₂⁺ (150amu).

A series of TD spectra is shown in Figure 4.19 for the As⁺ (75amu) detected mass fragments following increasing exposure of the GaAs surface to molecular chlorine. One distinct peak is clearly apparent, at 700-750K. The uptake curve for these spectra is shown in Figure 4.20 and shows a rapid rise in signal at low chlorine coverage whilst at increased coverage the signal increases slowly. This is identified as the As β peak and differs from the Ga β in that complete saturation does not occur. The peak intensity rises slowly over very large exposures of chlorine. The As β peak increases in intensity up to exposures of 1000L. Continued chlorine exposure causes a reduction in the rate of increase of peak intensity without saturation of the state.

A series of TD spectra for the AsCl⁺ (110amu) detected mass fragment with increasing Cl₂ exposure is shown in Figure 4.21. It is noticeable that a decreasing signal is immediately apparent upon starting the desorption experiment. This is due to spontaneous desorption of products at 300K. A desorption state exists below 300K and low temperature TDS results are presented in section 4.5.4.3 to witness this statement. A peak is observed at a similar (high) temperature as that of the β peak for the As mass fragment in Figure 4.19. An uptake curve for AsCl for this high temperature β desorption is presented in Figure 4.22. The curve displays a steady rise in signal as the chlorine exposure is increased.

TD spectra for the more highly chlorinated As mass fragments were then studied. The AsCl₂ spectra are shown in Figure 4.23 revealing that at low
chlorine coverages only one peak is observed. This arises at approximately 680K and grows in intensity with increasing chlorine exposure. At exposures of 250L another state centred at 450K appears. These two states correspond closely with the α and β peaks of the Ga-containing fragments and possess energies of desorption of similar, although not identical, values i.e. 119 and 187 kJ mol$^{-1}$ for the α and β states respectively. A similar series of curves are observed for the AsCl$_3$ (180amu) mass fractions. The curves for AsCl$_2$ uptake are presented in Figure 4.24 and show that the β state saturates at an exposure of approximately 25L whilst the α state continues to populate at increasing exposures of molecular chlorine.

In addition to the arsenic chloride mass fragments, arsenic may be lost in a molecular form. The existence of both dimeric and tetrameric arsenic is well known. The TD spectra shown in Figure 4.25 for desorption of the As$_2$ mass fragment with increasing chlorine exposure reveals only small losses of this species from the surface. A single desorption peak is found at 700K which rises rapidly at exposures of chlorine up to approximately 25L and then rises at a slower gradient. The uptake curve is presented in Figure 4.26 for the peak area of the As$_2$ mass fragment versus chlorine exposure. Initial dosing with the halogen results in a high initial gradient but prolonged exposure shows a reduction in the rate of loss of this phase.

### 4.5.4.3 Adsorption of Cl$_2$ on GaAs at 100K: Arsenic containing Desorption Products

Evidence from adsorption studies of chlorine on GaAs in the previous section suggest that the spontaneous evolution of some species occurs at temperatures below 300K. Results are presented in this section to isolate adsorption states at low temperatures. Liquid nitrogen cooling was employed to cool the crystal surface to 100K. The AsCl$_x$ (x=0-3) mass fractions were recorded. A typical spectrum is shown in Figure 4.27 for AsCl. The spectra shows an intense broad peak labelled γ arising at 160K. The less intense broad state with a peak maximum between 410-450K equates to
the \( \alpha \) state observed in the 300K adsorption studies in the previous section. At low exposure of chlorine the \( \alpha \) state appears before the \( \gamma \) state populates. It is also noticeable that no \( \beta \) state is observed. The uptake curves for AsCl peak signal intensity are plotted against exposure to chlorine and are presented in Figure 4.28. The \( \gamma \) peak populates rapidly upon exposure to 7L of Cl\(_2\) (2.9 x 10\(^{15}\) molecules cm\(^{-2}\)) and continues to populate at a reduced rate upon increasing chlorine exposure. The \( \alpha \) state also populates rapidly to a maxima around 7L, but this state saturates at higher chlorine doses. The activation energies of desorption associated with these states can be calculated by use of the Redhead equation [4.48]. The \( \gamma \) state has \( E_{\text{des}} = 42 \) kJ mol\(^{-1}\) whilst the value for the \( \alpha \) state is 115-128 kJ mol\(^{-1}\). The \( \gamma \) state has a desorption energy that may be expected for a physisorbed species as in the case of Br\(_2\) adsorption on Si(001). The appearance of this peak for AsCl\(_x\) species, however, witnesses a low temperature reaction.
Figure 4.19 Thermal Desorption Spectra of As⁺ (75amu) mass fragment at increasing exposures of Cl₂

Figure 4.21 Thermal Desorption Spectra of AsCl⁺ (110amu) mass fragment at increasing exposures of Cl₂
**Figure 4.20** Uptake Curve for TDS Spectra of As showing Peak Area plotted as a function of Chlorine Exposure (derived from spectra in Figure 4.19)
Figure 4.22 Uptake Curve for TDS Spectra of AsCl showing Peak Area plotted as a function of Chlorine Exposure (derived from spectra in Figure 4.21)
Figure 4.23 Thermal Desorption Spectra of $\text{AsCl}_2^+$ (145amu) mass fragment at increasing exposures of $\text{Cl}_2$.

Figure 4.24 Uptake Curve for TDS Spectra of $\text{AsCl}_2$ showing Peak Area plotted as a function of Chlorine Exposure (derived from spectra in Figure 4.23).
Figure 4.25 Thermal Desorption Spectra of $\text{As}_2^+$ (150amu) mass fragment at increasing exposures of $\text{Cl}_2$
Figure 4.26 Uptake Curve for TDS Spectra of As2 showing Peak Area plotted as a function of Chlorine Exposure (derived from spectra in Figure 4.25)
Figure 4.27 Thermal Desorption Spectra of AsCl⁺ (110 amu) mass fragment at increasing exposures of Cl₂ at low temperatures (100K)
Figure 4.28 Uptake Curve for TDS Spectra of AsCl showing Peak Area plotted as a function of Chlorine Exposure at Low Temperatures (100K)
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4.5.5 Ion Interactions with Chlorine/GaAs Surfaces

4.5.5.1 Bombardment of Chlorine/GaAs(001) by Argon Ions - Gallium containing Desorption Products

Clean GaAs(001) surfaces were exposed to a flux of molecular chlorine and then irradiated with argon ions and neutrals generated from the AS10 source described previously. The perturbations of the adsorbate covered surface by the argon ions were studied by measurement of thermal desorption spectra for a fixed chlorine dose with increasing ion exposure. This gave information on the rate of loss of a particular species, or the change in the nature of desorption products.

The Ga (69amu) mass fragment was initially investigated. Two constant chlorine exposures of 0.5 and 150L were used and TD spectra are presented in Figures 4.29 and 4.30 respectively. The 0.5L exposure exhibits only the β state whereas the 150L dose also shows a small α state. Irradiation of these surfaces was performed using 550eV Ar+ ions from the VSW AS10 sputter gun with a beam flux of 3μA cm⁻² s⁻¹. The descending spectra show surfaces that were exposed to increasing ion doses. The peak areas from these spectra are plotted as semi-log values versus the ion dose. These are shown in Figures 4.31 and 4.32 for 0.5L and 150L exposures respectively. It is clear that the peak area decreases with increasing ion exposure, but closer inspection reveals that for 150L coverage, the β state peak area increases at initial ion dose conditions. For 0.5L coverage peak area remains constant initially, followed by erosion of the β state. The appearance of a broad peak at 550-600K is apparent at high ion dose, in addition to the β peak. This desorption feature is described as the β₁ desorption peak.

The GaCl⁺ mass fragment signal was similarly investigated and the TD spectra for increasing ion exposure are shown in Figure 4.33 with the equivalent semi-log peak displayed in Figure 4.34. The chlorine exposure for this set of TD spectra was 0.5L. Increased ion irradiation revealed that the peak
area increased initially with ion dose. Further ion bombardment resulted in gradual slow erosion of the phase. The $\beta_1$ state appeared during this course of ion exposures, although this overlaps with the $\beta$ peak. At high ion doses ($>10^{17}$ ions cm$^{-2}$) a broad low temperature peak is observed at approximately 480K. This is the value at which the $\alpha$ GaCl$_2$ state occurs. The erosion of the GaCl peak is not linear and the low cross-section values varies with adlayer coverage.

The GaCl$_2$ (139amu) peak studied is believed to derive from GaCl$_3$. The mass spectrometer signal, however, has a greater intensity than GaCl$_3$ thus is easier to study. The TD spectra at increasing ion exposures are presented in Figure 4.35 with the semi-log plot of ln peak area versus ion dose displayed in Figure 4.36. This set of spectra reveal a characteristic broad GaCl$_2$ peak at approximately 480K. The effect of ion irradiation is very rapid removal of this phase to the effect that an ion dose of $4.5 \times 10^{13}$ argon ions cm$^{-2}$ removes 90%.

The spectra obtained for the ion beam bombardment experiments are discussed in detail in a subsequent section. Similar experiments were performed, however, using neutral argon beams and the results are presented below.

### 4.5.5.2 Bombardment of Chlorine/GaAs(001) by Ar Neutrals - Gallium containing Desorption Products

Similar experiments were performed to those in the previous section, but an Ion Tech saddle field FAB source was employed. A range of beam energies and beam densities were used to study the effect that different conditions cause on the adsorbate covered surface. A constant initial surface coverage was studied with a clean GaAs(001)(4x1) reconstructed surface was studied (150L of chlorine molecules).

The GaCl (104amu) mass fragment was studied in detail. The gallium trichloride and its associated dichloride cracking fragment, however, were
found to possess very rapid erosion characteristics and therefore useful information was not obtained using this technique. The TD spectra for the GaCl fragment after an increasing neutral beam exposure to a 1kV beam generated from a 3mA discharge and possessing an equivalent beam density of 6.4×10^{13} \text{Ar}^0 \text{cm}^{-2}\text{s}^{-1} are shown in Figure 4.37(a). The spectra show the erosion of the high temperature peak at 680K with argon neutral bombardment. Increasing ion dose leads to a broadening of the peak and an increasing signal background at temperatures above 600K. At irradiation levels of greater than 5×10^{16} \text{Ar}^0 \text{cm}^{-2} the desorption peak maximum decreases to 650 K and GaCl signal is detected at 400 K upon commencement of the heating cycle. In addition, the mass spectrometer detects a strong GaCl signal prior to TD spectra being recorded.

Figure 4.37(b) shows the TD spectra for irradiation of the adsorbate-surface with a 1kV neutral beam generated from a 40mA discharge current with an equivalent beam density of 5.6×10^{14} \text{Ar}^0 \text{cm}^{-2}\text{s}^{-1}. It is observed that the characteristic desorption peak is almost obscured by the raised background level. There is a noticeable GaCl signal after beam irradiation. Figure 4.37(c) shows exposure of the 150L exposed surface with a higher energy (2.5kV) beam of argon neutrals generated from a 40mA discharge. The equivalent beam density of 34\mu A \text{cm}^{-2}\text{s}^{-1} is identical to the beam flux employed at the lower energy. Observation of the GaCl desorption peak reveals erosion and broadening of the desorption curve alongside a significant shift to lower temperature desorption. This occurs at 550-600K with increasing neutral dose and results in removal of the high background levels observed in Figures 4.37(a) and (b). A curve showing the peak area (ln) as a function of increasing neutral irradiation is shown in Figure 4.38 for these three sets of spectra displayed in Figures 4.37(a)-(c).

To investigate the effects of significantly higher chlorine exposures to the GaAs surface extremely large dose of molecular chlorine (>50kL) was undertaken. This surface was then irradiated with 1kV argon neutrals at a beam density of 6.4 \times 10^{13} \text{cm}^{-2}. The resultant TD curve is displayed in Figure 4.39. The GaCl signal observed shows the high temperature peak at a lower
temperature (580K) as described previously. In addition to this the profile of the peak is sharp compared to the broad character of the curves shown earlier. Further work was not be performed due to the detrimental effects to the performance of the UHV system by these high exposures of molecular chlorine.

4.5.5.3 Bombardment of Chlorine/GaAs(001)- Arsenic containing Desorption Products

The thermal data from the study of molecular chlorine adsorbed on GaAs(001) shows the major desorption products are removed below ambient temperature (300 K). The AS10 ion beam source was employed in this phase of experimentation with a 550eV beam of argon ions produced with a beam density of 3μA cm⁻² s⁻¹.

The irradiation of a 750L chlorine covered GaAs surface for the As (75amu) mass fragment is shown in Figure 4.40 with the non-irradiated peaks appearing at 500K(a) and 650K (b) respectively. A high background peak appears at temperatures above 700K. Bombardment of the surface leads to rapid but not complete erosion of the α peak with slower subsequent erosion of the β peak. The semi-log plot of ln peak area versus ion dose is shown in Figure 4.41. Ion bombardment appears to reduce the background signal produced at high temperatures. The AsCl₂ desorption intensity is also studied after ion beam irradiation of the surface. Figure 4.42 shows a series of TD spectra following increasing ion exposure. The two shallow peaks observed appear to be only slowly eroded by the argon ions and this is verified by the plotted erosion curve in Figure 4.43.

The results obtained for thermal reactions and ion-assisted perturbation are now discussed to develop mechanistic descriptions of the surface processes leading to etching of GaAs. Implications for device processing are also discussed.
Figure 4.29 Thermal Desorption Spectra for Ga (69amu) as a function of Ar⁺ Ion Irradiation (0.5L chlorine exposure)

Figure 4.31 Semi-log plot of Thermal Desorption Peak Intensities for Ga as a function of Irradiation by Argon Ions (550eV following chlorine exposure (0.5L) of GaAs(001) surface
Figure 4.30 Thermal Desorption Spectra for Ga (69amu) as a function of Ar⁺ Ion Irradiation (150L chlorine exposure)

Figure 4.32 Semi-log plot of Thermal Desorption Peak Intensities of Ga as a function of Irradiation of Argon Ions (550ev) following chlorine exposure (150L) on GaAs(001)
Figure 4.33 Thermal Desorption Spectra for GaCl (104amu) as a function of Ar⁺ Ion Irradiation (0.5L chlorine exposure)

Figure 4.34 Semi-log plot of Thermal Desorption Peak intensities for GaCl as a function of irradiation by argon ions (550V) at 0.5L chlorine coverage on GaAs
Figure 4.35 Thermal Desorption Spectra for GaCl$_2$ (139amu) as a function of Ar$^+$ Ion Irradiation (150L chlorine exposure)

Figure 4.36 Semi-log plot of Thermal Desorption Peak Intensities for GaCl$_2$ as a function of Irradiation by Argon Ions (550eV) following chlorine exposure (150L) of GaAs(001) Surface
Figure 4.37(a) Thermal Desorption Spectra for GaCl (104amu) as a function of Ar neutral Irradiation (3mA, 1keV)

Figure 4.37(b) Thermal Desorption Spectra for GaCl (104amu) as a function of Ar neutral Irradiation (40mA, 1keV)

Figure 4.37(c) Thermal Desorption Spectra for GaCl (104amu) as a function of Ar neutral Irradiation (40mA, 2.5keV)
Figure 4.38 Semi-log plot of Thermal Desorption Peak Intensities of GaCl as a function of Irradiation by Argon Neutrals following chlorine exposure of GaAs(001) surface (150L)
Figure 4.39 Thermal Desorption Spectra for GaCl (104amu) as a function of Ar neutral Irradiation (3mA, 1keV) at large chlorine exposure (>50kL)

Figure 4.40 Thermal Desorption Spectra for As (75amu) as a function of Ar+ Ion Irradiation (750L chlorine exposure)
Figure 4.42 Thermal Desorption Spectra for AsCl$_2$ (145amu) as a function of Ar$^+$ Ion Irradiation (150L chlorine exposure)
4.6 Analysis and Discussion

The results presented in the previous section are now discussed in order to form an understanding of the nature of the chemical processes at the Cl$_2$/GaAs interface during thermal and ion-assisted etching. The adsorption process, structure of the adsorbed phase on the surface, and the reaction products are all considered. Furthermore, the surface stoichiometry during thermal and ion-assisted reactions of halogens with GaAs surfaces is of considerable significance. The nature of Cl$_2$ reaction on GaAs surfaces is still generating controversy in terms of the detailed processes occurring at the surface. A number of methods have been used to elucidate the pertinent mechanisms. Firstly, the technique of TDS may be used in conjunction with AES, XPS and LEED. A number of researchers have also employed modulated molecular beam (m.b.) studies to determine kinetic parameters and to elucidate the timescale of some of the fast processes that occur upon ion irradiation of the surface. Furthermore, scattering techniques such as LEIS have been utilised to probe the structure of the surface region. It has been noticed from the literature that many investigations of the Cl$_2$/GaAs system do not appear to consider surface reconstruction structures to be an important parameter in the determination of the reaction chemistry. In addition, the conditions under which experiments have been performed differ greatly, thus leading to what at first sight appear to be contradictory observations. This discussion also considers m.b and LEIS results, as well as TD data, thereby forming a coherent picture of the thermal and ion-assisted etching processes using the new results achieved during this study to complement existing studies on this etching system.

4.6.1 Chlorine Adsorption on the GaAs(001) Surface:

The results presented in the previous section (4.5.2) for TDS, AES and LEED analysis of the Cl$_2$/GaAs adsorption system are now discussed in order to clarify the current state of understanding of this complex reactive system. It is convenient to assess the nature of the desorption products in terms of,
firstly, Ga-containing desorption products and secondly the As-containing desorption products.

4.6.1.1 Analysis of Desorption Products

The TD data for Ga-containing desorption products indicates adsorption of molecular chlorine on GaAs(001) appears to be at least a two stage process. The first process is the formation of a β state for the Ga and GaCl detected mass fractions as shown in Figures 4.11 and 4.13. No signal is detected for GaCl$_2$ or GaCl$_3$ mass fragments at this high (~700K) temperature. This desorption peak is believed to correspond to the formation of a strongly bound chemisorbed state. This β state signal is observed to saturate rapidly and is fully populated (0.5L) at low exposures. The saturation coverage occurs at an exposure of approximately 5L of Cl$_2$, which equates (assuming a sticking coefficient of unity) to a surface coverage of $1.12 \times 10^{15}$ Cl$_2$ cm$^{-2}$. This is in reasonable agreement with known XPS uptake studies [4.50]. Following saturation of the β state, a low temperature peak populates and is designated as the α state. The sticking probability of Cl$_2$ forming this phase is considerably lower than the initial sticking coefficient which exists for the population of the β state. Furthermore, the Ga-α state does not saturate upon prolonged chlorine exposure. This behaviour strongly suggests the β phase is a two dimensional chemisorbed adlayer consisting of chlorine to surface Ga bonds. The GaAs(001)(4x1) Ga-rich reconstruction is observed to change to the (1x1) structure upon adsorption of molecular chlorine. This shows strong agreement with other researchers [4.51]. Drathan et al [4.28] showed that this change in reconstruction results in a surface with a greater concentration of As ($4x1 \theta_{AS}=0.22$; $1x1 \theta_{AS}=0.50$). Clearly As segregates to the surface upon adsorption of Cl$_2$ on the GaAs surface. Margaritondo et al have also shown the preferential adsorption of Cl$_2$ onto As sites of the GaAs(110) cleavage plane [4.58]. TDS data, however, supports bonding of chlorine to the Ga-rich surface. The TD data for the As mass fragment reveals similar behaviour to the Ga and GaCl fractions, although at low surface concentrations. A high temperature adsorption phase
is observed which fully saturates at high chlorine exposure. This fragment appears to derive from both the As$_2$ and the halogenated AsCl$_x$ (x=1-2) desorption products. This As-β state is observed at a slightly higher temperature than the GaCl desorption peak thus strongly implying that As$_2$ is lost to restore the stoichiometry of the surface region. This As$_2$ loss allows the surface to reconstruct from the (1x1) to the (4x1) surface phase rather than remain As-rich state. At increased Cl$_2$ coverages this high surface concentration of arsenic formed by segregation may compete to desorb as As$_2$ or AsCl$_3$. The chlorine dose required to saturate the As β state, however, is approximately 2000L and corresponds to an impinging flux of $4.5 \times 10^{17}$ molecules cm$^{-2}$. This value is much more than is required to form a single AsCl layer on the surface and this amount of chlorine is unlikely to exist in the surface region at any time. This suggests that spontaneous desorption of AsCl$_3$ occurs at 300K with a concurrent excess of As at the surface region. This high As concentration at the surface allows chlorine molecules to continue to adsorb to the surface at high exposure.

Thermodynamic considerations support desorption of As$_2$ rather than arsenic chlorides and this is witnessed by experimental evidence. Figure 4.44 [4.52] presents thermodynamically predicted product phase diagrams for the Cl/GaAs system at 300K. In chlorine deficient systems the As$_2$ species is preferentially formed rather than AsCl$_3$. Calculations were not performed, however, for less halogenated AsCl species. Furthermore, GaCl$_2$ is thermodynamically predicted at low halogen concentrations. Thermodynamic calculations for CVD gas phase reactions of GaAs and Cl$_2$ show that As$_4$ is formed preferentially to As$_2$ and AsCl$_3$ when an excess of GaAs is present [4.53]. These are computations for gas phase reactions, however, and may not be applicable for a surface reaction.

The Ga α state signal is proposed to be due to the growth of a 'corrosion' phase caused by mixing of the chlorine and GaAs in the surface region. The process that occurs shows analogous behaviour to the Mott-Cabrera field-assisted diffusion mechanism [4.54] observed in the previous analysis of the silicon-bromine adsorption system. Figure 4.45 presents a plot of $1/X$ (X= α
state peak area) versus In Cl$_2$ exposure for the low temperature Ga$_2$ desorption peak observed in Figure 4.15. This plot clearly shows a linear trend over an extended region of prolonged halogen exposure. This is preceded by a period of non-conformity to this model as the monolayer to corrosion layer phase transition occurs. The observed features are attributed to the formation of an electrochemical potential between the corrosion layer and the bulk GaAs structure. This potential is less than that expected for a corrosion layer-metal interface, thus build up of this phase is comparably slow. There is no spontaneous desorption (or etching) of this phase at room temperature and hence the growth of the Ga-α state appears to represent the α GaCl$_x$ phase, where x>2. A similar α state for the GaCl$_3$ detected mass fraction is also observed and thus the thermodynamically preferred GaCl$_3$ species also exists (see accompanying Table 4.1).

If the TD data is compared to published cracking patterns [4.54(a)] information may be obtained on the gallium containing desorption products. Table 4.2 presents product distribution data (corrected for isotopic and sensitivity effects) for the gallium containing desorption mass fragments at 15L and 150L Cl$_2$ exposure. In the case of the lower dose, the intensity of the GaCl$_3^+$ signal is less than would be expected from the published cracking information and therefore some GaCl$_2$ may be expected as a desorption product. Furthermore, there appears to be a strong GaCl fragment and thus the reaction products may consist of GaCl$_x$ (where x=1-3). At high coverages the cracking patterns show reasonable agreement with the published data. This indicates that at high chlorine coverages, the desorption product consists mainly of GaCl$_3$ in the low temperature regime. It is possible, however, that this state also represents desorption of GaCl$_2$.

The use of molecular beam modulation experiments can provide an insight into the kinetics of the thermal reaction process. Balooch et al [4.55] measured the reflected chlorine and reaction product signals using in-situ mass spectrometry, as a function of GaAs substrate temperature. They calculated the total reaction probability for thermal reaction of Cl$_2$ and GaAs to be 0.002 at 300K. At 450K the reaction probability had increased to 0.3 corresponding to
emission of AsCl₃ and GaCl₃. It was observed that the reaction rate for formation of the trichloride species decreased rapidly at high temperatures. Thermal etching at increasing rates continuing due to the formation of both the gallium and arsenic monochloride species. This is clearly in agreement with the TDS results obtained in this study. At temperatures of 700K the total reaction probability is approximately 0.5 with no evidence of saturation of the reaction rate. Balooch et al [4.55] employed a modulated Cl₂ beam at 20Hz with a flux of \(1.2 \times 10^{15}\) molecules cm\(^{-2}\) which is equivalent to a 5L dose per pulse. TD studies have shown this exposure to be enough to form a Cl monolayer on the GaAs surface. At low substrate temperatures AsCl₃ and GaCl₃ were detected whilst at high temperatures (700K) they detected AsCl and GaCl as shown in Figure 4.46.

Recent TD experiments by Liberman et al [4.56] of the reaction of the GaAs(110) with Cl₂ suggest that no GaCl₃ species are desorbed. For the case of GaAs(100) our adsorption studies at 350K in Figure 4.15 and those of French et al [4.50] at 175K show desorption of GaCl at between 300-500K. A molecular beam study of Cl₂ with GaAs (orientation not specified) by Hou et al [4.57] has fuelled the controversy regarding the thermal reaction mechanism. They observed only three neutral reaction products, GaCl₃, AsCl₃ and As₄. Arsenic trichloride is detected at low temperatures, whereas As₄ is detected at high temperatures, although the coverage dependence of reaction products is not addressed.

4.6.1.2 Mechanism for Thermal Etching based on TDS Studies of GaAs/Cl₂

A model for thermal etching is proposed on the basis of TDS results presented in this study. A schematic of this mechanism is shown in Figure 4.47. Three regimes of surface coverage of Cl₂ on GaAs are considered.

(i) low coverage 
(ii) medium coverage 
(iii) high coverage 

sub-monolayer 
5-15L 
'corrosion' layer >15L
Chapter 4: Analysis and Discussion

The basis for the model is that Ga and As loss due to thermal etching must be equal to maintain stochiometry. To be able to regenerate a consistent reconstructed surface this must be a reasonable assumption, although some thermal etching studies [4.55] have shown that at typical etching temperatures a gallium rich surface may be found. This effectively limits the rate of subsequent reaction, and is consistent with the lower vapour pressure of GaCl₃ compared to AsCl₃.

The low coverage regime shown in Figure 4.47(a) shows a strongly bound gallium monochloride phase which is formed upon dissociative chemisorption of the chlorine on the surface gallium of the GaAs(001)(4x1) reconstructed surface. Thermal desorption studies of this phase from Figure 4.13 reveal a GaCl reaction product with surface stoichiometry maintained by desorption of As₂. The evidence for desorption of As₂ at low Cl₂ exposures comes from the TDS spectra of the detected mass fragments As⁺ and As₂⁺ as shown in Figures 4.19 and 4.25.

The medium coverage regime shown in Figure 4.47(b) may be described by a thin layer of chlorinated GaAs. The impinging flux in this regime is between 1 x 10¹⁵ and 1 x 10¹⁶ chlorine molecules cm⁻². The adsorption of molecular chlorine over half monolayer coverages lifts the (4x1) reconstruction thus exposing As to the chlorine impinging on the surface. Margaritondo et al [4.58] have shown that chlorine preferentially chemisorbs to As sites and hence a process of surface segregation is most probable. Recent studies by Mokler et al, however, show that chlorine preferentially adsorbs on the Ga defect sites of an As rich surface [4.59]. The gallium is lost as the trichloride as deduced from the TD spectra for GaCl₂ and GaCl₃ fragments. The gallium dichloride is assumed to be found as part of the fragmentation pattern of GaCl₃ in the mass spectrometer. The arsenic is lost as As₂, but at high temperatures a residual sub-monolayer coverage is left which is tenaciously bound to the surface and may desorb as the arsenic monochloride (AsCl) species. This state exists when sufficient population of the surface is allowed. The sticking coefficient of molecular chlorine rapidly decreases after monolayer saturation has occurred. The desorption products at low
Chapter 4: Analysis and Discussion

temperature are revealed to be GaCl$_3$ and AsCl$_3$, whilst after depopulation occurs at high temperatures the monochlorides of gallium and arsenic are the last desorption products alongside the arsenic dimers desorbed to maintain surface stoichiometry.

The desorption of the molecular chlorine fragment (70amu) at high coverages has also been studied and found to desorb with increasing linearity during the course of a thermal desorption cycle. At medium to high coverages there is some controversy over the detection of arsenic monochloride as a desorption product rather than desorbed arsenic. TDS studies show a high temperature AsCl desorption peak (Figure 4.21) and Balooch et al [4.55] also detect an AsCl 'parent' signal in their modulated beam studies. The degree of chlorine coverage on the GaAs appears to be a significant factor in the desorption products observed as shown in the previous discussion on coverage regimes. Most modulated beam studies of thermal and ion-assisted processes are only able to select a limited range of conditions. This study has covered a large range of temperature and exposures in order to resolve the ambiguities raised by the existing modulated beam and scattering experiments.

As mentioned previously, there is considerable debate upon whether dimeric or tetrameric arsenic is the species that desorbs at high temperature to maintain stoichiometry of the GaAs. Hou et al [4.57] claim to have observed As$_4$ during a molecular beam study at surface temperatures of 550K. The crystal orientation of the GaAs and details of molecular beam flux are not reported in their study and hence the applicability to this discussion is tempered by a lack of knowledge of precise experimental conditions. The results in this study have shown an absence of As$_4$ species, although this fragment's mass unit is on the limit of detectability for the 300amu mass spectrometer. As$_3^+$ species were not observed and hence it is assumed that As$_4$ is not a reaction product. No other reports of tetrameric arsenic detection exist in the literature for this thermal etching reaction apart from recently reported thermal reactions by Liberman et al [4.56]. Chatillon and Bernard [4.53] performed thermodynamic calculations for the GaAs-Cl system.
for application to the CVD growth of GaAs thin films and predicted that at 550K GaCl₃ and As₄ should be the major reaction products. Hou et al [4.57] utilised a very high chlorine exposure for their observations of arsenic trichloride in this reaction system.

Ha et al [4.60] have described the reaction of GaAs with chlorine as a two step process where the first step consisted of a rapid chlorination of all 'dangling bonds' on the GaAs surface to form surface bonded dihalides such as GaCl₂ and AsCl₂. The rate controlling second step produced volatile AsCl₃ which covered the surface at high Cl₂ pressures. These experiments were performed under real etching conditions at chlorine fluxes of up to $4.5 \times 10^{21}$ molecules cm⁻² s⁻¹ at crystal temperatures of 300-450K. The desorption activation energy for the reaction is quoted as 59kJ mol⁻¹ at pressures of 10 torr, whilst at lower pressures this value increased to 99kJ mol⁻¹. These values are low compared to our rate limiting value of 119kJ mol⁻¹ for GaCl₃ desorption. The pressure gap, however, is eight to ten orders of magnitude. Evidence for a precursor mediated etching reaction between Cl₂ and GaAs(110) surface has recently been presented by DeLouise [4.61,4.62]. Using angle resolved supersonic beam scattering techniques to study the dynamics of this reaction have revealed a key intermediate to be (Cl₂)ads. Implications of this are that, even at high flux conditions, the reaction rate may become Cl₂ flux limited since a lower concentration of surface intermediate species will be available for reaction.

The ion provoked modifications to this thermal etching mechanism are now considered.
Figure 4.44 Thermodynamically Predicted Reaction Product Phase Diagrams for the GaAs/Cl₂ System
Figure 4.45 Mott-Cabrera Plot of 1/Peak Area versus lnE for GaCl2
Figure 4.46 AsCl$_x$ and GaCl$_x$ Ions detected mass spectrometrically as a function of surface temperature.

[M. Balooch, D.R. Olander and W.J. Seikhaus
Figure 4.47 Schematic showing the Desorption Products for the Thermal Etching of GaAs with molecular chlorine at varying surface coverages.
### Table 4.1 Thermodynamic Data for GaCl\textsubscript{x} Species

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</tr>
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Table 4.2 Cracking Patterns of Gallium/Gallium Chloride Mass Fragments (15L and 150L chlorine exposure)

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<tbody>
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<td>β</td>
<td>α</td>
<td>β</td>
<td></td>
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4.6.2 Beam Assisted Reactions of GaAs with Halogens

With a good understanding of the adsorption process and subsequent thermal reactions of chlorine on GaAs it is now possible to discuss the results presented in section 4.5.5 for inert ion and neutral irradiation of this surface. The results are considered in the overall context of surface engineering of sub-micron device structures. A number of real etching applications utilise ion, neutral, electron and laser sources to enhance the reaction rate. It is clear that the etching mechanism of the Cl₂/GaAs/Ar⁺ reaction is critical to the discussion and modification to any of the existing etch technologies. The analysis of ion beam cross sections for loss of the desorption phase is a useful method for providing mechanistic information.

4.6.2.1 Ion/Neutral Beam Induced Cross Sections

Inspection of the data presented previously for ion/neutral beam irradiation of the chlorine/GaAs(001) surface region suggests that simple erosion of the surface states in the reverse order of formation does not occur. Furthermore, it is clear that conversion of the strongly bound phases to the more weakly bound states as proposed previously for the silicon/bromine system does not occur. The behaviour of the desorption states upon irradiation, however, still exhibit some intriguing features. This is particularly true of the increases in intensity for the strongly bound GaCl phase. Extended ion/neutral exposure leads to the eventual removal of all bound forms on the surface. An ion dose of approximately 1x10¹⁷ ions cm⁻² is necessary to achieve this, although some states such as the low temperature GaCl₂ phase deplete very rapidly. The perturbations to the surface during this period of ion bombardment may have a profound and sometimes damaging effect on the surface region of the GaAs.

The nature of ion interactions may be considered by derivation of the cross section of desorption of phases from the surface region. This method has been demonstrated in the previous chapter to be useful for the determination
of ion-assisted reaction mechanisms. This data also provides a complementary database to observations obtained from modulated ion beam and LEIS studies. Thus, a complete understanding of the qualitative chemical and physical processes which result from a CAIBE-type etch can be obtained. The expression used to obtain these cross sections has been described in Section 3.5.3.1 (Equation 3.3). The cross sections for loss/gain of intensity of desorbed phases are presented in Table 4.3.

The effect of ion bombardment of the surface as detected through the TDS spectra of Ga (69amu) is compared for two chlorine exposures. Firstly, a Cl$_2$ dose of 0.5L which corresponds to coverage of less than one monolayer and secondly a 150L dose, which has been shown to induce the formation of a highly chlorinated 'corrosion' layer at the surface. The low coverage surface when bombarded with 550eV Ar$^+$ ions yields the linear plot of Figure 3.31. The cross-section of desorption ($\sigma_1$) value obtained is $0.4\text{Å}^2$ over extended ion irradiation. Under initial bombardment (up to $2\times10^{14}$ Ar$^+$ cm$^{-2}$), however, the peak area does not erode upon ion impact. Furthermore, the higher coverage surface (150L) described in Figure 3.32 intriguingly shows an initial increase ($\sigma_2=2.5\text{Å}^2$) of the Ga$^+$ ion signal closely followed by an erosion process ($\sigma_3=1.6\text{Å}^2$). The GaCl$_2$ signal as plotted in Figure 3.34 also clearly exhibits this behaviour. The cross section for loss of the phase ($\sigma_5$) is $0.4\text{Å}^2$. This shows excellent agreement with the Ga loss ($\sigma_1$) and indicates that the signal derived from the tightly bound Ga-Cl species actually increases with low exposures of ions. Furthermore, the cross section for gain of the phase increases with Cl$_2$ exposure. The adsorption of chlorine is expected to lower the surface binding energy and hence reaction products should be more easily sputtered leading to a decrease in peak area of the detected signal. This process does occur at higher ion doses but low ion exposure actually increases the density of tenaciously bound Ga-Cl at the surface. It is clear that there are several possible mechanisms by which Ga-Cl concentration is increased. Firstly, ion bombardment may lead to segregation of Ga and As within the surface region resulting in the formation of a roughened Ga-rich surface. Secondly, intermixing of chlorine on the surface into the bulk may lead to formation of GaCl in the near surface
region. It is possible that AsCl\textsubscript{x} species donate Cl atoms to unbound Ga atoms at the perturbed surface. Thermodynamic data strongly suggests that this does not occur because AsCl\textsubscript{3} should spontaneously desorb from the surface. AsCl\textsubscript{x} species are observed occupying high temperature states and thus published gas phase thermodynamic data [4.52] may not be applicable. Ion enhanced sputtering of AsCl\textsubscript{x} from the surface may give rise to the effect by concurrently depleting the chlorine concentration in the surface region, whilst simultaneously increasing the gallium concentration at the surface. This scenario has been tentatively suggested by Balooch et al [4.55] as a limiting effect for purely thermal etching processes.

With regard to the removal of higher halides of gallium from the surface, there is considerable debate from modulated beam studies [4.55,4.64-65] whether the major ion induced desorption product is GaCl\textsubscript{2} or GaCl\textsubscript{3}. It is clear from this debate that GaCl\textsubscript{3} is the major thermal desorption product and hence the GaCl\textsubscript{3} signal detected largely derives from the GaCl\textsubscript{3} molecule. The transient cross section for ion-induced loss of the GaCl\textsubscript{3} phase is obtained by measuring the effect of ion impact on the GaCl\textsubscript{2}\textsuperscript{+} mass fragment. The data for ion induced desorption of GaCl\textsubscript{2} from the α state reveals a very fast ion induced erosion process with a cross section (σ\textsubscript{7}) of 126Å\textsuperscript{2}. This effectively means that all GaCl\textsubscript{3} is removed from the surface after 1 x 10\textsuperscript{14} Ar\textsuperscript{+} ions cm\textsuperscript{-2} of 550eV ion energy have impacted on the surface. It is known that the density of a Ga monolayer on the GaAs(100) surface is 6.26 x 10\textsuperscript{14} atoms cm\textsuperscript{-2}. The ratio of Ar\textsuperscript{+} ions to Ga surface sites is approximately 1:6. This ion coverage effectively clears the surface of all weakly bound species. In addition to this 'clearing' effect, bond breaking and incorporation of chlorine atoms into the surface is likely due to the collisional cascade processes resulting from ion impact on the surface. The rise in the density of GaCl species at initial ion impact is known to occur up to an ion dose of 5 x 10\textsuperscript{15} Ar\textsuperscript{+} ions cm\textsuperscript{-2}. Mass balance requires some Cl originally bound as GaCl\textsubscript{3} to be converted to GaCl during this initial ion bombardment regime.

Further investigation of the irradiation of Cl\textsubscript{2} dosed GaAs surface (150L) was performed using an Ion Tech FAB 114 neutral source with argon as the
energised gas. This source was used because of the greater range of beam energies and higher beam flux than the AS10 hot filament ion source used in the ion beam studies. Furthermore, there is considerable evidence that neutral beams are more effective for CAIBE-type etching of semiconductor systems due the reduction of electrical and optical damage to the sub-surface region. The inert neutral beam source was used in this study at three settings; 1kV (3mA), 1kV (40mA) and 2.5kV (40mA), thus the ion flux as well as ion energy were varied. The erosion curves presented in Figure 4.34 show cross-sections for loss of the GaCl phase which increase as both a function of neutral beam density and beam energy. It is clear from comparison of the 1kV beams at different ion flux (3mA $\sigma_9$; 40mA $\sigma_{10}$) that the cross sections for loss of the GaCl $\beta$ state shown in Table 4.6.1 increases with the higher equivalent ion flux. The cross section for loss also is larger as the beam energy increases as can be observed from the 40mA discharge at beam energies of 1kV ($\sigma_{10}$) and 2.5kV ($\sigma_{11}$) respectively.

4.6.2.2 Mechanisms for Ion Assisted Etching of GaAs with Cl$_2$

It is clear that enough information is available from TDS experiments of ion bombarded surfaces to consider the nature of the changes induced by the impinging beam. The model for thermal etching in the previous section ascribes GaCl$_3$ desorption to the presence of a multilayer corrosion phase containing GaCl$_x$, AsCl$_x$ (x=1-3), Cl and Cl$_2$. This phase changes rapidly upon beam exposure. A number of possible processes may occur which result in the loss of this phase by a fast event. Firstly, the energetic beam may sputter erode this weakly bound 'corrosion' layer. This enhancement of the sputter yield is due to the reduction of the surface binding energy caused by adsorption of chlorine upon the semiconductor surface. It is known that the impinging beam also causes ion induced mixing processes to occur into the sub-surface region. Data for the gas phase products suggests that GaCl is not the thermodynamically [4.52] or kinetically [4.60] preferred reaction product, however, it is likely that energy from the impacting ion provides the driving force to overcome the barriers for GaCl formation. A reaction of the form,
The reaction of fresh GaCl₃ adsorption with GaAs is thus being promoted by the ion beam. Further exposure of the surface to the ion beam causes the eventual complete removal of the GaCl phase. The above reaction under equilibrium conditions clearly inhibits ion-assisted etching. This is caused by formation of high temperature desorption products from the low temperature GaClₓ desorption phase. In order to produce the observed enhancement of the reaction the ion bombardment must support a fast etching process through some other mechanism. A reaction mechanism scheme is suggested which is consistent with the TDS data obtained. This contains three steps which are outlined in equations 4.2-4.4;

\[ \text{GaCl}_{(ads)} \xrightarrow{i} \text{GaCl}^*_{(ads)} \]  \[4.2\]

\[ \text{GaCl}^*_{(ads)} + \left\{ \frac{(x-1)}{2} \right\} \text{Cl}_2 \rightarrow \text{GaCl}^*_{x(ads)} \]  \[4.3\]

\[ \text{GaCl}^*_{x(ads)} \rightarrow \text{GaCl}^*_{x(g)} \]  \[4.4\]

The initial step (Eqn 4.2) in the proposed reaction sequence is the excitation of the adsorbed GaCl state by the ion beam. This is followed (Eqn 4.3) by interaction of gas phase Cl₂ with the activated surface to form an adsorbed species GaClₓ possessing a fast desorption rate. Clearly this activated state may also return to the initial state before reaction may take place. The final step (Eqn 4.4) of the ion-induced reaction sequence describes the emission of the GaClₓ species into the gas phase. This emissive event may occur via a thermal desorption process or by enhanced sputtering by a second impinging ion. The three combined reaction steps are fast (milliseconds) compared with the timescale of the TDS experiment (seconds). Studies on the InP(100)/Cl₂ system [4.66] show a similar mechanism to that predicted by the above scheme. They reveal, however, that the sputtered products change from In and P₂ to InCl and P₄ when chlorine is introduced to the etching sequence.
They also detect a change in peak profile for the InCl thermal desorption peak, which gradually merges into an intermediate binding energy to the α and β states at increasing ion beam exposure. It is clear, however, that beam exposure of greater than 20s completely removes the adsorbed surface phases and thus this is a relatively fast loss process.

4.6.2.3 Comparison of TD Mechanism with Other Studies

The use of modulated beam techniques and LEIS have generated considerable debate towards the description of a comprehensive mechanism for ion assisted etching of GaAs with halogens. This section incorporates the complementary aspects of other studies into the TD derived etching mechanism, whilst discussing those aspects of other studies that are at variance with this model.

Balooch et al [4.55] have suggested that the ion induced reaction step is,

\[ \text{GaCl}_3^{(\text{ads})} + i \rightarrow \text{GaCl}_3^{* (\text{ads})} \]  

where the excited reaction product possesses a high desorption rate constant. They measured the excitation cross-section as \(5.4 \times 10^{-13} \text{ cm}^2\), which corresponds to one ion causing emission of 100% all GaClₓ molecules within a 40Å radius around the point of ion impact. Clearly thermal desorption and modulated beam studies give rise to differing models of ion-induced reaction. The reconciliation of these models may be attempted purely by relating the degree of halogenation of the excited gallium species to the chlorine concentration in the etch system. The Cl₂/Ar⁺ ratio is critical to the gallium reaction product obtained. TD and modulated beam experiments possess a series of fundamental differences which have led to a number of inconsistencies in previously proposed etch mechanisms. The TD experiments show thermally derived information on the surface perturbed by the ion beam whereas modulated beam experiments measure emission mechanisms from the ion damaged surface. Furthermore,
continued Cl$_2$ adsorption upon an activated surface during the MB experiment is clearly representative of a CAIBE-type etch process. This ion-induced etch reaction process is shown in Figure 4.48 and describes the time dependent surface concentration of GaCl$_3$. This exhibits build up and subsequent depletion of the GaCl$_x$ species. The As concentration in the substrate is generally modeled as constant. This is clearly at variance with the arsenic segregation model of Orrman-Rossiter [4.67], but is in agreement with the predictions of Ameen and Mayer [4.68].

Previous studies by McNevin and Becker [4.64] investigated the kinetic mechanism of the ion-assisted reaction using a modulated beam technique. The pulse intervals were 12ms on and 12ms off, with ion fluxes of 1-10 x 10$^{14}$ ions cm$^{-2}$ s$^{-1}$ and chlorine fluxes of 2 x 10$^{12}$- 4 x 10$^{14}$ molecules cm$^{-2}$ s$^{-1}$ thereby exposing the surface to a range of Ar$^+$/Cl$_2$ ratios from 0.25-500. They proposed a model assuming that As is saturated with adsorbed Cl atoms as demonstrated by Margaritondo et al [4.58].

$$\frac{1}{2} \text{Cl}_2 + \text{As}_{(s)} \rightarrow \text{AsCl}_{(s)} \quad [4.6]$$

A surface reaction step then follows with the surface species with a precursor form of chlorine on the surface via a Langmuir-Hinshelwood type reaction.

$$\text{Cl}_2 \rightarrow \text{Cl}_2(\text{s}) \quad [4.7]$$

$$\text{AsCl}_{(s)} + \text{Cl}_2(\text{s}) \rightarrow \text{AsCl}_3(\text{s}) \quad [4.8]$$

$$\text{Ga}_{(s)} + \text{Cl}_2 \rightarrow \text{GaCl}_2(\text{s}) \quad [4.9]$$

Desorption of the surface phases occur via the steps

$$\text{AsCl}_3(\text{s}) \rightarrow \text{AsCl}_3 \uparrow \quad [4.10]$$

$$\text{GaCl}_2(\text{s}) \rightarrow \text{GaCl}_2 \uparrow \quad [4.11]$$
This study detected no trace of GaCl₃ in the reaction products, although this may be due to the low chlorine surface concentrations. This model clearly shows the ion induced reaction is enhancing the desorption step rather than contributing to the degree of halogenation of the surface. This model assumes an unreasonably high surface diffusion coefficient in order to explain the difference between incident chlorine flux and the Cl concentration in the desorbed product obtained during the experiment.

Balooch et al [4.55] observed a GaCl₃ ion-assisted etch product in their modulated beam studies. They also found evidence for a gallium-rich scale on the surface which is removed by ion stimulated desorption. They used an incident beam intensity of 1 x 10¹⁷ chlorine molecules cm⁻² s⁻¹ with a 2.5Hz modulated ion beam (20mA cm⁻²; 3.5keV) which equates to an ion dose of 1.28 x 10¹⁴ ions cm⁻². This equates to a Cl₂/Ar⁺ ratio of greater than 300:1, therefore, the reaction conditions are diametrically opposed to those employed by McNevin and Becker [4.64] This is closely comparable in CAIBE terms to the 150L adsorption experiments presented earlier. The desorption of GaCl₃ by thermal processes is proposed by Balooch et al as rate limiting. The cross section of loss of desorbed phase as calculated by Balooch is 5.4 x 10⁻¹³ cm⁻² whilst our value is 1.26 x 10⁻¹⁴ cm⁻².

O'Brien et al [4.65] analysed product waveforms obtained from modulation of the incident ion flux. This method was used because of the suitability in detecting mechanisms which respond quickly to the ion flux such as collisional cascade sputtering or thermal desorption due to 'thermal spike' processes. They found the major gas phase products during these experiments to be GaCl₂ and GaCl₃. The GaCl₂ emission waveform obtained is displayed in Figure 4.49 in terms of three possible models.

(a) collisional cascade (CC)
(b) thermal desorption (TD)
(c) thermal desorption followed by a first order surface process
Two TOF lengths of 14.0 and 21.5 cm were recorded and were shown to agree with a collisional cascade model completed in under 3ms with a surface binding energy of 0.08eV. They also observed AsCl₃ as shown in Table 4.1 as being emitted mainly by thermal desorption processes with some contribution by collisional cascade sputtering. The product waveforms reveal the contributions of emission types. These are similar to those found for silicon halides (Figure 3.5) and show the initial processes following closely to CC type followed by slower TD processes.

The nature of the near-surface region must also be considered as well as the emission products when analysing the mechanisms of ion assisted etching. Damage produced by these ion processes have serious implications for complex device fabrication methods. LEIS gives important information on the state of the etched surface which is complementary to TD and modulated beam studies. This is particularly true of surfaces exposed to RIBE-type processes. Orrman-Rossiter and Armour [4.67] have shown that bombardment of the GaAs(001) surface with low energy (18-508eV) Cl⁺ ions produces an As-rich surface layer that is covered by a monolayer of Cl. This is in agreement with the findings of Margaritondo et al [458] which suggests that the chlorine atoms bind preferentially to As atoms at the GaAs surface. The surface preparation, however, is critical to bonding at the surface. This is clear from the contradictory results obtained in this study and in the steady state experiments. Orrman-Rossiter used two different methods to clean the surface. Firstly, Ne⁺ ion sputtering with the 5KeV analysis beam and no subsequent annealing. Their second method utilised simultaneous irradiation of the sample with 200eV Ar⁺ ions at a crystal temperature of 523K. Both methods were found to produce surfaces which were amorphous and damaged in the near surface region. TD experiments clearly show GaCl monolayer formation at low Cl₂ coverages for a CAIBE-type process, whilst RIBE-like ion bombardment tends to cause As segregation to the surface.

A mechanism was suggested for interaction between a Cl⁺ ion and the GaAs(001) surface. Firstly irradiation of the surface with Cl⁺ ions forms an As
rich surface layer. Detected species also include Cl, Cl₂, AsClₓ and GaClₓ. After further Cl⁺ bombardment a Cl covered surface upon an As rich layer exists with an As depleted region with implanted Cl. Bombardment with Ne⁺ ions causes an eroded (etched) surface with emitted species Ga, As, Cl, GaClₓ and AsClₓ. The As depletion in the sub-surface region also increases in response to prolonged Ne⁺ bombardment. Ameen and Mayer [4.68] studied the segregation of group V elements in RIE processes on GaAs and InP using LEIS and sputtered neutral mass spectrometry (SNMS) and found that adsorption of chlorine altered the chemical potential at the surface. Species with lower latent heats of vapourisation such as AsClₓ tend to volatilise from the surface leaving GaClₓ moieties at the surface. The beam energies for this study are much lower than those used by Balooch et al [4.55] and the chlorine flux upon the surface is much reduced. The conditions used almost certainly produce GaCl in preference to the gallium trichloride.

4.6.2.4 Comparison of Ion/Neutral Beam assisted Etching vs Laser assisted Etching Processes

The issue of ion beam versus laser etching is a complex and much discussed subject. Photochemical etching of GaAs certainly has favourable points when compared to plasma or reactive ion etching and these have been outlined by Jackman [4.69]. Laser etching possesses advantages such as high etch rates, low damage and the possibility of maskless etching. It is clear, however, that both RIBE and CAIBE allow considerable control over the etch environment. Furthermore, ion/neutral beam sources may be used as simple and inexpensive add-on components to existing in-situ processing equipment. In view of the increased competitiveness of CAIBE versus laser etching, it is of considerable interest to consider similarities and differences between the chemistry provoked by the differing beam sources. In addition, the mechanisms by which these processes occur may have significant implications for reduction of damage induced by these processing steps.
Liberman et al [4.56,4.70] have performed studies on the interaction of Cl₂ with the GaAs(110) surface both with and without laser irradiation, with particular emphasis on low laser fluences on physisorbed layers. Illumination of the Cl covered surface at 85K with 193nm ArF excimer radiation causes desorption of Cl atoms and formation of AsCl₃, whilst at 351nm XeF irradiation produces much smaller quantities of AsCl₃ and Cl flux. Using an excimer pumped dye laser, visible light of 535nm was also employed resulting in no reaction product formation on the surface. A mechanism of surface reaction was proposed for 193nm reaction where photoemission of electrons from the surface initiate dissociation of the Cl₂ physisorbed layers.
Figure 4.48 Schematic of Ion-Assisted Processes at varying chlorine coverages on GaAs
4.6.3 Summary and Implications for GaAs CAIBE Processes

A CAIBE precursor must clearly exhibit a reactive nature towards the semiconductor surface and also provide a passivating surface layer in order to absorb the majority of the kinetic energy of the impinging ion beam. Chlorine has been shown to be highly reactive towards a clean Ga-rich GaAs surface. An ideal CAIBE precursor may be one that is less reactive but displays dissociative adsorption behaviour on the surface. This gives rise to a passivated surface layer. This ideal behaviour is particularly desirable for maskless etching reactions where a focused ion beam is required to promote the reactivity at selected areas on the substrate. It has been demonstrated that ion beam mixing in the case of GaAs/Cl₂ etching is not a positive step towards enhanced etch rates. The promotion of the emission products from the surface is caused by ion enhanced adsorption processes and subsequent 'clearing' effects from the surface. There is a clear ambiguity between this reaction mechanism and that observed for the reaction of silicon with halogens.

The CAIBE process does not benefit from prior fragmentation of the precursor on adsorption unlike the plasma, RIE and RIBE processes. The many ultra-stable gases used in plasma etching e.g. CF₂Cl₂ and other Freon gases may be unsuitable due to weak or absent chemisorption processes. Molecules such as CCl₄ have been utilised as precursor materials and have been shown to possess the ability to dissociatively chemisorb on Si(100) [4.71]. Approximately two layers of the fragmented species were present on the surface and their desorption characteristics were similar to those obtained for chlorine interactions on Si(100) surfaces [4.72]. Beam assisted reaction gave rise to further adsorption followed by decomposition of the molecule leaving carbon residues on the surface. Any strategy using halogenated carbon compounds as precursors must ensure that a stable carbon containing fragment is produced. Halogenated precursors such as 1,2 dichloroethane [4.73] have shown considerable promise in removing gallium fragments from the surface. A β-hydride elimination may occur resulting in desorption of alkene molecules.
It is clear that the inevitable effect of any CAIBE-type etch process is the partial intermixing of the adsorbed phase into the sub-surface region. The surface is then activated to give ion-enhanced adsorption of reactive species which readily desorb. In view of the ever decreasing size of GaAs device structures and the ease which the material may be damaged, it is evident that physical perturbations of the host lattice will have serious implications for the electronic and optical properties of the material. This problem may be partially alleviated by use of a low energy ion beam that impinges on the surface at energies less than the sputtering threshold. This energy for GaAs is approximately 10eV, although for a halogenated adlayer this value is reduced to approximately 2eV. The adlayer may, however, passivate the surface and therefore a purely chemical process may occur at energies of a few tens of eV. The development of low energy ECR type ion sources will greatly assist in damage free etching. The hot filament and Saddle Field ion/neutral sources utilised in this study are suitable for large scale etching processes but appear to be inappropriate for etching of shallow channel devices.
CHAPTER 5

SURFACE REACTIONS OF HYDROCARBONS ON Si(100): APPLICATION TO DEPOSITION OF DIAMOND, DIAMOND-LIKE AND SILICON CARBIDE THIN FILMS

5.1 Introduction

5.2 Properties and Applications of Diamond and Related Wide Band Gap Materials

5.3 Deposition Methods and Growth Mechanisms of Diamond and Other Related Wide Band Gap Compounds

5.3.1 Deposition Methods
5.3.1.1 Chemical Vapour Deposition (CVD)
5.3.1.2 Plasma Assisted CVD (PACVD)
5.3.1.3 Ion Beam Deposition

5.3.2 Deposition of Silicon Carbide

5.3.3 Mechanisms of Diamond Synthesis

5.4 Adsorption of Hydrocarbons on Surfaces

5.5 Hydrocarbon Adsorption on the Si(100)(2x1) Surface; A TDS and AES Analysis

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5.5.2 Adsorption Studies of Ethene (C\textsubscript{2}H\textsubscript{4}) on Si(100): Results

5.5.3 Bombardment of the Ethene-Si(100) Surface with Argon Neutrals: Results

5.5.4 Bombardment of Ethene/Si(100) Surface with Atomic Hydrogen Neutrals: Results

5.6 Analysis and Discussion

5.6.1 Adsorption and Thermal Studies of Ethene (C\textsubscript{2}H\textsubscript{4}) on Si(100)

5.6.2 Thermal Processes on the Ethene/Si(100) Surface
5.1 Introduction

Diamond may be grown either at high pressures into an equilibrium state [5.1], or at low pressures into a metastable state. Thin film growth of diamond may be achieved using techniques utilising the latter pathway. Most deposition methods make use of an 'activated' mixture of hydrocarbon radicals and atomic hydrogen created in any one of numerous thermal [5.2-5], plasma [5.6-9], electron [5.10,5.11] or ion assisted [5.12-14] processes. Whilst in pursuit of high quality diamond films, a new class of materials, the diamond-like carbons (DLC)[5.15], have emerged; these may be classified as hydrogenated (a-C:H) or non-hydrogenated (a-C) carbon films. This chapter explores the properties, applications and methods of deposition of diamond and DLC films. In addition, the mechanism of silicon carbide (SiC) deposition is also addressed. The growth processes of all these films are discussed in terms of the surface reactions of activated and non-activated hydrocarbons such as ethene \( \text{C}_2\text{H}_4 \) and methane \( \text{CH}_4 \) with a Si(100) substrate. The mechanisms which control adsorption of hydrocarbon precursors, their reaction with the surface and subsequent thin film growth under these thermodynamically metastable conditions are of significant interest for improvement of layer processing for optical and microelectronic devices. Although applications exist for homoepitaxial films, the deposition of heteroepitaxial diamond films are of particular interest for integration into
existing VLSI processing. Also, the protection of fragile optical components by these materials is an important large area use for these films. A study of the reactions of ethene on silicon, which may lead to an understanding of the formation of buffer layers of SiC for subsequent growth of diamond is of significant interest. The possibility of ethene as a precursor for diamond thin film deposition is also examined. Energetic neutral bombardment by Ar° and H° beams of the ethene/Si(001) surface region is investigated and discussed with respect to the induction or enhancement of chemistry via perturbations to the surface region.

5.2 Properties and Applications of Diamond and Related Wide Band Gap Materials

Elemental carbon can exist in at least six crystalline forms; α and β graphite, diamond, hexagonal diamond (Lonsdaleite), chaoite and carbon (VI) [5.16]. In addition, there are also the novel class of carbon 'cage-like' structures known as fullerenes [5.17]. The two most naturally abundant forms of carbon are α-graphite(hexagonal) and diamond. The appearance and structure of these two forms differ greatly, resulting in the widely contrasting physical properties which are listed in Table 5.1. There are a number of striking differences in the properties of these two materials. Firstly the hardness of diamond is well known, whilst graphite is relatively soft. Diamond possesses high electrical resistivity and high thermal conductivity, whilst graphite has high electrical conductivity and moderate thermal conductivity. Structurally, α-graphite consists of planar hexagonal nets of trigonally bonded (sp²) carbon layered in ABAB sequences as shown in Figure 5.1. Van der Waals type bonding between these layers accounts for the weak interplanar bonding and hence graphite's characteristic properties. In diamond, each carbon atom is tetrahedrally (sp³) surrounded by four equidistant neighbours. The diamond structure, shown in Figure 5.2, consists of two interpenetrating f.c.c. lattices offset along the <111> direction by one quarter of the diagonal unit length.
Diamond-like carbon films, however, do not possess long range order and hence are usually classified as amorphous. A widely accepted structural analysis, the 'fully constrained network' (FCN) model [5.18], describes a-C:H as a random, but fully constrained sp²/sp³ network with terminating hydrogen atoms. An alternative to the FCN model, is the 'defective graphite' (DG) model [5.19]. Here, the structure is described as analogous to graphite, but allows for a stochastic arrangement of non-aromatic defects which may induce strong π-electron localisation. This leads to strengthening of the interplanar bonds and hence improvements in the physical properties observed for DLC.

Diamond and DLC films have structural, optical, mechanical and electronic properties that make them eminently suitable for a multitude of microelectronic and optical applications. The properties of DLC are presented in Table 5.1 alongside those of diamond, α-graphite and β-silicon carbide. Diamond possesses high thermal conductivity, high electrical resistivity, extreme hardness and is chemically inert. The wide band gap of diamond (5.5eV) makes it a material of great potential for devices operating at higher frequencies than present Si or GaAs structures can achieve. Diamond has been shown to have very rapid response times when exposed to laser pulse illumination [5.20]. The carrier lifetime is short, leading to rapid signal decay hence enabling high frequency operation. Natural crystals were measured at 125-220ps whilst synthetic diamond was observed to have a 55ps response time, thereby exhibiting characteristics suitable for high voltage (a few kV) switching and generation of ultrashort electric pulses or microwave bursts. Devices of this type have been fabricated and characterised [5.20-23], taking advantage of diamond's favourable properties of high dark resistivity, high carrier mobility [5.24] and high breakdown field strength[5.25,5.26]. Diamond also exhibits high microwave conductivity [5.27] and is far less susceptible to radiation effects [5.28]. This is due to the low absorption of high frequency electromagnetic radiation and the high Young's modulus of elasticity which is a measure of the lattice bond strength. Impact avalanche and transit time (IMPATT) diodes fabricated from semiconducting diamond have been shown to have comparable power conversion efficiencies.
to both Si and GaAs devices. The superior thermal conductivity and higher operating voltage also leads to devices of potentially greater power handling capacity [5.29,5.30].

A multitude of devices based on diamond have been fabricated including point contact transistors and permeable base transistors [5.31]. Shiomi et al [5.32] report the fabrication of a MESFET device using a p-type doped diamond layer. Many of these devices, at present, are constructed from homoepitaxial films i.e. diamond films on single crystal diamond substrates. The recent promise of diamond deposition onto existing electronic and optoelectronic materials such as Si and GaAs has provoked a renewal of interest in such potential applications as heterojunction diodes [5.33], thermistors [5.34] and light emitting diodes [5.35]. Thin film Al/diamond Schottky diodes with high breakdown voltages (>400V) have also recently been reported [5.36], thus illustrating diamond's use as a dielectric material. This is particularly useful for the development of GaAs device structures as this material has no native insulating oxide.

A p-n junction fabricated from diamond is a particularly attractive possibility. There are many instances of boron p-type diamond films for use in device structures [5.37,5.38]. A common method for the introduction of boron during the growth process is by plasma decomposition of boron hydride in a CVD process. There is considerable difficulty in the preparation of high quality n-doped diamond films. Recently, reports of synthesis by hot filament CVD using a diphosphorus pentoxide dopant have emerged [5.39]. In addition, several attempts to interstitially incorporate lithium atoms has resulted in charge compensation by intrinsic acceptor states [5.40].

The selective area deposition of diamond films has been achieved by using either reactive ion etching of the deposited film or amorphous silicon masking and subsequent deposition of the diamond film by EACVD and microwave plasma CVD methods [5.41].
Silicon carbide also has a number of important applications within microelectronics and also as a material for large area radiation 'hard' coatings. There is particular emphasis on its use as a buffer layer between deposited diamond films and the semiconductor substrate. It also has many other applications e.g. light emitting diodes [5.42], transistors [5.43] and high frequency/high power devices [5.44]. Silicon carbide deposited by CVD, is also an important material in synchrotron radiation beam lines [5.45]. The highly polished nature of SiC surfaces results in less scattering in the vacuum ultraviolet than is found for metal-coated glass mirrors. The radiation stability, both optical and mechanical, of both diamond and SiC renders membranes made from these materials suitable for use as potential x-ray lithography mask carriers. This has been assessed by measurement of the Young's modulus after broad band irradiation from a synchrotron source [5.46].
### Table 5.1.1 Properties of Diamond and Other Related Wide Band Gap Materials

<table>
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<th></th>
<th>Diamond</th>
<th>DLC</th>
<th>α-graphite</th>
<th>β-silicon carbide</th>
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</thead>
<tbody>
<tr>
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<td>amorphous</td>
<td>hexagonal</td>
<td>cubic</td>
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<td>a</td>
<td>3.567</td>
<td>sp²/sp³</td>
<td>2.47</td>
<td>4.360</td>
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<tr>
<td>c</td>
<td>6.79</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Density</strong></td>
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<td>1.8-2.0</td>
<td>2.26</td>
<td>3.21</td>
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<td>900-3000</td>
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<td>1.8-2.2</td>
<td>II 2.15</td>
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<td>10⁶-10¹⁰</td>
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Figure 5.1 Structure of Graphite
Figure 5.2 Structure of Diamond (including a sub-cell)
5.3 Deposition Methods and Growth Mechanisms of Diamond and Other Related Wide Band Gap Compounds

Diamond, DLC and silicon carbide thin films may be deposited by a variety of methods; the most important of which are now briefly discussed. These techniques are grouped according to the nature of the deposition process.

5.3.1 Deposition Methods

5.3.1.1 Chemical Vapour Deposition

Chemical vapour deposition (CVD) describes a class of reactions involving the decomposition of a suitable chemical precursor, or mixture of chemical precursors, on a heated surface giving rise to the desired deposit. Surface temperatures of the order of 1250K are typically required for diamond CVD growth. This method may be further sub-divided into groups according to the method of activation of the vapour phase leading to the chemical decomposition. A hydrocarbon/hydrogen gas precursor may result in diamond synthesis via thermal [5.2-5.4], electron assisted [5.10,5.11] or hot filament CVD [5.4]. A typical CVD reactor utilising the latter activating process is shown in Figure 5.3 and is the most commonly used of the above CVD techniques for deposition of diamond films. The layers grown using this technique tend to result in higher growth rates and superior properties than the thermal and electron assisted processes. The hot filament process has been described as more closely related to Plasma Assisted CVD than conventional CVD [5.47].

5.3.1.2 Plasma Assisted CVD (PACVD)

Plasma assisted CVD is a process that utilises electrical energy within the CVD environment. The substitution of electrical energy for thermal energy makes it possible to dramatically reduce the deposition temperatures for thin film growth. This technique has been used to deposit diamond and a-C:H thin films by decomposition of the precursor mix using radio frequency (rf)
self biased PACVD [5.48-5.51], which is a variation of the rf sputtering method [5.52]. This technique produces higher impact energies than inductively coupled plasmas and hence causes enhanced decomposition of molecular ionic species within a small reaction zone [5.53] leading to dissipation of a high power density ($10^6 \text{W cm}^{-2}$) in the region of the substrate. The hydrocarbon used in the deposition process is, therefore, generally not an important parameter for film growth, although film growth is dependent upon the atomic ratios in the plasma.

Other variations of PACVD include DC [5.6] and microwave [5.7-5.9,5.37,5.54,5.55] approaches; the latter usually employs Electron Cyclotron Resonance (ECR) microwave sources at pressures of $10^{-3}$-$10^{-5}$ torr with ion energies of several tens of volts, in contrast with the several hundreds of volts obtained from rf plasma sources. The ECR technique operates on the principle that microwave energy is coupled to the natural resonant frequency of the electron gas in the presence of a static magnetic field. The benefits of this source are that it is electrodeless and also possesses a highly controllable collisionless plasma. Higher coupling efficiencies are obtained with a microwave ECR source over conventional rf techniques thus producing plasma densities in the range $10^{11}$-$10^{12}$ cm$^{-3}$. Control of the ion energy produced by the ECR source may be enhanced by rf biasing the substrate. A simple dc bias causes charging of the insulating diamond (or DLC) film thus reducing the accelerating potential.

5.3.1.3 Ion Beam Deposition

This group of deposition processes rely on ion beam processes to either sputter deposit or modify a deposited thin film. It may be sub-divided into several techniques such as ion beam sputtering, dual beam sputtering and ion bombardment evaporation deposition [5.12-5.14]. Non-hydrogenated diamond-like films may be deposited by sputtering of a carbon target in a rf plasma [5.56] or by an Ar$^+$ beam [5.57]. The basic sputtering process involves the physical removal of a target material by an energetic impinging beam. A variety of beam sources are used such as ions, neutrals,
electrons or photons although the term 'sputtering' usually refers to the use of ion beams. Sputtering is a mature technology which has many applications in thin film deposition, for example magneto-optical storage media, transparent conducting coatings and wear resistant coatings etc. An advantage of this genera of techniques is the ability to successfully upgrade from research size deposition coaters to production scale processes. Sputtering techniques which utilise parallel plate electrodes are favoured for film deposition due to their favourable low cost, process simplicity, process control and thin film uniformity.

5.3.2 Deposition of Silicon Carbide

The growth of silicon carbide thin films is important as they may be used as interlayers between diamond films and optoelectronic materials such as zinc sulphide, zinc selenide or electronic substrates such as silicon [5.58]. A major obstacle to the growth of silicon carbide films on silicon is the very large lattice mismatch (20%) between β-SiC (4.36Å) and the silicon substrate (5.43Å)[5.59]. A buffer layer of α Si/C alloy may be deposited by thermal reaction at 1670K of the silicon surface with propane [5.60] or by sputter coating the surface with SiC [5.61], although the latter is difficult due to contamination problems introduced when sputtering and CVD processing methods are present on the same deposition system. Bozso et al [5.62] have deposited SiC films by CVD of ethene on Si(100) and performed kinetic studies. A schematic of the observed growth regimes is shown in Figure 5.4. They found that an α 'Si-C' alloy forms on the surface at substrate temperatures below 940K whereas at temperatures greater than 940K surface segregation of a silicon layer above the SiC film occurs. A temperature dependent decrease in the sticking coefficient of ethylene on Si(100) may cause a reduction in the rate of reaction at the surface, thus leading to a slower SiC growth rate. CVD of films by decomposition of C₂H₄ on Si(100) has been monitored by XPS [5.63] and shows a reduction of film growth efficiency after a 30Å layer has formed. This was attributed to a diffusion limited growth process.
5.3.3 Mechanisms of Diamond Synthesis

A significant effort has been employed to improve the growth rate of diamond films and their properties, whilst a direct observation of the mechanisms of growth has yet to be achieved. It is generally agreed, however, that a nutrient gas of hydrocarbon and hydrogen must be transformed into an activated (i.e. excited) state to enable diamond deposition to occur [5.64]. The process is initiated by activation of the surface by reaction with atomic hydrogen. The active surface site may then capture a hydrocarbon molecule or radical. Mechanisms for organisation of hydrocarbon decomposition into the diamond structure have been proposed by Frenklach and Spear [5.65], and Tsuda et al [5.66]. The former model assumes the presence of a propane like 'kernel' for diamond-like growth which is activated by atomic hydrogen for subsequent capture of acetylenic species such a scenario is shown in Figure 5.5. The 'kernel' is the smallest step that can initiate growth of the diamond structure, and may consist of two, three or four carbon atom chains with the two terminal carbon atoms in the chain bonding to the adjacent surface carbon atoms. The kernals may either be propane-like (Figure 5.5(a)) or propene-like (Figure 5.5(b)). The two and four carbon atom initiation sites are depicted in Figure 5.5(c),(d) and introduce strain to the growth surface. The model proposed by Tsuda et al [5.66] uses quantum calculations and assumes a methylated surface exists with the methyl cation providing a positively charged active site. Additional capture of methyl radicals leads to diamond-like growth with the positive charge of the surface preserved. These models do not adequately explain why such a large excess of atomic hydrogen is required for diamond growth. Piekarczyk and Yarbrough [5.67] recently proposed a model of diamond deposition from hydrocarbon-hydrogen mixtures by application of thermodynamic analysis to the CVD process. A four stage process is suggested where (i) activation of the hydrocarbon-hydrogen mixture occurs followed by (ii) transport of the active species to the growth surface. The deposition step (iii) produces $sp^3$ and $sp^2$ hybridised carbon on the surface, with (iv) etching of the co-deposited $sp^3$ carbon by the excess atomic hydrogen.
Figure 5.3 Schematic of Hot Filament Deposition Technique

Figure 5.4 Three temperature ranges of SiC growth on Si(100) from Ethene
Figure 5.5 Diagram of initiation kernels in Diamond thin film deposition.

after
5.4 Adsorption of Hydrocarbons on Surfaces

Most methods of diamond and DLC thin film deposition utilise mixtures of hydrocarbons and hydrogen; the two most commonly employed are CH₄/H₂ and C₂H₂/H₂. Silicon carbide, whether used as an intermediate layer for diamond growth [5.58] or deposited as a semiconducting material in its own right [5.68] may be prepared by CVD growth from ethene, C₂H₄. The fundamental aspects of the interaction of these precursors with solid surfaces is, therefore, of significant interest in order to develop, an understanding of the mechanism and hence enable the optimisation of growth processes. A number of adsorption studies have been performed on metal, metal oxide and semiconductor surfaces. It is important to fully understand the structure and bonding of the hydrocarbons, methane, ethene and acetylene before considering aspects of their adsorption behaviour. Methane, CH₄, possesses four C-H sp³ bonds arranged at the corners of a tetrahedron as shown in Figure 5.6(a), C₂H₄ consists of a coplanar sp² σ-bonded structure with one π-bond formed by an atomic orbital pair extending in a direction normal to the plane. This form of structure is shown in Figure 5.6(b). Acetylene, C₂H₂, is a linear σ-bonded molecule with two additional π-bonds formed by pₓ and pₜ molecular orbitals thus forming a carbon-carbon triple bond (Figure 5.6(c)).

The adsorption and subsequent reaction of unsaturated hydrocarbons on transition metal surfaces has been studied due to their efficacy as catalysts for hydrogenation processes [5.69], with the most effective being the group VIII metals [5.70,5.71]. The mechanism of bonding between ethene and platinum is illustrated in Figure 5.7. The configuration of atomic orbitals is shown as the olefinic species approaches the metal surface. Bonding occurs due to donation of electrons from the π-bond of ethene to the unoccupied 5d₆s₆p² orbital of platinum, whilst a 'backbond' forms from the occupied 5dsp orbital of platinum to the anti-bonding π-orbital of ethene. In this example the 'backbonding' (or retrodative bonding) is so strong as to dissociate the C₂H₄ at the surface [5.72]. This behaviour may be modified by pre-adsorption of potassium, an electron
donor, on to the platinum surface [5.73]; the surface on becoming 'electron-rich' is less inclined to sharing of the \( \pi \)-electrons from ethene. The weakly bound ethene molecule does not dissociate on the surface, which is advantageous in some catalytic reactions. Ibach and Lehwald [5.74] showed that valuable surface structural information could be obtained for acetylene, ethene and molecular hydrogen on Pt(111). They found that adsorption of ethene below room temperature gave an essentially di-\( \sigma \) bonded surface complex, but at around 300K a structural conversion to an ethylidene \((\text{CH}_3\text{CH}=)\) species takes place. This species was also found to form on heating, when the surface was exposed to hydrogen prior to dosing with acetylene at low temperatures. An intermediate for this reaction was found for this process; 2-ethyl-1-yldiene \((-\text{CH}_2\text{C}=)\) i.e.

\[
\text{CH}_2=\text{CH} \longrightarrow -\text{CH}_2-\text{C}= \longrightarrow \text{CH}_3-\text{CH} = \quad [5.1]
\]

The adsorption of the molecules acetylene and ethene have been extensively studied on other metals [5.75]. For example, the interaction with Fe surfaces is particularly well known in the Fischer-Tropsch synthesis reaction [5.76], known as coal liquefaction, where an iron catalyst with hydrogen present at high temperature and pressure converts CO to alkanes. This would normally be a difficult reaction to perform due to the strength of the C-O bond. Seip et al [5.75], using TDS and HREELS methods, found that acetylene and ethene, on bonding to a Fe(111) surface, both exhibited strong rehybridisation towards sp\(^3\), and decomposed at 230K and 250K respectively following different reaction pathways. They suggested that the chemisorption of these species was controlled by small differences in the geometric and electronic properties of the adsorbate-metal system.

Ethene and acetylene were also studied on Ni(110) surfaces [5.77]. The bonding of these gases with the surface at 80K was found to differ, because although both molecules were distorted, ethene formed an approximately sp\(^3\) gas hybridisation state whereas acetylene became sp\(^2.5\) hybridised. This hybridisation represents a contribution of \( \sigma \) and \( \pi \) orbitals that is intermediate in nature to the conventional sp\(^2\) and sp\(^3\) orbitals. Ethene decomposed to a
$\text{C}_2\text{H}$ species at 300K and then underwent further dissociation to form CH groups before finally leaving an atomic carbon deposit on the surface.

Further surface studies of metal-olefin surfaces have been performed using EELS techniques [5.78-5.81]. Most of the reactions studied proceed via a rehybridisation mechanism, as previously discussed, resulting in a di-$\sigma$ bonded surface complex. An exception is the example of ethene adsorption on Pd(111)[5.79], where it has been noted that very little distortion from the gas phase occurs at 150K. This is closely related to behaviour exhibited by ethene on noble metal surfaces such as Ag(110)[5.82] and Cu(100)[5.83], where $\pi$-bonding parallel to the surface occur upon low temperature adsorption. Upon heating, the ethene desorbs with no decomposition taking place. Studies employing near edge x-ray absorption fine structure (NEXAFS) have shown that acetylene and ethene lie flat on Cu surfaces with a weakening of the carbon saturated bond [5.84].

Early studies of adsorption of hydrocarbons on silicon surfaces were initiated due to interest in electronic factors in catalysis reactions, such as evaluation of surface conductivity, field effect mobility and dopant effects. These studies were only possible on semiconductor surfaces. Hence, Klimesch et al [5.85] performed studies on the $\text{C}_2\text{H}_4$/Si(111) system using TDS, AES and electrical characterisation methods. They observed that adsorption at 300K occurs without dehydrogenation. Subsequent thermal treatments resulted in desorption of 20-30% of the ethene from the surface while the remaining adsorbate underwent a two step dehydrogenation, at 660K and 800K, ultimately resulting in C-C scission.

Froitzheim et al [5.86] used HREELS to demonstrate associative adsorption of $\text{C}_2\text{H}_4$ on the Si(111)7x7 surface at 300K. Thermal dehydrogenation was observed at 660K, but was not completed until 760K. Studies of the adsorption kinetics [5.87] of propene, propane and methane on Si(100)2x1 at 120K show that the latter two molecules have zero sticking probabilities, whilst propene adsorbs strongly on the surface. The adsorption of propene on Si(100) is strongly enhanced by pre-treatment of the surface by Ar$^+$.
bombardment [5.88]. LEED and EELS have been used to study the adsorption and thermal decomposition of ethene on silicon (100)c4x2, (100)2x1, and (100)9° vicinal surfaces [5.89]; the adsorbate molecule was proposed as configuring with di-σ type bonding to the adjacent silicon atoms on the 'dimer' reconstructed surface. Post-adsorption heat treatment at 650K found loss of 40% of the ethene phase via desorption, with the remainder decomposed to \( \text{CH}_x \) and SiH. Furthermore, heating to 1000K resulted in the formation of a silicon carbide phase with H being completely removed from the surface. Yoshinobu et al [5.89] also studied this system. They found that ethene chemisorbs and thermally dehydrogenates on the terraces of a vicinal surface rather than the steps.

Cheng et al [5.90] directly determined the absolute monolayer coverages of acetylene and ethene on Si(100) finding both molecules to have saturation surface coverages at 105K of \( 2.5(+/-0.2) \times 10^{14} \) molecules cm\(^{-2} \); this is consistent with one hydrocarbon molecule per dimer site. Further studies by Cheng at al [5.91], using isotopic mixing techniques, found the dominant process on Si(100) is the desorption of an intact ethene molecule, with SiC formation being only a minor process. Less than 1% isotopic mixing occurs on thermal treatment between 500-950K. The recombination reaction

\[
2\text{CH}_2 \text{(ads)} \rightarrow \text{C}_2\text{H}_4 \text{(ads)} \rightarrow \text{C}_2\text{H}_4 \text{(g)} \quad [5.2]
\]

was found to be insignificant in the mechanism of desorption of ethene from silicon surfaces.

Theoretical studies using computational methods [5.92] show that there are significant barriers to dissociation, therefore, the chemisorbed ethene positions itself across the 'dimer' surface and thus the bridged di-σ configuration is preferred.
Figure 5.6 Bonding in Hydrocarbons illustrating (a) sp³ (b) sp² and (c) sp bonds
Figure 5.7 The formation of $\pi$-electrons on ethene and their bonding to the d orbitals of a transition metal (a) atomic orbitals of $\pi$-electrons in ethene (b) molecular orbitals of $\pi$-electrons in ethene, and (c) overlap leading to bonding between $\pi$-electrons of ethene and d electrons of platinum

(after S.R. Morrison The Chemical Physics of Surfaces Plenum 1990)
5.5 Hydrocarbon Adsorption on the Si(100)(2x1) Surface: A TDS Analysis

5.5.1 Introduction

The current literature on the interaction of hydrocarbons with semiconductor and metal surfaces has been briefly discussed in the preceding section. The surface chemistry of reaction processes leading to diamond, DLC and SiC growth, utilising hot filament activation of hydrocarbon precursors and bombardment of surfaces with energetic hydrogen and argon neutral beams has received little attention in the literature. A complete study of the mechanism for adsorption of ethene on Si(100) and the thermal and ion assisted processes are of considerable importance to the development of processing of these materials for semiconductor device applications. This is due to the need for controllable diamond thin films of sub-micron thickness without the abrasive pre-treatments that are generally used in current processes.

In order to observe the nature of the hydrocarbon-silicon surface region, a number of surface spectroscopic probes have been used. A comprehensive study of thermal desorption data is presented for ethene adsorption on the Si(100) surface. Methane was found not to adsorb to the silicon surface without the additional use of hot filament activation.

5.5.2 Adsorption Studies of Ethene (C\textsubscript{2}H\textsubscript{4}) on Si(100): - Results

TD spectra for the C\textsubscript{2}H\textsubscript{4}/Si(100) system were obtained for the mass fragments, C\textsubscript{2}H\textsubscript{4}+, H\textsubscript{2}+, H+, and CH\textsubscript{3}+ as detected in the quadrupole mass spectrometer (QMS). These spectra were obtained by plotting signal intensity for a predefined mass versus temperature using a linear heating rate of 10 K s\textsuperscript{-1}. Figure 5.8(a) shows a series of TD curves of the C\textsubscript{2}H\textsubscript{4}+ (28amu) detected mass fragment after increasing exposure of ethene upon an atomically clean Si(100) 2x1 reconstructed surface. These spectra reveal a solitary desorption
peak, labelled the α peak, upon exposure to increasing amounts of ethene. This peak appears at 470K and exhibits an asymmetric peak shape, thereby indicating a first order desorption process. The peak area of the desorbed species increases with continued exposure to ethene. A graph of ethene uptake calculated from the TD spectra is shown in Fig. 5.8(b). This is derived by plotting the area under the desorption peak against the ethene exposure, as measured in Langmuirs. Monolayer coverage from this plot appears to be achieved at approximately 0.75L exposure which equates to 3 x 10^{14} molecules cm^{-2}. The exact position of monolayer completion is not clearly defined from this uptake curve as complete saturation of the desorbed state is not observed. The position of monolayer coverage was defined as the point where the change in the rate of adsorption was greatest. The energy for desorption of the C_2H_4 (28amu) peak calculated from the Redhead equation [5.93] is 124 kJ mol^{-1}.

Further insight into the adsorption processes of ethene on silicon may be acquired by studying the TD spectra representing the loss of the H_2^+ mass fragment. The silicon surface was exposed to increasing amounts of ethene, and the resultant spectra are presented in Figure 5.9(a). An uptake curve of data derived from these TD spectra is plotted versus increasing ethene dose and is shown in Figure 5.9(b). The loss of molecular hydrogen occurs as a broad peak starting at 470K with a more prominent peak visible at 650-700K. The latter peak is labelled the γ_1 peak. This follows second order kinetics as the leading edge of the desorption peak occurs at increasingly lower temperatures following progressive exposure of ethene to the silicon. This type of behaviour is expected from an associative desorption reaction occurring on the surface.

A series of TD spectra is presented in Figure 5.10 for the mass fragment corresponding to H^+ (1amu), with the corresponding uptake curve derived from these spectra plotted in Figure 5.11. These spectra show a desorption peak at approximately 480K. The peak area increases upon continued exposure to ethene. A further desorption peak is also visible at approximately 680K corresponding to the γ-H_2 peak identified in Figure 5.8(b). It is clear
from Figure 5.10 that the C\textsubscript{2}H\textsubscript{4} species is the major thermally desorbed product from the surface. The uptake curve shown in Figure 5.11 reveals a rapid uptake of H\textsuperscript{+} derived from ethene, i.e. the \( \alpha \) peak, until approximately 10L followed by a sharp decrease in the rate of adsorption. This state does not saturate at high coverages. The \( \gamma \)-H\textsuperscript{+} peak also shows a rapid uptake to 10L followed by the complete saturation of the desorption peak.

The presence of other mass fractions was observed upon thermal desorption from the ethene exposed Si(100) surface; a series of TD spectra is shown in Figure 5.12(a) for the methyl (CH\textsubscript{3}\textsuperscript{+},15amu) species. An uptake curve is shown in Figure 5.12(b) for peak area data derived from these TD spectra plotted against ethene dose. The signal intensity, however, is very weak and may be attributed to fragmentation of the parent C\textsubscript{2}H\textsubscript{4} molecule within the spectrometer.

### 5.5.3 Neutral Beam Bombardment of the Ethene-Silicon Surface: - Results

The effect of energetic neutral beam bombardment on the Si(100) surface covered with adsorbed ethene has been investigated. Irradiation of this surface was performed after exposure to a fixed C\textsubscript{2}H\textsubscript{4} dose (3L). A fast atom beam (FAB) saddle field source was used to provide a beam of energetic Ar\textsuperscript{0} neutrals. The beam energy was maintained at 1.7kV with a discharge current of 40mA; the system pressure was 2x10\textsuperscript{-3} mbar whilst the beam source was operating. The FAB source was positioned 100mm from the Si surface and the neutral beam was incident on the surface at an angle of 45\textdegree with a beam flux of 34\textmu A cm\textsuperscript{-2} s\textsuperscript{-1}.

The TD spectra for the desorption of the C\textsubscript{2}H\textsubscript{4}\textsuperscript{+} (28amu) mass fragment after neutral beam irradiation are presented in Figure 5.13(a). The accompanying erosion curve is shown in Figure 5.13(b) and is obtained from the In peak area data plotted against the ion dose. Exposure of the surface with argon neutrals results in spectra which reveal a change in the peak shape. This manifests itself as a broadening of the desorption curve on the high temperature side. The peak height decreases upon continued neutral
exposure, but the broadening results initially in an increase in the ethene peak area as shown in Figure 5.13(b). The subsequent loss of the detected mass fragment upon increasing beam exposure is not linear with respect to the ion dose.

TD spectra are presented for the $H_2^+$ detected mass fragment upon irradiation of the ethene-silicon surface in Figure 5.14(a). It should be noted that there is a background of molecular hydrogen signal when the sample is taken through a blank dose and exposure to argon pressure, $2 \times 10^{-3}$ mbar. This blank dose causes the $\gamma$ peak to become more prominent than those observed in the adsorption studies i.e. Figure 5.9(a). Inspection of the spectra following beam irradiation suggests there is considerable perturbation of the surface. The three spectra for desorption of $H_2$ presented in Figure 5.14(a) consist of:

(A) a Si(100) surface exposed to 3.5L of ethene + blank dose

(B) the adsorbate-surface created in (A) exposed to a 1.7kV $Ar^0$ beam at an equivalent current density of $34\mu m \, cm^{-2}$ for 20s. ($1.08 \times 10^{16} \, Ar^0 \, cm^{-2}$)

(C) as (B), except 100s beam exposure ($5.45 \times 10^{16} \, Ar^0 \, cm^{-2}$)

Three TD peaks may be identified from these series of spectra; they are described as $\gamma_1$, $\gamma_2$ and $\gamma_3$ in respective order of increasing desorption temperature. A qualitative observation of these spectra show $\gamma_2$ (715K) to be the most prominent desorption phase, with $\gamma_1$ appearing at 500K subsequent to neutral beam exposure. The peak $\gamma_3$ at approx. 900K is difficult to resolve due to overlap with the high temperature tail of $\gamma_2$. Bombardment of the adsorbate-surface region for 20s under the previously described conditions showed no difference in the height of $\gamma_2$ but an increase in the FWHM of 30%. Further exposure (100s) to the argon neutrals resulted in still more peak broadening. The $\gamma_1$ peak follows the same trend as $\gamma_2$ by increasing area. A semi-log plot of peak areas versus Ar exposure highlights the enhancement of the desorption peak intensity of molecular hydrogen.
from the surface. This plot is derived from Figure 5.14(a) and is presented in Figure 5.14(b). This confirms that initial enhancement of peak size occurs is greater than at prolonged beam exposures.

The erosion of CH$_3$ and C$_2$H states were studied by exposure of an ethene (50L)/Si(100) surface to Ar$^0$ neutrals. Figure 5.15 shows both peaks from both species showing no movement of desorption peak position. Considerable erosion of the detected mass fragment signal from species desorbed from the surface is shown.

The implications of the above results and the interactions of neutral beams with hydrocarbon-silicon surfaces are discussed in section 5.6. However, further experiments, involving bombardment with an energetic hydrogen-based beam were carried out and are described below.
Figure 5.8(a) Thermal Desorption Spectra for C2H4 (28amu) from Si(001) following exposure to ethene (in Langmuirs)

Figure 5.8(b) Uptake Curve for TDS Spectra of C2H4+ (28amu) from Si(001) at varying exposures of ethene (in Langmuirs)
Figure 5.9(a) Thermal Desorption Spectra for H2 (2amu) from Si(001) following exposure to ethene (in Langmuirs)

Figure 5.9(b) Uptake Curve for TDS Spectra of H2+ (2amu) following exposure to ethene (in Langmuirs)
Figure 5.10 Thermal Desorption Spectra for H (1amu) from Si(001) following exposure to ethene (in Langmuirs)

Figure 5.11 Uptake Curve for TDS Spectra of H+ (1amu) following exposure to ethene (in Langmuirs)
Figure 5.12(a) Thermal Desorption Spectra for CH₃ (15amu) from Si(001) following exposure to ethene (in Langmuirs)

Figure 5.12(a) Uptake Curve for TDS Spectra of CH₃⁺ (15amu) following exposure to ethene (in Langmuirs)
Figure 5.13(a) Thermal Desorption Spectra of C2H4 (28amu) from 3L dosed Si(001) surface following irradiation by Ar neutrals (1.7keV)

Figure 5.13(b) Thermal Desorption Spectra of 3L exposed C2H4 (28amu) on Si(001) following irradiation by Ar neutrals (1.7keV)
Figure 5.14(a) Thermal Desorption Spectra showing Enhancement of $H_2^+$ signal due to Ar° neutral bombardment of the 3L dosed ethene/Si(001) surface

Figure 5.14(a) Semi-logarithmic graph of Enhancement of $H_2^+$ signal due to Ar neutral bombardment of the 3L dosed ethene/Si(001) surface
Figure 5.15 Thermal Desorption Spectra showing erosion of CH$_3^+$ (15amu) and C$_2$H$^+$ (25amu) due to Ar$^0$ bombardment of ethene/Si(001) surface
5.5.4 Bombardment of Ethene/Silicon Surface with an Energetic Atomic Hydrogen-based beam - Results

The first set of experiments performed were irradiation of adsorbed ethene on Si(100) by 1kV atomic hydrogen neutrals generated by the Ion Tech FAB source. This type of beam source was used due to the high probability of producing small quantities of hydrocarbon, in addition to the excitation of hydrogen, within the discharge region. This phenomenon is due to the beam source possessing graphite anode rods and is discussed in detail later in the chapter. TD spectra are presented in Figure 5.16 and show the desorption trace of C\(_2\)H\(_4\) from the silicon surface after 30L exposure of ethene. Subsequent bombardment by energetic (1kV) species from this source (hydrogen-based beam) results in a significant increase in intensity of the desorption signal. In addition, a second desorption peak labelled the \(\beta\) state arises at higher temperatures (535K). Figure 5.17(a)-(d) shows results for a similar experiment conducted with a 9L exposure of ethene upon the Si surface, 5.17(a), followed by irradiation with the 500eV hydrogen-based beam for 20s, 5.17(c), and 200s, 5.17(b), respectively. The spectra reveal an increase in the intensity of the desorption of the peak for ethene from the surface exposure of atomic hydrogen neutrals increases. A control spectra, 5.17(d), was taken by dosing the silicon with 9L of ethene followed by exposure of the sample to a pressure of 2 x 10\(^{-3}\) torr of molecular hydrogen leaked through the FAB source. The magnitude of this ethene desorption peak is less than that produced by normal exposure or by neutral irradiation, although a significant degree of peak broadening takes place. Figure 5.18 presents data derived from the desorption curves in Figure 5.17 and are plotted as peak area versus H\(^0\) neutral dose. They show the enhancement of ethene desorbed from the surface after neutral irradiation. Prolonged exposure to the hydrogen-based beam results in the ethene desorption peak increasing without apparent saturation.

A series of experiments were performed such that the mass fragments for methane (16amu) and methyl radical (15amu) were investigated. Ethene
was dosed (9L) onto the silicon surface. The surface was then bombarded with the energetic (500eV) hydrogen-based beam from the FAB source. Control experiments were performed by TDS of the clean silicon surface and also the bombarded, but undosed, surface. Figure 5.19(a) shows thermal desorption spectra for the methane (16amu) signal following adsorption of 9L ethene upon the silicon surface. There is no discernible peak on the mass spectrometer partial pressure scale of $10^{-10}$ torr. Irradiation of the surface with 500eV atomic hydrogen neutrals results in a TD spectra as shown in Figure 5.19(b) which exhibits a broad desorption peak centred at 480 K. A secondary peak also appears at approximately 750K. A control TDS curve is shown in Figure 5.19(c) for bombardment of the surface without prior adsorption of ethene. This reveals desorption peaks of similar intensity except that the broad high temperature desorption state appears at approximately 800K. A further control was performed as shown in Figure 5.19(d) by dosing the surface with silicon, followed by exposure to an overpressure of molecular hydrogen equivalent to that during bombardment. The surface was not exposed to the energetic neutral beam. The TD spectra reveal a methane peak of an intensity of an order of magnitude lower than that obtained by irradiation with the hydrogen neutrals. This small methane concentration may derive from filament induced processes within the UHV system.

The behaviour of the TD spectra for the methyl mass fraction (15amu) is similar to that observed for methane. The spectra are presented in Figure 5.20 and confirm the observations from Figure 5.19. The CH$_3$ species was thought to derive from the methane as ionised on entry at the mass spectrometer. The TD curve shown in Figure 5.20(d) reveals a desorption peak at least an order of magnitude smaller than that observe for the methane species.

Whilst these results do not show hydrogen neutral perturbation of the adsorbate region, they may have important applications for the growth of diamond films. In particular, the enhancement of the methyl species may allow a hydrogen-based beam source of this type to be used for diamond film deposition. This is discussed more fully in section 6.4.
Figure 5.16 Thermal Desorption Spectra of (a) C$_2$H$_4$ (28amu) from a Si(001) Surface exposed to 30L of ethene; (b) as (a) followed by 1kV H$^0$ neutral bombardment
Figure 5.17 Thermal Desorption Spectra of (a) C$_2$H$_4$ (28amu) from a Si(001) Surface exposed to 9L of ethene; (b) as (a) followed by 0.5kV H$^0$ neutral bombardment for 200s; (c) as (b) except 20s bombardment; (d) as (a) followed by exposure to 1mtorr H$_2$

Figure 5.18 Graph showing effect of hydrogen neutral dose on surface ethene concentration on Si(100)
Figure 5.19 Thermal Desorption Spectra of (a) CH₄ (16amu) from a Si(001) Surface exposed to 9L of ethene; (b) as (a) followed by 0.5kV H⁰ neutral bombardment for 20s; (c) as (b) except no ethene dose; (d) as (a) followed by exposure to 1mtorr H₂

Figure 5.20 Thermal Desorption Spectra of (a) CH₃ (15amu) from a Si(001) Surface exposed to 9L of ethene; (b) as (a) followed by 0.5kV H⁰ neutral bombardment for 20s; (c) as (b) except no ethene dose; (d) as (a) followed by exposure to 1mtorr H₂
5.6 Analysis and Discussion

The following sections discuss the results obtained from measurement of the adsorption process and the thermally desorbed products. The implications of these results and the subsequent beam modification processes observed at the interface of ethene/silicon are considered with particular emphasis on new growth strategies for SiC, diamond and diamond-like thin films. A few recent TDS studies have been performed on aspects of adsorption of unsaturated hydrocarbons on silicon by other researchers [5.91,5.94] with particular emphasis on application to catalytic dehydrogenation reactions. However, the use of ethene as a precursor for deposition of silicon carbide films and possible use as a reactant for growth of interlayers for heteroepitaxial diamond and diamond-like films is of burgeoning significance [5.58].

The nature of the adsorption process and the subsequent thermal reaction with silicon surfaces is therefore of increasing importance for fabrication of microelectronic device quality layers. The techniques of TDS and AES lend considerable support at an atomic level to deposition data available in the literature. The use of electron energy loss spectroscopies (e.g. HREELS) has also been of great value in leading to an understanding of the surface processes of the C$_2$H$_4$/Si(100) system [5.89].

5.6.1 Adsorption and Thermal Studies of Ethene (C$_2$H$_4$) on Si(100)

The first mass fragment studied was the parent molecule, ethene (28amu), some of which was observed to thermally desorb intact from the surface. Auger analysis of the surface subsequent to desorption did not show carbon as an impurity. The clean working surface was then obtained by heating to 1200K for several minutes. The observed desorption peak at 470K shown in Figure 5.8(a) is in broad agreement with previous studies, although Cheng et al [5.91] measured the desorption peak at 600K shown in Figure 5.21 using a low heating rate of 2 K s$^{-1}$. This heating rate is low in comparison to the
22 K s\(^{-1}\) linear rate used in this study. Klimesch et al [5.85], studying ethene on Si(111) found desorption occurring from two states (\(\alpha_1\) and \(\alpha_2\)) at 600K and 420K respectively as presented in Figure 5.22, although the low temperature process appears to be at the same temperature as a peak attributed by the authors to desorption of molecular hydrogen from the sample support mounts. Klient and Brzoska [5.94] found no distinct desorption peak for ethene on Si(111), as may be observed in Figure 5.23, but reported a broad low intensity loss of the adsorbed phase across an extended temperature range. Analysis of the ethene desorption spectra from the Si(100) and Si(111) surfaces reveals that the loss of ethene from Si(100) occurs by a one step desorption process at low temperature (470K) whereas removal of the ethene molecule from the Si(111) surface occurs as a broad two step process which does not decrease in intensity until molecular hydrogen starts to desorb from the surface. This process occurs at approximately 800K. A detailed understanding of the nature of bonding between the ethene molecule and the reconstructed silicon surface is essential in order to lay the foundations for the discussion of the initial phases of thin film growth.

Cheng et al [5.90] calculated a saturation monolayer coverage of \(2.5 \times 10^{14}\) molecules cm\(^{-2}\): one ethene molecule per Si dimer site in close agreement with the value obtained in this study. It is clear, however, that after saturation further adsorption occurs although the sticking coefficient is much reduced. This desorption has previously been attributed to an associative process [5.93], with hydrogen present in surface hydrocarbon fragments combining to form molecular hydrogen which may subsequently thermally desorb. This data agrees well with the results of Klimesch et al [5.85] presented in Figure 5.10 which show a linear trend for desorption of molecular hydrogen at ethene coverages of greater than one monolayer. The similarity in intensity to the cracking pattern for ethene in the system as illustrated in Table 5.2 provides evidence for this assertion. Assignment of the \(\gamma_1\) and \(\gamma_3\) states to a particular bonding position or surface process is not clear from these spectra and requires a complementary technique such as EELS to fully describe the vibrational states at the surface, and hence the bonding.
The adsorption position of the ethene molecule upon the dimer of the Si(100) surface is diagrammatically represented in Figures 5.24(a) and 5.24(b) and is witnessed by EELS and LEED evidence presented by Yoshinobu et al [5.89]. Figure 5.24(a) shows an ethene molecule bonded at the surface in a di-σ arrangement to an individual Si dimer pair with the plane of the ethene parallel to the (011) plane. An alternative site is presented in Figure 5.24(b) and shows the ethene molecules bonded between adjacent Si dimers and hence occupying a recessed position on the surface. The description presented in Figure 5.24(a) is suggested to be the preferred orientation of the adsorbate on the surface. Theoretical calculations [5.92] support the experimental evidence [5.89]. The single desorption peak as presented in Figure 5.8(a) provides further evidence that chemisorption to only one type of surface site on Si(100) exists. Thus each ethene molecule bonds to one surface dimer.

5.6.2 Thermal Processes on the Ethene/Si(100) Surface

The formation of thermally stable surface phases of SiC is of particular interest for application to thin film deposition processes, both as an intermediate layer for diamond growth and as a radiation hard semiconductor material. The thermal reaction of ethene with silicon is a particularly important method of growth of these thin films. Having discussed the nature of bonding between ethene and the Si(100) surface it is necessary to consider how the process of thermally induced dehydrogenation of the hydrocarbon at the surface might occur. On Si(111)7x7, ethene dehydrogenates at temperatures greater than 450K and C-C bond scission occurs at approximately 800K [5.86]. Furthermore, it is interesting to observe reports of only partial loss of the intact ethene molecule from both Si (111)[5.87] and Si(100) [5.91] surfaces. This is accompanied by dehydrogenation of 60-80% of the remaining ethene bound to the surface by a process which is attributed to thermal processes. This implies either the existence of more than one bonding state of ethene to the surface, or a competitive process between desorption of the ethene molecule and a thermal dehydrogenation reaction. It has been demonstrated using.
HREELS that the ethene is bound to one surface site [5.88]. It has also been observed that the surface reconstruction of Si(100) is not lifted upon adsorption of ethene in the sub-monolayer regime, whilst further exposure of ethene result in coverages of greater than 1ML which tend to lift the surface reconstruction. The Si(100) dimer surface may, therefore, allow ethene to bond at intra-dimer sites once monolayer coverage is achieved. This assertion based on LEED observations is supported by TDS data shown in Figures 5.8(b) and 5.10 witnessing that the uptake of ethene on the surface does not saturate. The subsequent loss of ethene at low temperature may then originate from these inter-dimer sites, whereas the strongly bound dimer sites on increasing temperature allow C-C bond scission to occur whilst further heating leads to dehydrogenation. The nature of a competitive process is not easily verified by thermal desorption studies, and discussion is not found in the literature to account for these observations.

The TD spectra for H⁺ (1amu) presented in Figure 5.10 shows two peaks of interest. Firstly, a prominent desorption peak at around 470K which represents hydrogen formed from dissociation of the ethene molecule through ionisation in the mass spectrometer. Secondly, a less intense broad peak at higher temperatures is also observed which corresponds to H₂ produced during the dehydrogenation process occurring at the ethene/silicon surface. The TDS spectra for both the C₂H₄ (28amu) and H₂ (2amu) mass fragments support this analysis. The uptake curve shown in Figure 5.11 reveals a saturation of the H⁺ signal derived from molecular hydrogen. This possibly indicates that the dehydrogenation reactions may only occur at sub-monolayer regimes. This agrees with a model of only ethene molecules bonded to the dimer undergoing dehydrogenation.

Clearly, the nature of thermal reactions of ethene with the Si(100) surface is not straightforward. A mechanism has been proposed which is in agreement with the observations from TDS, LEED and AES studies and also draws from other researchers studies using complementary methods such as vibrational spectroscopic techniques. The effect of energetic particle beams on these adsorbate-surface systems are now considered.
5.6.3 Beam Bombardment of Ethene on Si(100) by Ar Neutrals - Discussion

The use of ion beam assisted techniques for the deposition of diamond and diamond-like films is well established [5.12-5.14]. A brief review of the method employed has been described in section 5.3. The synthesis of diamond films by these methods usually involves the use of carbon ion beams, or sputter processes on carbon targets. An interesting variation to these forms of thin film deposition may be possible by utilising the surface processes which occur upon ion bombardment of an adsorbed hydrocarbon phase on single crystal silicon. The effect of inert ion beams on adsorbed hydrocarbon phases has not been previously studied and similarly, the effect of irradiation of these surfaces with energetic neutral beams of atomic hydrogen has not been considered. The bombardment of adsorbed layers of ethene on Si(100) by energetic argon neutrals are considered first, followed by analysis of surface processes induced by H° bombardment in section 5.6.4. The section examines perturbations of the ethene-Si(100) surface resulting from bombardment by low energy (<2kV) argon neutral particles.

The nature of ion/neutral bombardment of adsorbate-surface systems has been discussed in previous chapters with respect to enhancing etching reactions of halogens with semiconductors. This section is fundamentally different from these preceding discussions due to the resultant application being thin film deposition rather than layer removal. Nevertheless, the physical processes that occur when an energetic ion/neutral beam impinges on the surface are essentially the same to those previously described systems. These have also been reviewed in section 1.4. Numerous competing processes occur as a consequence of collisional cascade type processes. Due to the relative lack of volatility of silicon-carbon alloys compared to the silicon-halogen system, processes such as intermixing of elements within the surface region may provide a greater contribution than sputtering processes i.e. the surface binding energy at the interface may actually increase.

The initial experiments witnessed the effect of neutral beam bombardment on the C₂H₄ covered silicon surface. The semi-log erosion curve, shown in Figure 5.13(b), for loss of the C₂H₄⁺ detected mass fragment upon neutral bombardment of the surface does not show a linear trend and hence does not
exhibit exponential decay of the surface phase. Intriguingly, a plot of ln peak area of the ethene mass fragment versus the neutral argon beam dose reveals an increase in signal upon initial beam exposure. This peak area increase is visibly due to broadening of the desorption peak rather than an increase in peak height. A similar plot of peak height versus neutral beam dose reveals gradual erosion of the ethene peak. The process of beam impact thus appears to perturb the strength of bonding of ethene to the silicon surface and this may be due to several reasons. Firstly, the increase in the peak width of the 28amu mass signal may result from diffusion of the ethene to a sub-surface position due to disruptive beam effects such as recoil implantation or enhanced diffusion of carbon containing species to the bulk. These processes are unlikely because the C_2H_4 molecule may be expected to fragment after Ar^0 beam exposure. Furthermore, the ethene molecule is known to be reluctant to undergo associative desorption after the C-C bond has undergone scission at the surface [5.91]. The impact of an energetic high mass particle such as a 1keV argon neutral would be likely to cause intra-molecular bond breaking and intermixing of carbon fragments in the sub-surface region and therefore reduce the amount of intact C_2H_4 available for desorption. Another explanation is possible if the second desorption peak is offset to slightly higher temperatures (550K) than the primary peak is considered. This may be caused by ethene desorbing from sub-surface voids formed during cascade processes. Amorphisation of the surface region clearly alters the nature of bonding between ethene and silicon, and results in intermixing. A schematic of surface and sub-surface processes that occur in this adsorbate/surface system are depicted in Figure 5.25.

The impact of the energetic argon neutrals does alter the proportion of ethene on the surface which may desorb as an intact entity, and that which decomposes or dehydrogenates on the surface and subsequently sputters to leave a clean Si surface. In order to examine the implications of this statement, the desorption spectra for loss of molecular hydrogen from the surface after argon neutral irradiation of the adsorbate-surface region for the C_2H_4/Si(100) system are considered. The TD spectra showing the effect of argon bombardment on the surface resulting in changes in the nature of desorption of molecular hydrogen are presented in Figure 5.14(a). These spectra clearly show that neutral bombardment enhances the
dehydrogenation reaction at the surface. There are two reasons for this assertion. Firstly, the peak area of loss of molecular hydrogen increases upon prolonged neutral irradiation although the amount of ethene adsorbed at the surface is constant. The second argument is the enhancement of the $\gamma_1$ peak at 500K which shows that there is a mechanism which causes associative desorption of molecular hydrogen at lower temperatures than the purely thermal process described by previous researchers on the ethene/Si(100) system [5.91,5.94] and as verified by the thermal studies presented earlier in this chapter. The position of the $\gamma_1$ peak coincides with the temperature for desorption of ethene molecule, and the broadening effect of neutral bombardment may be linked by a competitive desorption process of both molecular hydrogen and ethene at this temperature induced by the impinging energetic neutral beam.

The effect of further irradiation of the surface as shown in Figure 5.14(a) is to accelerate the loss of molecular hydrogen from a surface bound ethylenic species. The high temperature $\gamma_3$ desorption peak is due to the final dehydrogenation of the surface after the initial dehydrogenation of ethene on the surface. At this stage the surface has no ethene adsorbed, but residual hydrogen bound to the surface and incorporated into the sub-surface region may associatively desorb at these temperatures.

It is clear from the preceding analysis that the use of an ion beam to perturb the surface region of the ethene-silicon adsorbate system results in some sputtering of the intact adsorbate from the surface, and some dissociation of the molecule leaving residual carbon at the surface region. The latter process may result in the growth of silicon carbide thin films. Another feature of ion enhanced processes is the intermixing of silicon and carbon to a significant depth, thus enhancing the SiC thin film growth process. Bozso et al [5.62] have proposed a mechanism for the growth of SiC at various temperature regimes and this is shown schematically in Figure 5.5. This figure shows SiC deposition within the temperature range 850-940K. The most efficient of these growth ranges is the high temperature region at over 1000K (Figure 5.5(a)). The mechanism involves three layers one of which is the silicon substrate with diffused carbon. The overlayer consists of a silicon carbide thin film with a further layer of silicon at the surface which segregates to the surface at these
high temperatures. A barrier to low temperature growth is the replenishment of the growing layer with silicon atoms. A possible method of low temperature silicon carbide growth may result from bombardment of the growing surface with energetic argon neutrals. The impact of the particles may cause intermixing of the silicon and carbon within the surface region, thus allowing enhanced diffusion processes of silicon to the surface. The irradiation may also promote crystallinity due to the high local surface temperatures during ion bombardment. These may be at lower temperatures than those achievable using conventional thermal CVD processes. Bozso et al [5.62] observed that at 940K the 22.5eV plasmon loss peak indicative of the SiC phase had developed. This was attributed to the diffusion processes in the bulk starting to dominate the kinetics of the surface reaction. Modification of the surface region is likely due to ion-enhanced diffusion processes which may dominate over thermal diffusion; thus resulting in lower processing temperatures.

In summary, a number of observations have been recorded for bombardment of the ethene/Si(001) surface;

- Argon neutral bombardment shows a clear enhancement of the dehydrogenation reaction at the Si(001) surface.
- Associative desorption of molecular hydrogen is induced at lower temperatures (<500K)
- Simple sputtering of C$_2$H$_4$ (28amu) from the surface
- bombardment by 1.7kV Ar neutrals is sufficient either to sputter erode surface carbon or allow incorporation into the sub-surface region. A SiC phase is not formed at these energies and formation of such films would require the use of lower energy beams to avoid sputtering processes occurring.
5.6.4 Bombardment of the Ethene/Si(100) surface with an energetic Hydrogen-based beam: Discussion

The adsorption of ethene has been well characterised in section 5.4 and the nature of the bonding of ethene to the surface has been established. Bombardment of these states with a low energy hydrogen-based neutral beam has been described in section 5.5.4 providing interesting observations and exciting implications for diamond deposition processes. Hydrogen was passed through the fast atom beam (FAB) saddle field source resulting in the formation of energetic hydrogen/hydrocarbon species. Thermal desorption results presented in Figures 5.19 and 5.20 provide evidence for the formation of small quantities of energetic hydrocarbon species also occurs during the excitation process. It is believed that methane is the major product of a reaction of atomic hydrogen with the graphite anodes of the FAB source. Methane does not stick to the Si(001) surface and hence the presence of methane at the surface may occur only as a result of associative surface desorption or by adsorption of an excited modified methane molecule which does stick. The former explanation is a likely explanation for this observation. The output of the beam source consists of energetic molecular hydrogen, atomic hydrogen and hydrocarbon species. Recombination of atomic hydrogen formed in the beam source is most likely at the pressures employed for discharge to occur.

Gould [5.95] studied the kinetics of this reaction and proposed a mechanism which involves the formation of CH$_4$ produced by a surface complex consisting of a reaction of atomic hydrogen with chemisorbed hydrogen present on the graphite surface. It was suggested that additional chemisorbed H rapidly reacts with this surface complex, leading to the desorption of methane. This favours a reaction of the type,

\[
\text{CH}_3\text{ads} + \text{H}_{\text{ads}} \longrightarrow \text{CH}_4(\text{g})
\]

Pairing of the surface complexes causes formation of a stable site-blocking species thus limiting CH$_4$ evolution at that site. A further study of the reaction of graphite with atomic hydrogen [5.96] showed that thermal reaction up to 800K produced solely methane, whereas acetylene was
observed as the reaction product at temperatures greater than 1000K.

Figures 5.16 and 5.17 show bombardment of ethene adsorbed to the Si(100) surface by a hydrogen-based beam. Bombardment with these species enhanced the ethene desorption peak. There are several possible explanations for this observation. Firstly, the FAB source is producing olefinic or acetylenic species as well as methane in the saddle field region. The nature of the energetic beam causes these species to either stick to the surface. The broad peak observed at 550K may result from associative desorption of ethene from carbon units at the surface. Alternatively, bombardment may form voids in the sub-surface region which contain ethene driven into the surface by exposure to the neutral beam. Broad beam bombardment may also cause ion-induced desorption of background ethene in the chamber, thus effectively increasing the dose of the crystal. This latter explanation is believed to be unlikely as great care was taken to expose only the crystal surface to the beam. The bombardment of an adsorbate covered surface is unlikely to result in sputter desorption or implantation due to the low mass of the hydrogen neutrals. The FAB appears to produce small amounts of hydrocarbon as evidenced by observation of TD spectra of the mass fractions 15 and 16, relating to methane and methyl species as presented previously in Figure 5.19 and 5.20 respectively. This has important implications for the possible growth of diamond thin films using an ion beam method. Typical hot filament activated hydrocarbon/hydrogen mixtures are of the order of 1% of the former component. The formation of similar mixtures with an energetic component may allow carbon based thin films to be fabricated.

To summarise this section, bombardment of an ethene/silicon surface with a hydrogen-based neutral beam leads to an increase in the methyl mass fragments desorbed from the surface.
Figure 5.21 Thermal Desorption Spectra of $\text{C}_2\text{H}_4$ and $\text{H}_2$ from $\text{C}_2\text{H}_4$ adsorbed on Si(100) at 105K.

after C.C.Cheng et al  Surface Science 231 177 (1990)
Figure 5.22 (a) showing desorption of ethene (28amu) and hydrogen (2amu) after exposure to Si(111) (b) uptake curve derived from desorption spectra shown in (a).

Figure 5.23: Thermal Desorption Spectra of ethene adsorbed on Si(111)7x7 with increasing exposures. Insert graph is an Arrhenius plot indicating 2nd order desorption.

after
Ch.Klient and K.Brzoska Surface Science 231 289 (1990)
Figure 5.24 Structural Models for Ethene Chemisorbed on Si(100) after Yoshinobu et al. J.Chem. Phys. 87 7332 (1987)
Figure 5.25 Processes occurring on the ethene/Si(001) surface during argon neutral irradiation
5.7 Summary

The preceding discussion has elucidated several key features of the ethene/Si(001) system and energetic beam modifications to this surface.

- Ethene (\(\text{C}_2\text{H}_4\)) adsorbs on the Si(001)(2x1) surface with an approximate monolayer coverage of \(3 \times 10^{14}\) molecules cm\(^{-2}\). Further ethene exposure results in multilayer formation, but with a greatly reduced sticking probability. Methane (\(\text{CH}_4\)), however, does not adsorb to the Si surface.

- Some ethene thermally desorbs intact at 470K (\(E_{\text{des}} = 124\ \text{kJ mol}^{-1}\)), with the remainder decomposing at 680K and releasing molecular hydrogen as a desorption product.

- Bombardment of the ethene/Si surface with Ar neutrals results in sputter removal of intact ethene molecules. Enhancement of the 2 amu QMS signal reveals Ar neutral bombardment increasing the proportion of ethene decomposing on the surface. A number of beam induced processes occur at the gas-solid interface (Figure 5.25).

- Bombardment of the ethene/Si surface with an energetic beam of hydrogen neutrals reveals an increase in the ethene concentration on the surface.

- Furthermore, the methane concentration at the surface is greater than that expected from comparison with ethene cracking patterns. The presence of excess hydrogen may prevent decomposition of the ethene adsorbed on the surface.

- The process of forming energetic hydrogen neutrals within the FAB source gives rise also to a small component of hydrocarbon species.

It is clear that the interaction of simple hydrocarbon gases and a silicon surface are complex. Processes induced by energetic particle beams have been investigated and qualitatively characterised. The introduction of hydrogen into these systems provides a considerable volume of future work in order to assess the influence on growth of diamond and other carbon-based thin films.
5.8 Further Work: The Surface Chemistry of Filament Activation Processes for diamond Thin Film Deposition

It is desirable to apply the knowledge of hydrocarbon adsorption on Si surfaces and their possible thermal or ion beam modifications to their use in hydrocarbon/hydrogen mixtures in real growth processes of metastable diamond and diamond-like films. Furthermore, the TDS/LEED/AES approach may supply considerable insight into the hot filament CVD process.

An insight into the results that may be obtained and some discussion of their implications is presented here. These are of sufficient interest to suggest that a comprehensive surface study of the complexities of these activated processes is pursued in future work.

5.8.1 'Activation' Processes for Hydrocarbon/Hydrogen Mixtures in Diamond Thin Film Deposition

It has been mentioned previously that it is necessary to activate hydrocarbon/hydrogen gas mixtures for synthesis of metastable diamond. The most commonly used methods can be divided into thermal and non-isothermal processes. The former group include hot filament CVD and techniques using high temperature, high pressure "thermal" plasmas such as DC and AC arc discharges or microwave high pressure plasma jets [5.97]. The second group consists of low pressure DC, RF and ECR plasma assisted CVD methods, which possess high electron temperatures but low ion and neutral energies. A discussion of the thermal processes is presented, with particular emphasis on 'hot filament' CVD growth.

5.8.2 Hot Filament Activation

Hot filaments are extensively used to activate gas mixtures which may be used for diamond thin film synthesis via CVD techniques [5.64]. Thermal activation of hydrocarbon/hydrogen mixtures such as CH$_4$/H$_2$ and C$_2$H$_2$/H$_2$ performs a key role in the CVD process by providing atomic hydrogen for
reconstruction of the growing diamond surface and formation of nucleation sites of a graphitic nature [5.1]. Dissociation of molecular hydrogen by a hot tungsten filament was first demonstrated by Langmuir and Mackay [5.98], whilst the increase in efficiency of dissociation of hydrocarbons by the filament in a hydrogen ambient was observed by Boudart et al in the late sixties [5.99]. A considerable time elapsed before diamond thin film deposition using hot filament CVD was demonstrated in 1982 by Matsumoto [5.100].

Although the deposition of diamond thin films by filament assisted CVD is now well established, little analysis of the underlying processes in the filament-region has been performed. Celii [5.101] used an IR laser absorption spectroscopy technique [5.102] to observe gas phase species formed during filament assisted growth. A 200:1 H$_2$/CH$_4$ mixture was found to contain acetylene and ethene consistent with the growth model of Frenklach and Spears [5.65], as well as methyl radicals, above the substrate surface. Ethane, C$_3$ hydrocarbons and methane radicals were not detected during the growth process, and the concentration of the CH, C$_2$ and C$_2$H species was not measurable. Celii [5.103] also employed resonance enhanced multiphoton ionisation (REMPI) [104] for the detection of atomic hydrogen. This is achieved when three 364.7 nm photons, which are resonant with the (1s--->2p) Lyman-α transition at 121.57 nm. These photons are absorbed with a further photon causing ionisation from the 2p level (3+1 REMPI). The concentration of atomic hydrogen was found to change with filament temperature and hydrocarbon mixture, whilst diffusion was regarded as the dominant mechanism of transport of atomic hydrogen to the substrate.

Sommer and Smith [5.105] have analysed the observations of Celii using a thermodynamic model to optimise important growth parameters such as temperature, pressure and reactant composition. A thermodynamical model based on quasi-equilibrium is used to describe the role of supersaturation of atomic hydrogen at the growth surface. They also propose that a non-carburising filament material such as rhenium is more suitable than the conventional tungsten and tantalum filaments. The prohibitive cost of rhenium has prevented replacement in most existing
filament deposition processes.

Wu et al [5.106] have recently measured the composition of reactant gases in a hot filament CVD process using gas chromatography and a quartz microbalance. The major chemical process for a feed gas combination of methane/hydrogen and acetylene/hydrogen was found to be a conversion process between methane and acetylene with ethane and ethene as reaction intermediates. A maximum ethene concentration was obtained at 2073K with acetylene being the major stable hydrocarbon at lower temperatures. Methane is the major reaction product at temperatures greater than 2173K.

A compositional chart of species present in the gas phase as a function of dissociation temperature [5.67] is shown in Figure 5.26. At temperatures of 1250K, where diamond is deposited, methane and H$_2$ are almost exclusively found. At filament temperatures above 1700K, C$_2$H$_2$ is the most abundant species, whilst C$_2$H dominates at 3200K and CH at 4800K.

5.8.3 Hot Filament Assisted Adsorption of Hydrocarbon on Si(100)- Results

This section presents results of adsorption from activated hydrocarbon/hydrogen gas mixtures. The filament employed in this study was coiled into a spiral and mounted several millimetres from the outlet of the dosing tube. The filament-substrate distance was set at 25mm. The filament needed extensive degassing at 5A set current for twelve hours. The relative proportion of methane and hydrogen increase as a function of filament temperature. This opposite trend is observed for olefinic and acetylenic species. By passing methane across a hot filament, and performing TDS studies of the surface, useful clues as to the surface chemistry during the diamond CVD growth process may be obtained.

Thermal desorption spectra for methane exposure to a Si(100) surface showed methane to have a sticking coefficient close to zero. Exposure of methane to the same surface with hot filament interposition, however, reveals surface hydrocarbon species. Figure 5.27 shows that a C$_2$H$^+$ (25amu) species is
detected on the Si surface. The build up of the C\textsubscript{2}H\textsuperscript{+} species on the surface does not appear to saturate with large exposures of activated methane. It was noticed that the C\textsubscript{2}H\textsuperscript{+} species was present upon exposure of the activated methane, but not observed when the methane precursor was unactivated. A desorption peak for C\textsubscript{2}H\textsuperscript{+} at 500K was observed, which was assumed to be indicative of desorption of ethene from the surface, however, the parent molecule was not detected. It therefore appears that an acetylenic species may bind to the surface as a result of adsorption of activated methane on a silicon surface.

The effect of neutral beam irradiation of the C\textsubscript{2}H\textsuperscript{+} surface state formed by activated methane adsorption on silicon is now examined. The bombardment of the characteristic C\textsubscript{2}H state with argon neutrals (1.7kV) is presented in Figure 5. 28 and reveals erosion of the surface phase upon increasing neutral beam exposure. A slight increase in the width of the desorption peak was observed at beam doses of 8x10\textsuperscript{16} neutrals cm\textsuperscript{-2}. It was also observed that after initial erosion of the surface C\textsubscript{2}H, this beam dose increased in both height and area. Furthermore, a small desorption peak was detected at approximately 760K and possibly indicating the formation of a strongly bound surface phase. The high temperature desorption state possesses a similar value to the final dehydrogenation step for thermal decomposition of ethene on silicon.

5.8.4 Surface Reactivity of Hot Filament Activated Methane

The gas phase chemistry of feed gas combinations for diamond film deposition has been studied by many researchers. The surface reactions during the growth process are less well understood and is of critical importance for the deposition of semiconductor quality layers. The thermal
desorption of surface species from a silicon surface after exposure to typical activated hydrocarbon/hydrogen mixtures has been performed. The surface reactivity of hot filament activated methane on silicon surfaces is a system of particular importance. Results previously presented in Figure 5.27 reveal the presence of an acetylenic species bound at the surface. A hot filament induced reaction of the type

\[ 2\text{CH}_4 \xrightarrow{\text{reaction}} \text{C}_2\text{H}_2 + 3\text{H}_2 \]

occurs. Thermodynamic data [5.67] predicts an equilibrium position for this reaction in favour of acetylene at high temperatures i.e. 2300K. The activated adsorption experiments in this study are quite clearly performed at surface temperatures below that required for thin film growth in order to be able to regenerate a clean surface. No other studies to our knowledge have been carried out previously for adsorption of activated species upon silicon surfaces. It is therefore of interest for application to deposition processes if growth of a diamond film may be promoted by methods other than hot filament or plasma activation. A particularly attractive alternative for selected area deposition is by controlling the layer growth at the surface rather than the gas phase. A possible strategy to achieve this may be the adsorption of a known activated precursor species, such as \( \text{C}_2\text{H} \), followed by neutral beam bombardment of the desired deposition area to induce the growth process. It is desirable to use neutral argon beams due to possible perturbation of the electronic properties of the layers and substrate material by ionic beams. Charging effects may also be undesirable in a process of this type. With this strategy in mind it is clearly appropriate to discuss the effect of neutral beam bombardment of the \( \text{C}_2\text{H}/\text{Si}(100) \) surface.

The adsorbed acetylenic species at the surface derived from the activated methane dose is rapidly sputter eroded by the neutral argon beam as previously shown in Figure 5.28. Some carbon containing species may be driven into an amorphised surface region as single carbon species. This may account for the increase in the TD peak area observed at high beam doses. Further beam bombardment inputs large amounts of localised energy via cascade type processes allowing associative desorption of carbon-
Figure 5.26 Composition of gas phase versus dissociation temperatures for 1% methane/99% hydrogen at 0.1 atm [5.67]
Figure 5.27 TD Spectra of C₂H⁺ (25amu) massfragment from a Si(001) surface dosed with CH₄ through a hot filament (12.5A)
Figure 5.28  TD Spectra of $C_2H^+$ (25amu) mass fragment from an Ar0 neutral irradiated $CH_4$ (hot filament,150L) /Si(001) surface
Chapter 6. Concluding Remarks

This investigation has employed the use of surface sensitive probes to examine the nature of thermal and ion-assisted reactions of halogens and hydrocarbons on semiconductor surfaces. The rationale behind these studies is twofold. Firstly, the real etching and deposition processes employed for device fabrication are generally developed along the lines of an empirical approach. The need for increasingly smaller devices exhibiting improved performance places considerable limitations upon the current methods of processing techniques. A detailed mechanistic knowledge of the desired reactions is required in order to improve these methods. The second reason for employing this surface approach is the current drive towards in-situ processing of complete device structures. This type of processing requires the sequential fabrication steps to be performed without removing the device from the processing environment. The deposition, etching, metallisation steps may all be carried out in multi-chamber vacuum systems. This alleviates problems of control over the interface and the prevention of particulates on the device.

This section deals with the strategic advances in device processing that can proceed with a thorough knowledge of the surface reactions of certain etching and deposition systems as developed in this thesis. The major problem of integration of these results with a real process is the so-called ‘pressure gap’ which is well known to both surface scientists and process scientists in the field of heterogeneous catalysis. The problem is not as severe in semiconductor processing and the equipment designed in this project circumvents many of the problems of mixing UHV and low pressure processing procedures. The design of two process/modification cells around a central RFA based analysis chamber allowed increased flexibility of the studies that could be performed. Furthermore, the processing cells also were capable of operating at UHV pressures when the TDS experiments were performed.
The studies of the halogenated etching reactions on Si and GaAs have illustrated the corrosive nature of the etchant gas. Clearly, spontaneous reaction of these etch precursors with the substrate occurs and thus for selective area etching these reagents are quite inappropriate. This is because the areas that are not processed still possess an adsorbed overlayer. Subsequent depositions on this surface then trap the adsorbate, which remains at the interface, thus possibly degrading device performance. Furthermore, the etching occurs in a non-discriminatory manner over the complete device structure. An alternative strategy would involve the investigation of inert precursors for CAIBE type processes. An example would be 1,2-dichloroethane which can undergo dissociative chemisorption at monolayer coverages \[6.1\]. Further exposure can lead to molecular physisorption, but essentially no corrosion phase is produced. This lends itself to the possibility of energy from ion or neutral beams to be selectively targeted in order to drive the chemistry on the surface. The advantages of CAIBE processes over RIBE and other etch processes are known to include extension of ion beam source lifetime, layer-by-layer etch control and maskless etching using focused ion beams. The use of carefully selected precursors to control etch chemistry can be envisaged. A combination of etch retarding and etch enhancement species may be used to control etch selectivity. A possible example would be the use of \(\text{Se}_2\text{Cl}_2\) which may act as a selective etchant of \(\text{Al}_x\text{Ga}_{1-x}\text{As}\) over GaAs.

In addition, to exercise control over the chemical reactivity of the etch precursor, it is also necessary to utilise low energy ion beams in order to reduce the physical influence of the impinging particle. It has been shown that the surface binding energy of GaAs is approximately 10eV, whilst that of the chlorinated surface is less than 2eV. Clearly, the use of 1keV beams is less than desirable since at such an energy, discrimination between a 2eV and a 10eV bound state will be very small. The development of low energy ion sources that can be used to improve etch processes is extremely important. Candidates here are ECR and r.f.plasma sources. Highly focused ion beams can currently be produced using liquid metal ion sources which typically operate at 30-50 keV. The relatively inert nature of the beam produced (often
Ga) may be ideal for low damage CAIBE processes if the beam energy can be considerably reduced. This would appear, to the author of this thesis, to be a highly desirable development that would enable low damage, maskless, highly localised etching to be achieved which is essential to the development of in-situ processing.

Beam energy is not the only means by which improved process quality, such as reduced substrate damage, can be achieved. It is apparent from this study that the exact nature of ion-beam induced processes which occur will be strongly influenced by the steady-state thickness and composition of the adsorbed layer. This layer both controls the etching chemistry (when very thin, physical sputtering dominates and when thick the sputter removal of chemically produced erosion products dominates) and controls the extent to which the energy of the incoming beam is transmitted to the underlying region resulting in perturbation and considerable electronic damage. A further point to consider is that spontaneous chemical etching does not leave memory effects or sub-surface damage, thus the resultant surface effectively has no knowledge of ever being processed.

In this context careful matching of the mass of the incoming beam to the mass of the adsorbate species present, whilst maximising the mis-match between the beam and the substrate could also be utilised to good effect. It is clear that the successful realisation of in-situ UHV based ion beam etching of structures requiring the minimum of damage will only be achieved by the further development of the surface chemical studies presented here, utilising more complex, carefully designed etching precursors. The inclusion of ligand species to modify surface reactivity will introduce new problems of contamination from by-products of the reactions and this issue must be carefully addressed.

The introduction of such “designer” chemistry must occur alongside low energy, highly focused source development. This emphasises the interdisciplinary nature of the tasks facing the research workers in this field.
A particularly understated problem faces the etching community in terms of the environmental toxicity of many commercially utilised etch gases. The Montreal protocol, recently ratified in London by 61 countries, bans the use of a number of classes of compound completely by the year 2005. In the UK this ban is due to be implemented by 1995. The CFC family of gases, such as Freon 12 and 13, are commonly used by GaAs/AlGaAs device engineers for discriminatory etching: this seems likely not to be possible once this ban is in place. Furthermore, routinely deployed reagents such as carbon tetrachloride are also to be banned. Since this list of compounds is almost certain to get longer, rather than shorter, in the future it is particularly important that surface chemical studies proceed which will identify useful, non-environmentally toxic etch precursors.

The use of surface probes to study reactions of hydrocarbons on silicon is a particularly underdeveloped area in terms of the potential wealth of knowledge to be uncovered. The potential uses of these studies have been reviewed here and subsequent analysis of results obtained on the ethene/Si system have resulted in considerable insights into how SiC thin films may be fabricated by ion beam methods. Further results on the hot filament assisted CVD process has led to an opening for extensive work to be performed on the nature of alkyl chain extension reactions. This is of very significant importance. For example, the primary problem facing diamond growth scientists currently is the inability to grow single crystal high purity diamond on good quality Si substrates. Substrates are extensively scratched to provide nucleation: polycrystalline growth will always result from this procedure. In the opinion of this author the only solution to this problem will be to fully identify the nature of the surface chemistry which gives rise to the onset of CVD growth and then to design Si surface structures that promote the desired adsorption and subsequent reactions without the use of arbitrarily scratched and highly defected substrate material. Only then will the true extent of any lattice mismatch problem between Si, SiC and diamond become apparent. UHV based attempts to grow high purity diamond layers can follow.
In conclusion, even though the application of surface science to electronic engineering has rapidly evolved over the past ten years, there is still a considerable amount of fundamental work on a number of key issues before surface engineering can be considered to be a mature science. This work has shown how the use of surface probes such as TDS, AES and LEED can contribute to the development of this area. Complimentary surface probes such as STM and the whole plethora of vibrational spectroscopies are envisaged to be an essential prerequisite for the continued maturation of this field.
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